Electronic structures of CsPb(X_{x}Y_{1-x})_{3} perovskites

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Abstract. We investigated electronic structures of CsPb(X_{x}Y_{1-x})_{3} perovskites, where X, Y = Cl, Br, or I, and \( x = 0, 1/3, \) or 2/3, based on the density functional theory (DFT) with generalized gradient approximation (GGA). The results show that these materials exhibit direct and inverted gaps, in the sense that the character of electronic states near the valence band maximum (VBM) is derived from atomic s-like orbital of Pb and p-like orbital of halide atom, whereas the character of states near the conduction band minimum (CBM) is derived from atomic p-like orbital of Pb in contrast with the electronic band structures of other common semiconductors. Their density of states also indicates that the optical transition in both absorption and luminescence are stronger.

1. Introduction

The use of solar cells to convert sunlight to electricity is increasing rapidly, but the relatively high cost of cells has given a new boost to research in photovoltaics (PV). Newer cell types that involve organometal halides have recently attracted a great deal of attention intensively \cite{1} as they hold strong solar absorption, low non-radiative carrier recombination rates and promise of drastic cost decreases. The efficiency of halide perovskite-based solar cells has increased rapidly, from 3.8\% in 2009 to 22.7\% in 2018 \cite{2, 3}. The basic building block of this perovskite is the ABX\textsubscript{3} perovskite structure. This simple structure consists of a 3D net-work corner-sharing BX\textsubscript{6} octahedra, where the A-cations (e.g., A = CH\textsubscript{3}NH\textsubscript{3}, NH\textsubscript{2}CH=NH\textsubscript{2}) are located in the larger 12-fold coordinated hales between the octahedron. It is typically composed of a metal cation (B = Sn, Pb, Ge) and its ligantanions (X = O\textsuperscript{2−}, Cl\textsuperscript{−}, Br\textsuperscript{−}, I\textsuperscript{−}, or S\textsubscript{2}\textsuperscript{−}). Moreover, the mixed - halide CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3−x}Br\textsubscript{x} were explored by Seok et al \cite{4}, they indicated that a low Br content gave the best initial efficiency due to a lower bandgap and reach the efficiency of 16.2\% by using the mixed - halide CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3−x}Br\textsubscript{x} with 10–15\% of Br. However, these materials still have a problem impeding them for commercialization which need to be solved i.e. they have found to be unstable under moisture, high temperature and ultraviolet soaking due to existence of organic molecule in their structure. Thus, in this work, we propose to replace an organic molecule with cesium to form CsPbX\textsubscript{3} and their alloys CsPb(X_{x}Y_{1-x})\textsubscript{3}, where X, Y = Cl, Br or I, and \( x = 0, 1/3 \) or 2/3. We choose cesium because it is the largest nonradioactive element that can hold the three-dimensional stable ideal-like perovskite structure.
2. Materials and methods
In this work, the first principle calculations were carried out within the framework of density functional theory (DFT) by using the PWSCF code as implemented in the QUANTUM ESPRESSO packages [5]. The effective interaction between valance electrons and ionic core of atom is described by norm-conserving pseudopotentials [6]. The lattice parameters, atomic positions, electronic band structures and density of states (DOS) of CsPb(X\textsubscript{x}Y\textsubscript{1-x})\textsubscript{3} were obtained by using the generalized gradient approximation (GGA) formulated by Perdew-Burke-Ernzerhofer (PBE) [7]. The single-particle Kohn-Sham wavefunction is expanded in the plane-waves basis set with a cutoff energy of 70 Ry and the corresponding Brillouin-zone integration is performed with $8 \times 8 \times 8$ Monkhorst-Pack mesh.

