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Design of Lead Hybrid Halide Perovskite for Solar Cells

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Abstract. Hybrid organic-inorganic halide perovskites solar cells have attracted extensive interest because of their outstanding properties, including an optimal band gap, high carrier mobility, and excellent optoelectronic merits. We study the electronic and crystal structural properties of hybrid organic-inorganic halide APbX₃ (A = Cs, methylammonium (MA), formamidinium (FA), X = I, Br) perovskites using first-principles calculations based on density functional theory. We find that halide atoms and A-site cations strongly affect their structural and electronic properties. The radius of a halide atom and the size of an organic molecule determine their lattice parameters and bond length. A relatively large halide atom can increase the value of the lattice parameters (a and b). Meanwhile, the electronic properties (band gap & carrier effective mass) of the Pb-based hybrid halide APbX₃ can be effectively modified by adopting appropriate A- and X-site atoms or organic sections. We predict that HOIPs may have outstanding potential in solar light harvesting with promoted power conversion efficiency due to a tunable band gap and excellent electronic properties.

1. Introduction

Renewable energy technologies are expected to play a significant role in sustainable economic development and reducing greenhouse gas emissions. Renewable energy is said to have increased from 20% to 28% of global electricity generation between 2011 and 2021 [1]. As one of the most abundant and cleanest sources, solar energy harvesting has attracted great attention in both industrial and academic fields [2]. Enhancing solar energy conversion efficiency is the most important mission for all photovoltaic materials. Hybrid organic-inorganic halide perovskites (HOIPs) have been intensively explored for several decades in the field of photovoltaics [3]. These perovskite materials can very efficiently capture energy from the sun because of their excellent electronic properties, such as long carrier diffusion length, tunable band gaps, and low exciton binding energy [4]. Since 2009, the power conversion efficiencies (PCEs) of solar energy have experienced a rapid increase, growing from an initial 3.8% to 25.2% as of 2022. [5]. Halide perovskites based on lead (Pb) have a general formula of APbX₃, where the cation A can be either organic (e.g., CH₃NH₃ or MA, NH₂CHNH₂ or FA) or inorganic (e.g., Cs), and X refers to a halide atom such as chlorine (Cl), bromine (Br), or iodine (I). Many notable achievements have been published due to significant efforts on related works over the last decade. Zhang et al. fabricated stable two-dimension (2D) HOIPs based on asymmetric organic molecules with a high PCE of 24.7% after 1000 hours of operation [10]. Singh et al. reported that by reducing dimensionality and heterostructure engineering, the stability of HOIPs can be significantly enhanced [11]. Fatima et al. also effectively improved the stability of CsPbI₂Br perovskite and promoted device performance via interfacial modification [12]. Song et al. replaced Pb with Sn atoms to achieve a new Sn-based HOIP (C₆N₂H₁₆Cl)₂SnCl₆ with excellent air stability [13]. Deng et al. reported an adjustable bandgap of 1.5–2.2 eV in Cs and Zn co-doped HOIPs [14]. Xu et al. investigate the defect tolerance of mixed metal



HOIPs, which have a long carrier lifetime of $>1 \mu\text{s}$ [15]. Although a lot of individual experimental and theoretical studies on HOIPs have been reported, there is no related research on Pb-based HOIP with different A cations and X ions.

In this study, based on density-functional theory (DFT), we systemically investigated the structural and electronic properties of APbX_3 with A being Cs, MA, and FA cations and X being I and Br ions, which are CsPbI_3 , MAPbI_3 , MAPbBr_3 , and FAPbBr_3 , respectively. Our research revealed a strong correlation between the sizes of the halide atoms (X) and the organic molecules MA/FA on the electronic and crystal structural properties of Pb-based hybrid organic-inorganic halides. Our findings also revealed that it is possible to selectively modify the electronic properties (including band gap and effective mass of carriers) by carefully selecting halide atoms.

2. Methods

We employed density-functional theory (DFT) first-principles calculations to investigate the properties of MAPbI_3 , MAPbBr_3 , FAPbBr_3 , and CsPbI_3 . The Monkhorst-Pack method was utilized to sample the first Brillouin zone and generate k-point meshes, with $5 \times 5 \times 3$ used for tetragonal crystal structure. Additionally, we applied the vdW-DF nonlocal density functional, while ensuring a consistent use of a cut-off energy of 500 eV to expand plane-wave bases. By fine-tuning the related parameters, we were able to achieve good convergence.

