First-principles investigations of structural stability and electronic band structure of CH$_3$NH$_2$BiI$_3$ for lead-free perovskite solar cell application

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Abstract. In this work, first principles density functional theory (DFT) was used to investigate the structural stability and electronic structures of CH$_3$NH$_2$BiI$_3$ lead-free perovskite. From the results, CH$_3$NH$_2$BiI$_3$ perovskite was predicted to be stable in monoclinic phase (space group $P2_1$) with lattice parameters, $a = 8.165$ Å, $b = 13.194$ Å, $c = 8.272$ Å, and $\beta = 90.03^\circ$. The formation enthalpy per formula unit ($\Delta H$) of CH$_3$NH$_2$BiI$_3$ was found to be 0.13 eV lower than the total $\Delta H$ of CH$_3$NH$_2$ molecule and bulk BiI$_3$, indicating its stability with respect to CH$_3$NH$_2$ and BiI$_3$. In addition, the chemical potential diagram shows the stable region of CH$_3$NH$_2$BiI$_3$, indicating that CH$_3$NH$_2$BiI$_3$ perovskite can be synthesized. From band structure calculations, CH$_3$NH$_2$BiI$_3$ has an indirect band gap of 1.58 eV which is comparable to 1.60 eV of CH$_3$NH$_3$PbI$_3$. However, the valence band maximum (VBM) was found to be mainly contributed by N 2p and I 5p, instead of the expected Bi 6s. It is relatively flat compared to the VBM of CH$_3$NH$_3$PbI$_3$, and thus has a larger hole effective mass. However, this theoretical prediction on monoclinic CH$_3$NH$_2$BiI$_3$ with enhanced structural stability, synthesizability, and small band gap suggests its capability to be a promising candidate in substituting the lead-based perovskite solar cells.

1. Introduction

CH$_3$NH$_3$PbI$_3$-based perovskite solar cell continues to attract great attention because its power conversion efficiency has been increased rapidly, from 3.8% in 2009 [1] to 22.1% in late 2017 [2]. However, the existence of the toxic Pb is not environmentally friendly. Recently, there are several lead-free candidates that have been proposed. Among all promising candidates, the Bi-based perovskite could be a potential candidate in replacing the Pb-based one since the contribution from Bi 6s (instead of Pb 6s) near valence band maximum (VBM) may share the same characteristic such as the excellent hole transport properties. This contribution from s orbital near VBM could be expected from other post-transition metals such as In, Sn, and Sb with the oxidation states of $+1$, $+2$, and $+3$, respectively. In addition, one more outermost valence electron of Bi than Pb atom are expected to introduce the stronger covalent bonding of Bi-I framework [3], which benefits structural stabilization.
There has been substantial interest in developing several Bi-based perovskites as the photovoltaic absorber candidates. For instance, the DFT investigation of Cs$_2$In(I)Bi(III)X$_6$ double perovskites (X= Halogen) predicted suitable materials properties, including direct band gap and small effective masses for both electrons and holes [4]. However, Cs$_2$In(I)Bi(III)X$_6$ was found to have low defect tolerance because the In(I)-based double perovskites are unstable against oxidation into In(III)-based compounds [5]. This might suggest that the post-transition metal which is stable as monovalent cation (when it replaces B-site of double perovskites) is very rare. Thus, Bi-based single perovskite (ABi(III)X$_3$) with the stable trivalent state of Bi and without the unstable monovalent cation may overcome the problem. Recently, CH$_3$NH$_2$BiI$_3$ cubic perovskite with structural stability, small band gap, and small electron effective masses has been predicted by DFT [3]. However, it has been reported that the most stable structure of this type of perovskite (such as CH$_3$NH$_3$PbI$_3$) is orthorhombic, containing 48 atoms (four formula unit, which is not a cubic perovskite) [6].

Therefore, in this work, we firstly seek the stable structure of CH$_3$NH$_2$BiI$_3$ using unit cell and atom positions obtained from the ground state crystallographic data of CH$_3$NH$_3$PbI$_3$ (space group Pnma) [6] as the initial structure for structural relaxation of CH$_3$NH$_2$BiI$_3$ (with removing one H and replacing Pb by Bi). DFT based on GGA and HSE06 was performed to investigate the electronic structures and structural stability of CH$_3$NH$_2$BiI$_3$ with its optimized structure. The predictions of synthesizability and electronic band structure of CH$_3$NH$_2$BiI$_3$ calculated in this work is expected to clarify its ability to be a novel lead-free perovskite candidate for the efficient and environment-friendly solar cells application.