3. Results and discussion
The highest PbX\textsubscript{6} octahedral symmetry of cubic cesium-based halide perovskites, CsPbX\textsubscript{3} (X = Cl, Br and I) plays an important role in structural properties. The symmetry of the mixing halide perovskites, adapting the formula as CsPb(X\textsubscript{x}Y\textsubscript{1-x})\textsubscript{3}, where X, Y = Cl, Br and I, and $x = 1/3$ and 2/3, was reduced and deviated from the cubic into tetragonal structures. If we consider the xz-plane across the center of cuboid, where contains the different species of halide atoms, we will find that the ratio of lattice constants (c/a) is close to the ratio of lattice constants of cubic CsPbX\textsubscript{3} and cubic CsPbY\textsubscript{3}. The GGA lattice constants for cubic CsPbX\textsubscript{3} and tetragonal CsPb(X\textsubscript{x}Y\textsubscript{1-x})\textsubscript{3} are shown in table 1. From our results, the equilibrium lattice constants for cubic perovskites agree well with the experiments within the percentage error less than 3%. Note that, the bonding strength between Pb and halide atoms can be sorted from stronger to weaker as Pb-Cl > Pb-Br > Pb-I, corresponding to an ability to attract electrons of halide atoms known as electronegativity.

Table 1. GGA lattice constants and band gaps of CsPb(X\textsubscript{x}Y\textsubscript{1-x})\textsubscript{3}, where X, Y = Cl, Br or I and $x = 0, 1/3$ or 2/3.

| Crystal | Lattice parameters (Å) | Band gaps (eV) |
|---------|------------------------|----------------|
|         | GGA               | Exp. | GGA   | Exp. |
| CsPbCl\textsubscript{3} | a = b = c = 5.738 | 5.605\textsuperscript{a} | 2.24 | 3\textsuperscript{c} |
| CsPbBrCl\textsubscript{2} | a = b = 5.736, c = 6.025 | 2.41 | - |
| CsPbClBr\textsubscript{2} | a = b = 6.019, c = 5.722 | 1.83 | - |
| CsPbI\textsubscript{2} | a = b = 5.748, c = 6.430 | 1.67 | - |
| CsPbBr\textsubscript{3} | a = b = c = 6.000 | 5.874\textsuperscript{b} | 1.77 | 2.3\textsuperscript{c} |
| CsPbIBr\textsubscript{2} | a = b = 5.997, c = 6.409 | 1.53 | - |
| CsPbClI\textsubscript{2} | a = b = 6.419, c = 5.696 | 1.54 | - |
| CsPbBrI\textsubscript{2} | a = b = 6.395, c = 5.974 | 1.49 | - |
| CsPbI\textsubscript{3} | a = b = c = 6.363 | 6.289\textsuperscript{b} | 1.44 | 1.73\textsuperscript{d} |

\textsuperscript{a}Moreira et al [8], \textsuperscript{b}Trots and Myagkota [9]
\textsuperscript{c}Kazuo Ges et al [10], \textsuperscript{d}Ahmad et al [11]

Then, the band structures of all CsPb(X\textsubscript{x}Y\textsubscript{1-x})\textsubscript{3} perovskites were also calculated by DFT-GGA. We have shown here only the band structures of CsPbCl\textsubscript{3} and CsPbClBr\textsubscript{2} calculations as examples of cubic and tetragonal structures respectively. This is because the band-characteristics of other compounds are similar. They exhibit direct band gaps as shown in figure 1 and figure 2. For the cubic phase it occurs at R point as seen in figure 1 whereas for the tetragonal structure of the mixed halide perovskite, it occurs at A point as seen in figure 2. Note that, both R and A points are at the corner of BZ cell. The GGA band gaps of CsPb(X\textsubscript{x}Y\textsubscript{1-x})\textsubscript{3} are also presented in table 1 and compared to the available experimental band gaps of CsPbCl\textsubscript{3},...
CsPbBr₃ and CsPbI₃. As expected, GGA band gaps underestimate the actual band gaps due to its self-interaction error. This is the well-known issue, however, GGA still give reliable results for lattice constants and can be used for preliminary analysis of DOS.