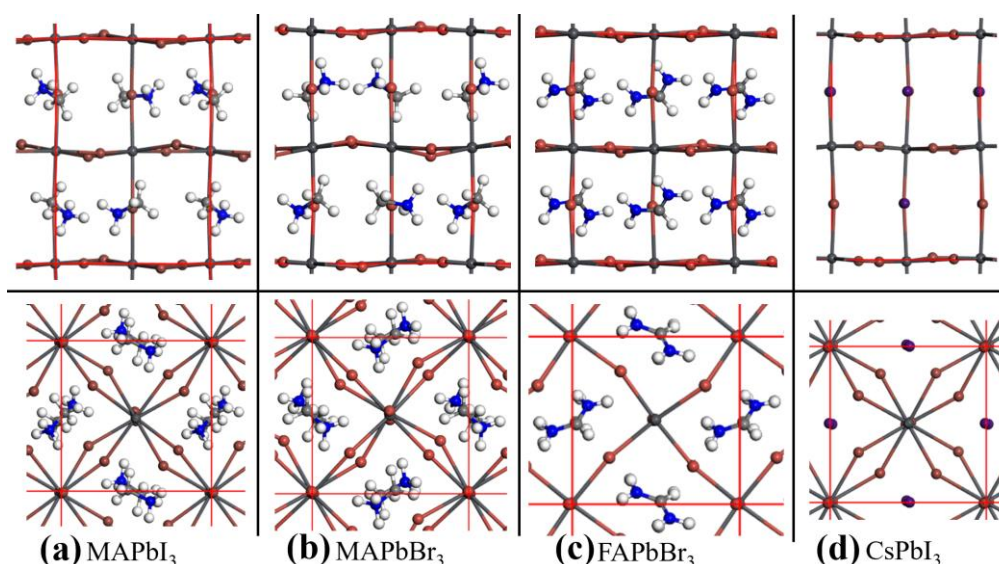


Figure 1. The optimized geometry structures of (a) MAPbI_3 , (b) MAPbBr_3 , (c) FAPbBr_3 (d) CsPbI_3 .

3. Results and Discussion

3.1. Optimized Structure

As mentioned above, the crystal structure of Pb-based HOIPs has the chemical formula APbX_3 , which consists of corner-linked PbX_6 octahedra and the A-site organic molecules (MA or FA). Under different temperature conditions, three kinds of phases (orthorhombic, tetragonal, and cubic) can be formed due to the distortion and rotation of organic molecules. Here, we studied the tetragonal phase of MAPbI_3 , MAPbBr_3 , FAPbBr_3 , and CsPbI_3 with space group $I4/mcm$ at room temperature in Figure 1. The relaxed geometries showed that these four Pb-based HOIPs with different organic molecules or halide atoms could induce various crystal structures. To ensure our calculations were reliable, we listed the bond lengths and lattice constants of these four crystal structures in Table 1. The calculated lattice constants were in good agreement with the reported data [16]. We found that the lattice constants a and b of PbI-based HOIPs were larger than those of PbBr-based HOIPs due to the relatively large radius of the I atom.

The lattice constants c depended on the size of the A-site atoms (MA, FA, and Cs). Interestingly, CsPbI₃ exhibited the largest value of the lattice constant c among these HOIPs, while FAPbBr₃ was the smallest one. Therefore, the large size of the A-site atom could lead to a relatively small c . The calculated bond length of Pb-Br indicated that organic molecules had a negligible effect on MAPbBr₃ and FAPbBr₃ due to their free distortion and rotation within the corner-linked PbX₆ octahedral cage. While the bond length of Pb-I in inorganic systems was obviously longer than that of MAPbI₃ and CsPbI₃, it was obviously shorter in organic systems. The reason might be that the small size of the Cs atom repelled the octahedral cage, stretching their bond length. The electronic properties of these four HOIPs were investigated based on the relaxed geometries.

Table 1. Calculated Lattice Constants (Å) and Bond Length of MAPbI₃, MAPbBr₃, FAPbBr₃ and CsPbI₃

	MAPbI ₃	MAPbBr ₃	FAPbBr ₃	CsPbI ₃
Pb-I	3.199	---	---	---
Pb-Br	---	3.04	3.05	3.25
Lattice Constant	$a=b=8.9$, $c=12.9$	$a=b=8.37$, $c=12.2$	$a=b=8.58$, $c=12.13$	$a=b=8.74$, $c=13.17$

