Materials Research Express

PAPER

Interstitial doping of K and Mn induced structural distortion and electronic properties changes in all-inorganic CsPbI\(_2\)Br perovskite

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Keywords: CsPbI\(_2\)Br perovskite, interstitial doping, structural distortion, electronic properties, first-principles calculations

Abstract

CsPbI\(_2\)Br and its derivatives are promising light harvesters for all-inorganic perovskite photovoltaic devices, whereas the effects of doping on local lattice structures and electronic properties of CsPbI\(_2\)Br remain unclear. Here the structural distortion and the electronic properties changes of CsPbI\(_2\)Br caused by the interstitial alkali-metal K and transition-metal Mn dopants were investigated from first-principles calculations. The bond lengths, bond angles, distortion magnitude and volume of both PbI\(_4\)Br\(_2\) octahedrons and dopant-occupied octahedral interstices, as well as density of states and crystal orbital Hamilton population were provided. We found that both the PbI\(_4\)Br\(_2\) octahedrons neighboring to Mn atom and the Mn-occupied octahedral interstice undergo a more significant structural distortion than those in the K-doped CsPbI\(_2\)Br. Contrary to the exothermic K-doping, the endothermic Mn-doping reduces the volume of Mn-occupied octahedral interstice by shrinking Mn-Br-I atomic plane and elongating Cs-Cs interatomic distance. The interstitial K-doping has little effect on the position and orbital component of valance band (VB) maximum and conduction band (CB) minimum of CsPbI\(_2\)Br, while the interstitial Mn-doping can not only shift up the VB edge by 0.41 eV but also introduce new unoccupied gap states (Mn-3d states) at the CB edge.

1. Introduction

Organic-inorganic hybrid perovskite solar cells (PSCs) have made a great progress on their certified power conversion efficiency (PCE), which increased from 3.8% to 25.7% in the past decade [1–4]. However, the thermally unstable and inherently volatile organic components in hybrid perovskite solar cells are the biggest obstacle to the commercial application in harsh operating environments. The replacement of organic components in hybrid perovskites with inorganic components (e.g., Cs\(^+\)) is a potential method to eliminate this obstacle. Hence, all-inorganic perovskites such as cesium lead halides CsPbX\(_3\) (X = Cl, Br and I) and so forth have been extensively explored for photovoltaic applications recently, due to their attractive optoelectronic properties and intrinsic thermal stability.

However, the application of all-inorganic halide perovskites into photovoltaic devices is still challenging. Although the bandgap (1.73 eV) of CsPbI\(_3\) matches better with the solar spectrum than that of CsPbBr\(_3\) (2.3 eV), the phase instability of the former is more notable. CsPbI\(_3\) usually undergoes the phase transition from (pseudo-) cubic black phases to non-perovskite yellow phase at room temperature, due to the insufficient size of Cs\(^+\) for holding the PbI\(_4\) octahedrons in its lattice [5–12]. Recently, some important methods such as functionalization/ doping, size-dependent, morphology control, alloying, and engineering have been used to improve the material properties. Among them, doping process has been subject of intensive research to make suitable material properties for use of it in wide range of applications [13–16]. For example, to improve the phase stability of cesium lead halide perovskites, the partial substitution of X-site anions in CsPbX\(_3\) perovskite was proposed [10, 17]. In the mixed-halide CsPbI\(_{3-x}\)Br\(_x\) perovskites, it was found that CsPbI\(_3\)Br has not only a suitable bandgap of 1.92 eV but also a considerably high ambient stability, implying that the composition engineering would be an...
effective strategy for stabilizing crystal [18]. Moreover, there have been many metal cations with smaller ionic radii including K\(^{+}\), Mn\(^{2+}\), Co\(^{2+}\), Zn\(^{2+}\), Ge\(^{2+}\), Sr\(^{2+}\), Eu\(^{2+}\) and Ba\(^{2+}\) introduced into the interstitial or substitutional sites of cesium lead halide perovskites, with various purposes like enhancing phase stability, manipulating crystallization process, passivating defects, optimizing energy band, suppressing ion migration, improving optoelectronic properties, etc [19–26]. It is worth noting that some experimental results showed that the alkali metal ion K\(^{+}\) prefers to substitute for Cs\(^{+}\), while some other researches proved from both experimental and theoretical perspectives that K\(^{+}\) ions are energetically to occupy the interstitial sites of perovskite lattices such as MAPbI\(_3\), FAMAPbI\(_2\)Br\(_{0.875}\)(CsPbBr\(_3\))\(_{0.125}\) and so on [27–29]. Besides this, Liu et al found that the transition metal ions Mn\(^{2+}\) are more likely to be inserted into the intertices of CsPb\(_3\)Br lattice during the growth of CsPb\(_3\)Br film, which was believed to be helpful for reducing the recombination loss of electrons and improving the extraction efficiency of holes [20]. As found in our previous work, the Fermi level enters the conduction bands of the CsPb\(_3\)Br system where a Mn atom was doped interstitially, making the system a n-type semiconductor material with enhanced conductivity [30].