Next, the total DOS and partial density of states (PDOS) were computed for analyzing the contribution of atomic-like orbitals to the band structure. The calculated PDOS of CsPbCl₃ and CsPbClBr₂, as shown in figure 3 and figure 4 illustrate that the VBM of all CsPb(XₓY₁−ₓ)₃ is mainly contributed from s-like orbital of Pb and p-like orbital of halides, whereas the CBM is mainly contributed from p-like orbital of Pb. This implies that the unique characteristic band structure of halide perovskites is “inverted” in the sense that its character is in contrast with the conventional semiconductors. For those common materials the CBM is primarily dominated by s-like orbital, whereas the VBM typically dominated by p-like orbital. Note that, in all CsPb(XₓY₁−ₓ)₃ compounds, the atomic-like orbital of Cs is far away from the band edges of VBM and CBM. This indicates that Cs, as the A-site cation, does not contribute to the band edges of halide perovskite. Actually, the significant role of Cs in the perovskite structure is to keep charge neutrality and to hold the stable three-dimensional structure. According to the dipole selection rule, the allowed transition occurs when those two states satisfied ∆l = ±1. Thus the transition from s-like of VBM to p-like of CBM of the halide perovskite is allowed and moreover it is a transition in the same atomic specie. This indicates that these halide perovskite compounds exhibit strong optical absorption and fluorescence emission between the edges of valence and conduction band.

Lastly, the band structure variation of CsPb(BrₓCl₁−ₓ)₃, when the compositional fraction x of Br was varied as x = 0, 1/3, 2/3 and 1, was investigated. As seen in figure 1, the CBM of cubic CsPbCl₃ is three-fold degenerate (not take spin degeneracy into account) whereas the VBM
is non-degenerate. This also happens in CsPbBr$_3$ and CsPbI$_3$. However, in case of tetragonal phase as shown in figure 2, the band near CBM turns to be two-fold degenerate. The degeneracy of CBM in cubic CsPbX$_3$ is relevant to symmetry of cubic under rotation with 90 degree around all axes of primitive basis, while the tetragonal structure has a rotational symmetry less than a cubic, i.e. the conventional unit cell of tetragonal is cuboid ($a = b \neq c$) thus although there exists a rotation symmetry of 90 degree around c-axis, there is no rotation symmetry of 90 degree when rotate around a- and b- axes resulting in degeneracy breaking of band near CBM. This splitting of band around CBM of tetragonal structures also occurs in CsPb(I$_x$Cl$_{1-x}$)$_3$ and CsPb(Br$_x$I$_{1-x}$)$_3$. The reason for this is that the CBM of halide perovskites is contributed from p-like orbital of B-site atom which has three-fold degeneracy, however if there is a perturbation to the system the splitting will occurs, and here the perturbation is due to mixing halide in perovskite. Although we expect strong optical transition in these perovskites, the band splitting near CBM might lower the transition intensity in CsPb(X$_x$Y$_{1-x}$)$_3$.

4. Conclusion
We investigated electronic structures of CsPb(X$_x$Y$_{1-x}$)$_3$ perovskites, where X, Y = Cl, Br or I, and $x = 0, 1/3$ or $2/3$, based on DFT with GGA approximation. We found that in case of $x \neq 0$, the cubic phase transform to the into tetragonal phase. From band structure and PDOS investigation, these materials exhibit direct and inverted gaps, i.e. the s-like orbital of Pb and p-like orbital of halide atoms are the main contribution to VBM, whereas the p-like orbital of Pb is the main contribution to CBM, which is in contrast with those in other common semiconductors. Moreover, electrons from Cs do not contribute to the band edges. This implies that the role of Cs is only to keep charge neutrality and to hold the structure stability. We also found that the optical transition in both absorption and luminescence of these materials should be strong because the transition can occur from s-Pb orbital in VBM to p-Pb orbital in CBM. In mixed halide perovskite, the symmetry reduction can lower the intensity of transition, but we can trade this weak point with the ability to tune band gaps. Balancing between the number of collected electrons corresponding to band gap and exciting electrons depending on the degeneracy at band edges is still challenge for further investigation.

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