3.2. Electronic Properties

The results of band structure along high symmetry k points in the first Brillouin zone of these four HOIPs systems are shown in Figure 2, indicating that all these studied Pb-based systems were direct band gap semiconductors. Meanwhile, their conduction band bottom (CBB) and the valence band top (VBT) are located in the Gama point. The band gap of MAPbI₃ is 1.60 eV, which is also consistent with the reported theoretical and experimental values [32]. There is a slight difference of 0.05 eV between the band gaps of CsPbI₃ and MAPbI₃, with the former having a slightly larger band gap. The band gap of PbBr-based systems is larger than that of PbI-based systems, which are 2.40 and 2.21 eV for MAPbBr₃ and FAPbBr₃, respectively. We demonstrate that MAPbI₃ exhibits the smallest band gap, and MAPbBr₃ owns the largest band gap in these four HOIP systems. Meanwhile, the band gap of CsPbI₃ is less than 0.56 eV for FAPbBr₃.

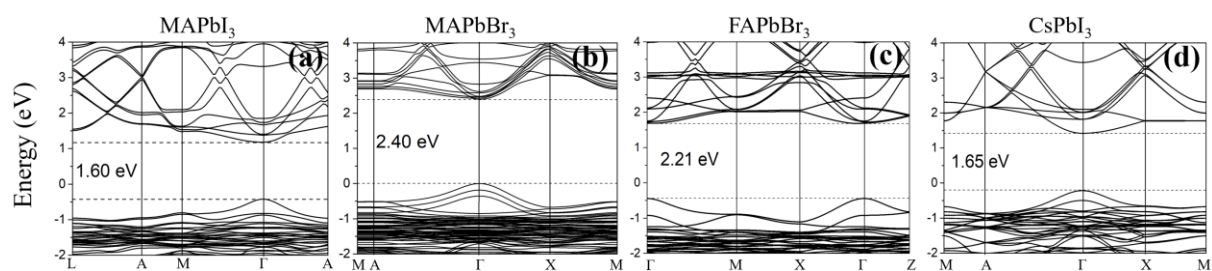


Figure 2. The calculated band gaps of (a) MAPbI₃, (b) MAPbBr₃, (c) FAPbBr₃ (d) CsPbI₃.

To better understand the origin of the valence- and conduction-band edge states of these four HOIPs systems, we further analyzed their PDOS. The VBT of MAPbI₃ was totally contributed by the I_{2p} electrons, while its CBB was mainly occupied by Pb_{2p} electrons (Figure 3a). CsPbI₃'s VBT was contributed equally by I_{2p} electrons and the Pb_{1s} electrons, whereas its CBB was still attributed by Pb_{2p} electrons, as in MAPbI₃ (Figure 3d). For MAPbBr₃ (Figure 3b), we found that both the VBT and CBB shifted to a higher energy level than MAPbI₃, which were from -0.48 to 0 eV and 1.12 to 2.4 eV, respectively. Its VBT was mainly contributed by Br_{2p} electrons and slightly by s states of Pb atoms, and its conduction band bottom was totally contributed by Pb_p electrons. Similar to CsPbI₃, the VBT of FAPbBr₃ was mainly occupied by Br_{2p} electrons and partially contributed by s states of the Pb atom, and its conduction band bottom was totally occupied by Pb_p electrons (Figure 3c). The organic molecular and Cs atom, in particular, had negligible changes to the valence- and conduction-band edge states. Based on the analysis of PDOS, we found that the CBB of all these four HOIPs systems always

stayed unchanged, which was decided by Pb_2p electrons, no matter what halide atoms or A-site atoms were replaced. It was seen that halides played an important role in the band gap of lead HOIPs materials. The large radius of a halide atom could effectively reduce the band gap of lead based HOIPs. By changing the type of X atom, we could flexibly modify their band gap and electronic properties.

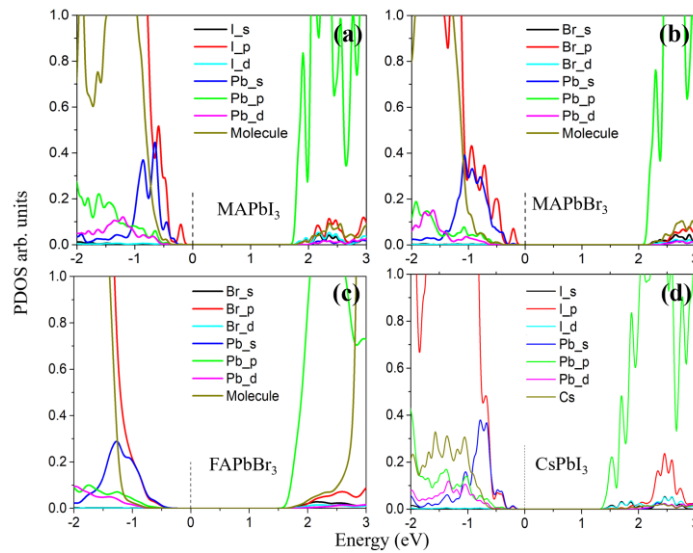


Figure 3. The PDOS of (a) MAPbI₃, (b) MAPbBr₃, (c) FAPbBr₃ (d) CsPbI₃.