2. Materials and methods

Crystallographic data of CH$_3$NH$_3$PbI$_3$ (space group Pnma) reported in Ref. [6] was adapted and used as an initial structure for the structural relaxation of CH$_3$NH$_2$BiI$_3$ under generalized gradient approximation (GGA) combined with Van der Waals correction (GGA-vdW) [7]. The relaxed structure of CH$_3$NH$_2$BiI$_3$ was then used to analyse its synthesizability and the corresponding electronic band structure.

In the details of the DFT calculation, the calculation were performed under the framework of the plane wave method implemented in Quantum-Espresso package [8], where electron-ion interactions are described using the optimized version of norm-conserving pseudopotentials under the approach of Ref. [9]. In the considered system, valence states included the C 2s and 2p states; H 1s state; N 2s and 2p states; Bi 6s, 6p, and 5d states; and I 5s, 5p, and 4d states. The generalized gradient approximation (GGA) with parameters obtained from Perdew-Burke-Ernzerhoff approach (PBE) was used. The energy cutoff of 80 was found sufficiently large for wavefunctions expansion. The k-point mesh with 4x2x4 Monkhorst-Pack grid was employed in this calculation.

To predict whether the proposed lead-free perovskite CH$_3$NH$_2$BiI$_3$ can be synthesized, it is necessary to specify the thermodynamic conditions (via chemical potential diagram) supporting the equilibrium growth of CH$_3$NH$_2$BiI$_3$ ($\mu_{\text{CH}_3\text{NH}_2} + \mu_i + 3\mu_i = \Delta H(\text{CH}_3\text{NH}_2\text{BiI}_3)$) and simultaneously preventing the occurrence of the possible competitive phases, that are BiI$_3$ ($\mu_{\text{BiI}_3} + 3\mu_i < \Delta H(\text{BiI}_3)$) and CH$_3$NH$_2$ ( $\mu_{\text{CH}_3\text{NH}_2} < \Delta H(\text{CH}_3\text{NH}_2)$), where $\mu_i, i = \text{CH}_3\text{NH}_2$, Bi, and I is the chemical potential of the constituent element and $\Delta H$ is the formation enthalpy per formula unit of the investigated compounds. Each $\mu_i$ was referred to its most stable phase, i.e. orthorhombic, monoclinic, and gas phase for I, Bi, and CH$_3$NH$_2$ respectively.

For electronic structure calculation, GGA, the Heyd-Scuseria-Ernzerhof (HSE) screened hybrid density functional[10], and spin-orbit coupling (SOC) correction have been used to calculate band gap of CH$_3$NH$_2$BiI$_3$ with the relaxed structures obtained under GGA-vdW. The HSE hybrid density functional with 25% portion of exact-exchange is suitable and previously used for the band structure calculation of CH$_3$NH$_2$BiI$_3$ cubic perovskite [3]. Thus, these parameter settings have been used throughout this work.
3. Results and discussions

It is surprising that the optimized crystal structure of CH₃NH₂BiI₃ predicted by this study’s calculation is monoclinic with space group P2₁, although the initial crystal structure used for structural relaxation is orthorhombic with space group Pnma (this space group has 8 symmetry operators) [6]. The lattice parameters at the ground state of CH₃NH₂BiI₃, a = 8.165 Å, b = 13.194 Å, c = 8.272 Å, and β = 90.03° are predicted. The obtained crystal structure of CH₃NH₂BiI₃ can be characterized by two space group symmetry operators, that are x, y, z and -x, y+1/2, -z. The crystal structure is shown in figure 1 (a). To the best of our knowledge, there is no report about CH₃NH₂BiI₃ with monoclinic symmetry (space group P2₁). Therefore, it is necessary to clarify that this novel lead-free perovskite discovered in this work can be synthesized by constructing its chemical potential diagram.

![Figure 1](image.png)

**Figure 1.** (a) Crystal structure of CH₃NH₂BiI₃ with space group P2₁. (b) The chemical potential diagram representing the available ranges of μ_Bi and μ_I for the successful preparation of monoclinic CH₃NH₂BiI₃. The stable region is represented by the narrow but long shape marked as red region.

