Density Functional Theory Study on the Electrical Properties of α-CsPbX$_3$ (X=I, Cl, Br)

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Abstract

All-inorganic perovskite solar cells have become more important in the commercialization of the photovoltaic devices. In this study the structural, electronic properties of inorganic metal halide cubic perovskites CsPbX$_3$ (X = I, Br, Cl) for perovskite solar cells are simulated using first-principles Density Functional Theory (DFT). The newly adjusted parameters make the calculations more accurate. These compounds are semiconductors with direct band gap energy. Results suggest that the α-CsPbX$_3$ (X=I, Cl, Br) have a wide bandgap adjustment range with potential application in solar cells and other optoelectronic energy devices. On the basis of the electronic properties, one can expect that the α-CsPbI$_3$ would be a better used to perovskite solar cell. α -CsPbCl$_3$ and α-CsPbBr$_3$ better suitable for others photovoltaic device.

Keywords: All-inorganic perovskite; α-CsPbX$_3$ (X=I, Cl, Br); electronic properties; DFT.

1.Introduction

All-inorganic perovskite solar cell materials have shown significantly improved performance in recent years. metal halide perovskites have drawn a great attention in the scientific community due to their remarkable performance in solar cells thanks to their outstanding opto-electronic properties such as suitable bandgap, high optical absorption, broad absorption spectrum, long charge diffusion lengths and high charge carrier mobility [1-5]. Metal halide perovskite materials are expressed as ABX$_3$ in chemical formula, where A and B are monovalent and divalent cations and X is a halogen anion [6].

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α-CsPbX$_3$ (X=I, Cl, Br) perovskite materials containing halogen elements are widely used in solar cells. Among them, the conversion efficiency of α-CsPbI$_3$ has reached 17.1% [7]. From the first report to the present, all inorganic perovskite α-CsPbI3, α-CsPbBr3, α-CsPbCl3, α-CsSnI3, α-CsGeI3 have been extensively studied, α-CsPbI3, α-CsPbBr3, α-CsPbCl3 showed good band gap and photoelectric conversion properties. Further development of α-CsPbX$_3$ (X=I, Cl, Br) semiconductor materials for other photovoltaic applications, a deeper and fundamental understanding the electronic properties of the semiconductors is necessary. Therefore, it is important to understand the difference in electronic properties between α-CsPbX$_3$ (X=I, Cl, Br) materials [8-11]. The investigation of the electronic properties of solids is important for better understanding the optical properties of the materials. The study of the electronic properties also reveals the response of a material to light. Therefore, the structure and electrical properties of the material are calculated by density functional theory. The results show that as the doping ionic radius increases, the band gap of α-CsPbX$_3$ (X=I, Cl, Br) decreases, the band gaps of CsPbI$_3$ (1.483eV), and CsPbBr$_3$ (1.782 eV) are suitable for use in solar cells.

2. Theoretical model and calculation method

The first-principles density functional theory (DFT), calculations have been performed using the plane wave pseudopotential method as implemented in CASTEP module of Materials Studio 2017[12-14]. The geometric structure of each α-CsPbX$_3$ (X=I, Cl, Br) sample was optimized using the generalized gradient approximation (GGA) and Perdew–Burke–Ernzerhof (PBE) functional with a cutoff energy of 500 eV [15]. The Brillouin zone was sampled with 8×8×8 Monkhorst and Pack k-points. The convergence thresholds of 1×10^{-5} eV/atom for the total energy, 0.03 eV/Å for the maximum force [16-18], 0.05 GPa for maximum stress, and 1×10^{-3}Å for the maximum displacements were used to optimize the geometry of crystal structure. Electronic properties of all samples were simulated based on the crystal structures.