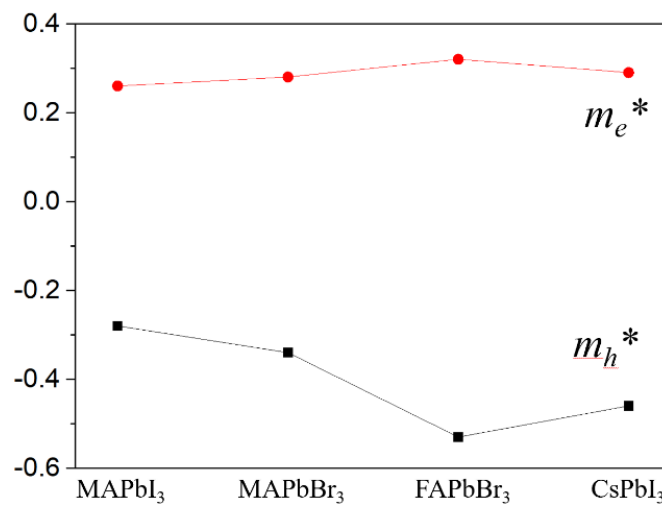


Figure 4. The calculated carrier effective mass of (a) MAPbI₃, (b) MAPbBr₃, (c) FAPbBr₃ (d) CsPbI₃.

3.3. Carrier Effective Mass

In Pb-based HOIPs, the effective mass of the charge carrier is a crucial factor that contributes to the performance of sun-light harvesting. In order to further explore the mechanism, the following equation is used to calculate the carrier effective masses (electron, m_e^* , and hole, m_h^*) of these four Pb-based hybrid organic-inorganic halide perovskites:

$$m^* = \hbar^2 \left[\frac{\partial^2 \varepsilon(k)}{\partial k^2} \right]^{-1} \quad (1)$$

where k is the wavevector and $\varepsilon(k)$ is the eigenvalues near the band edge of CBB or VBT. The results (Figure 4) showed that the m_h^* of the Pb-based HOIPs with organic molecular (MA and FA)

had a downward trend by replacing the I atom with a Br atom, then MA with FA. In other words, as an X-site atom's radius decreased (from I to Br) or the size of an organic molecular increased (from MA to FA), the m_h^* became heavier, potentially lowering the PCEs of Pb-based HOIPs, while it remained essentially unchanged in these four Pb-based systems for m_e^* . The m_h^* of CsPbI₃ was lighter than that of FAPbBr₃, but heavier than that of MAPbI₃ and MAPbBr₃. As a result, m_h^* was strongly dependent on the size of the halide atom and the A-site cation. We could effectively change their carrier effective mass by choosing the appropriate halide atom or organic molecule.

4. Conclusion

This paper used first-principles calculations-based DFT theory to investigate the structural and electronic properties of four tetragonal phases of Pb-based HOIPs (APbX₃), namely MAPbI₃, MAPbBr₃, FAPbBr₃, and CsPbI₃. We found that the values of the lattice constants *a* and *b* of PbI-based HOIPs depended on the radius of the halide atom. A relatively large halide atom could obviously increase the values of *a* and *b*, while the value of the lattice constant *c* was determined by the size of A-site cations, including organic molecular and Cs atoms. With the increased size of A-site cations, the value of *c* began to decrease. Meanwhile, organic molecules had no effect on the bond length of Pb-halide atom due to their free distortion and rotation. We also demonstrated that the electronic properties of these four HOIPs were greatly affected by lead and halide atoms. The large size of the halide atom could effectively reduce the band gap of Pb-based HOIPs due to the contributed band edge states. We could also reduce the carrier's effective mass by choosing the appropriate halide atom or organic molecule. Our predictions suggest that the properties (both structural and electronic) of hybrid organic-inorganic halide perovskite materials can be significantly altered through the process of halide atom doping or replacement. We expect that HOIPs may be outstanding alternatives to expensive silicon cells in the future.

Acknowledgments

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