The chemical potential diagram constructed based on the equilibrium growth condition of CH₃NH₂BiI₃, and the conditions excluding the formations of CH₃NH₂ and BiI₃ are shown in figure 1 (b). The ranges of μ_Bi and μ_I, satisfying all conditions necessary to allow the growth of monoclinic CH₃NH₂BiI₃ are found and highlighted as red area. Therefore the monoclinic CH₃NH₂BiI₃ is predicted to be synthesizable. In addition, the synthesizable region (red area) of the monoclinic CH₃NH₂BiI₃ is found to exhibit significantly wider shape than that of CH₃NH₂PbI₃ [11], indicating our proposed CH₃NH₂BiI₃ has higher ability to be prepared. This is because the ΔH of CH₃NH₂BiI₃ is found to be 0.13 eV lower than the total ΔH of CH₃NH₂ molecule and bulk BiI₃, while ΔH of CH₃NH₂PbI₃ is only 0.04 eV lower than the sum of ΔH from CH₃NH₂ and PbI₃ competitive compounds (obtained using GGA-vDW the same method as we used) [11]. However, the stable region still exhibits a narrow shape (only 0.13 eV of width), which reveals that it is still difficult to grow.

After the proposed lead-free perovskite has been clarified to be synthesizable, this predicted structure will be employed to investigate its electronic structure. Firstly, the GGA band structure has been computed and reported as shown in figure 2 (a). The material has an indirect band gap of 1.05 eV (predicted by GGA), where the VMB and CBM located at U (0.5,0,0,0.5) and Z (0.0,0,0,0.5) symmetry points, respectively. The significantly steep slope of band around CBM against the slope of band near VMB exhibits that electron effective mass is much lower than hole effective mass. The band near VBM is relatively flat compared to the VBM of CH₃NH₂PbI₃ [12], and thus has worse hole transport property. From projected density of states (PDOS) (see figure 2 (b)), the VBM was found to be mainly contributed by N 2p and I 5p, instead of the expected Bi 6s. Since small carrier effective mass is usually observed in the materials with the occurrence of spatially diffuse cation s-orbital near their VBM and CBM [13], the absence of the expected Bi 6s near VBM of CH₃NH₂BiI₃ leads to the discovery of the undesirable large hole effective mass (flat VBM).
However, since CH$_3$NH$_2$BiI$_3$ contains Bi which is the heavy element, the spin-orbit coupling (SOC) should be taken into account. Thus, the SOC correction has been performed and it is found that the band gap is deceased with the magnitude of 0.24 eV with respect to the GGA results. In addition, using HSE hybrid function increases the band gap by 0.77 eV (from 1.05 eV (GGA) to 1.82 eV). Therefore, the total change is 0.53 eV higher than GGA results. Finally, this estimation leads to the SOC-HSE band gap of 1.58 eV (see figure 2 (c)).

Figure 2. (a) GGA band structure, (b) GGA PDOS, and (c) band gaps (in eV) calculated in this work using GGA and various corrections for monoclinic CH$_3$NH$_2$BiI$_3$.

4. Conclusion
The synthesizability of monoclinic CH$_3$NH$_2$BiI$_3$ has been clarified by the validity of synthesizable area on the chemical potential diagram. The crystal structure of this stable phase (space group $P2_1$) has been presented in this work. This proposed lead-free perovskite has been predicted to have a narrow indirect band gap of 1.58 eV comparable with 1.60 eV of the widely studied CH$_3$NH$_3$PbI$_3$. In addition, the steep slope of band around CBM indicates that it has low electron effective mass while the flat shape of band near VBM reveals its large hole effective mass. Unfortunately, the Bi 6s is not the main contribution near VBM. Thus, the hole transport properties of this lead-free perovskite is not superior. From our PDOS calculation, elimination of N 2p from VBM, e.g. by replacing CH$_3$NH$_2$ with CH$_3$CH$_3$ molecule, might be a possible way to lower the hole effective mass because the flat VBM (large hole effective mass) is mainly contributed by N 2p. However, our theoretical prediction of the enhanced structural stability, synthesizability, and suitable band gap of this monoclinic CH$_3$NH$_2$BiI$_3$, still suggests its primary ability to be a candidate in substituting the lead-based perovskite solar cells.

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