3. Crystal structure

In the Fig. 1, show that crystal structure of perovskite. In the Table. 1, show that lattice constant of α-CsPbX$_3$ (X=I, Cl, Br) perovskite. The unit cell volume of α-CsPbBr$_3$ and α-CsPbCl$_3$ is smaller than that of α-CsPbI$_3$, because Cl (1.81Å) and Br (1.96Å) are smaller than the I (2.2Å) ion radius [18-19], the unit cell volume is reduced. This trend is consistent with the experimental results in other articles.
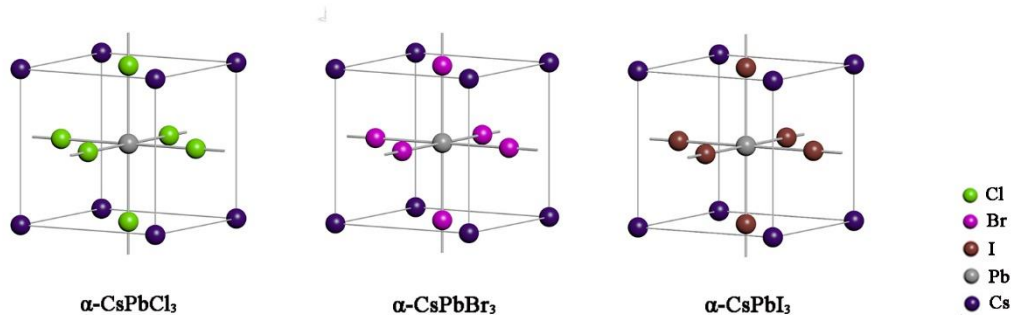

Figure 1: crystal structure of α-CsPbX$_3$ (X=I, Cl, Br). green, brownish, pink, grey, and purple spheres denote Cl, I, Br, Pb, and Cs, respectively.

Table 1: Calculated lattice parameters of α-CsPbX$_3$ (X=I, Cl, Br).

Formula	a	b	c	V
α-CsPbI$_3$	6.4043Å	6.4043Å	6.4043Å	262.6737Å^3
α-CsPbBr$_3$	5.9983Å	5.9983Å	5.9983Å	215.8197Å^3
α-CsPbCl$_3$	5.7341Å	5.7341Å	5.7341Å	188.5400Å^3

4. Electronic properties

In the Table. 2, show that bandgap value of α-CsPbX$_3$ (X=I, Cl, Br) perovskite. This work calculated bandgaps have a good agreement with previous theoretical works and experimental results [20]. In the Fig. 2~ Fig. 4, α-CsPbX$_3$ (X=I, Cl, Br) perovskites have a direct bandgap in cubic phase at the R point. The results show that dope ion radius decrease lead to causes the bandgap to increase which has been denoted in the band structure. The interaction between the p-orbital of the Cl and Br atom and the s-orbital of the Pb atom is greater than the interaction between the p-orbital of the I atom and the s-orbital of the Pb atom. In α-CsPbCl$_3$, the minimum value of the conduction band has a considerable upward shift, and the band gap of the compound is larger than that of α-CsPbBr$_3$ and α-CsPbI$_3$.The study of the electronic band structure suggests that the pattern of the band structure is almost not affected by difference in the radius of the halogen ions. Due to this characteristics, α-CsPbX$_3$ (X=I, Cl, Br) are suitable to be used in light emitting diodes as the band gap of these materials can easily be tuned by changing the halogen elements while the other properties remain almost same.
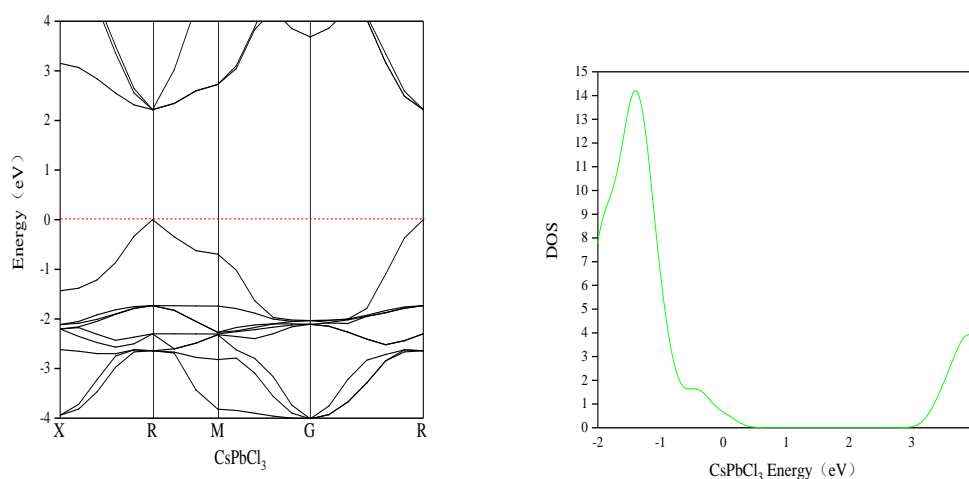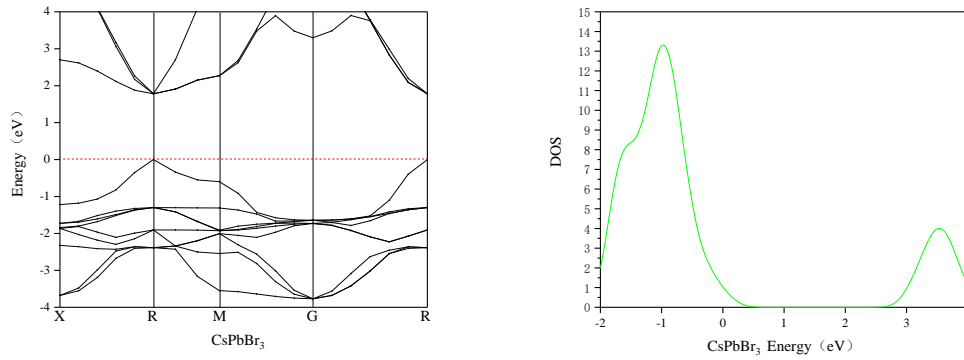

Figure 2: Band structure and DOS of α-CsPbCl$_3$.

Figure 3: Band structure and DOS of α-CsPbBr$_3$.

In order to study the electronic properties more carefully, their density of states have been shown in Fig. 2~ Fig. 4. On the picture of DOS, bandgap of each structure is clear too. The area where DOS is zero represents the bandgap which is the same as designated values in band structure of each compound.
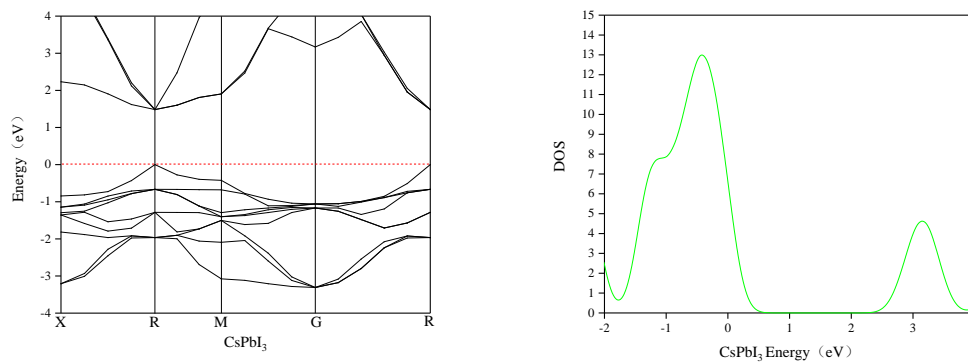

Figure 4: Band structure and DOS of α-CsPbI$_3$.

Table 2: Band gap of α-CsPbX$_3$ (X=I, Cl, Br) perovskite material.

Formula	This work Eg	Other work Eg	Experiment Eg
α-CsPbI$_3$	1.483eV	1.479eV	1.73 eV
α-CsPbBr$_3$	1.782 eV	1.796 eV	2.3 eV
α-CsPbCl$_3$	2.219eV	2.202 eV	3.0 eV

5. Conclusion

In this study, the structural and electronic properties of α-CsPbX$_3$ (X=I, Cl, Br) have been investigated using density functional theory simulation. Research indicates, the ionic radii of the halogen elements are different,

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this results in a difference in the unit cell volume of the α-CsPbX3 (X=I, Cl, Br) material, resulting in the band gap of α-CsPbX$_3$ (X=I, Cl, Br) tunable from 1.486eV to 2.219eV. The α-CsPbI$_3$ and α-CsPbBr$_3$ can be applied to solar cells due to the small band gap value. The ionic radius of the halogen element in α-CsPbX$_3$ (X=I, Cl, Br) does not change the band structure of α-CsPbX$_3$ (X=I, Cl, Br), because the band gap structure of the material is related to the lattice structure of the material, the change in ionic radius does not affect the lattice structure of the material, so the three materials have similar energy band diagrams, Therefore, α-CsPbX$_3$ (X=I, Cl, Br) is suitable for the light emitting diodes (LED). The three materials involved in this research have important guiding significance for the future development of solar cells and LEDs.

Acknowledgement

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