The lattice structure of CsPb\(_3\)Br is composed of the corner-sharing octahedral network of PbI\(_4\)Br\(_2\) with Cs atoms at the center of cub-octahedral cavities. As the framework of CsPb\(_3\)Br is mainly made up of the octahedral units of PbI\(_4\)Br\(_2\), so any changes in the framework structure could be reflected by the changes in Pb-I/Br bond lengths and/or I-Pb-Br bond angles of the octahedrons. The centrally coordinated octahedrons of PbI\(_4\)Br\(_2\) can widely affect CsPb\(_3\)Br’s properties due to the flexibility of octahedrons. Because of the size-mismatch and interplay between dopant and host atoms, the elemental doping inevitably causes charge redistribution and local distortion of host lattice via changing bond lengths and angles, and thus leads to considerable distortions in the high symmetric structure of CsPb\(_3\)Br and changes in physical properties. It has been demonstrated that there is a strong coupling between the structural distortion of perovskite and its magnetic behavior [31]. Therefore, finely controlling the structural distortion is much-needed to better functionalize CsPb\(_3\)Br perovskite. However, the interstitial doping induced changes in local lattice structures and electronic properties of CsPb\(_3\)Br remain far from clear at the atomic and electronic levels up to now. For this reason, the alkali metal element K and transition metal element Mn, which had already been used to improve the properties of perovskites experimentally [19, 20, 30], were chosen as representative dopants in the present work, to unravel the effect of interstitial doping on the structural and electronic properties of CsPb\(_3\)Br perovskite.

2. Computational details

Based on the previous optimized lattice parameters of CsPb\(_3\)Br unit cell (space group Pnma) including 1 Cs, 1 Pb, 2 I and 1 Br atoms [30], a 2 × 2 × 2 supercell of CsPb\(_3\)Br consisting of 40 atoms in total was built, in which one K or Mn atom was further doped into an interstitial site and thus the doping concentration is 2.5%. All calculations were performed within the framework of density functional theory (DFT) by using the Vienna ab initio simulation package (VASP) code [32] with a plane-wave basis. The electronic configuration of Cs, Pb, I, Br, K and Mn atoms is \([\text{Xe}]6s^1, [\text{Xe}]5d^{10}6s^26p^6, [\text{Kr}]4d^{10}5s^25p^6, [\text{Ar}]3d^{10}4s^24p^6, [\text{Ar}]4s^1\) and \([\text{Ar}]3d^34s^2\), respectively. The Perdew–Burke–Ernzerhof (PBE) functional of generalized gradient approximation (GGA) was used to describe the exchange-correlation interactions between electrons [33]. The electron–ion interactions as contained in atomic pseudopotentials were described by the frozen-core projector augmented wave (PAW) method. Integrals over the Brillouin-zone were performed on \(\Gamma\) -centered symmetry-reduced Monkhorst-Pack \(k\)-point meshes [34]. After a series of convergence tests, the plane-wave cutoff energy was set to 400 eV, and the grid of \(k\)-points employed for geometry optimizations and calculations of density of states (DOS) was taken as \(4 \times 4 \times 4\) and \(8 \times 8 \times 8\), respectively. Gaussian smearing with 0.1 eV smearing width was used to all structural relaxations and the tetrahedron method with Blöchl corrections was applied for all static total energy calculations and DOS calculations. Spin–polarization was considered in the calculations of Mn-doped CsPb\(_3\)Br due to the ferromagnetism of Mn atom.

In order to evaluate the difficulty of interstitial doping, the solution energy \(E_{\text{sol}}\) of K and Mn doped into CsPb\(_3\)Br was calculated. The solution energy here refers to the energy required for an atom to enter the octahedral interstice of CsPb\(_3\)Br lattice, and can be calculated as follows [35]:

\[
E_{\text{sol}} = E_X - E_{\text{pure}} - \mu
\]

where \(E_X\) and \(E_{\text{pure}}\) are the total energy of CsPb\(_3\)Br supercell doped with and without interstitial atom \(X (X = \text{K and Mn})\), respectively, and \(\mu\) is the chemical potential of \(X\) atom and was calculated with respect to equilibrium phase. If \(E_{\text{sol}}\) is positive, the doping process would be endothermic. Generally, an element with high positive \(E_{\text{sol}}\) is expected to have a low solubility in CsPb\(_3\)Br matrix. On the contrary, the doping process would be spontaneously exothermic when \(E_{\text{sol}}\) is negative.
E_{\text{sol}} can be further decomposed into the components of mechanical energy (E_{\text{M}}) and chemical energy (E_{\text{C}}) \cite{36}. The mechanical energy E_{\text{M}} is defined as the energy release of the lattice relaxation of CsPbI_{2}Br after the dopant is removed. Thus, E_{\text{M}} is represented by the doping induced change in total energy of CsPbI_{2}Br host lattice. The chemical energy E_{\text{C}} originates from the interaction of dopant with host lattice and is defined as the energy needed to remove the dopant without a relaxation of host lattice. E_{\text{C}} always improves the binding strength between dopant and host lattice. E_{\text{M}} and E_{\text{C}} were calculated as follows:

\[ E_{\text{M}} = E_{X\text{clean}} - E_{\text{pure}} \]

\[ E_{\text{C}} = E_{X} - E_{X\text{clean}} - \mu \]

Where \( E_{X\text{clean}} \) represents the total energy of CsPbI_{2}Br supercells which were the rest lattices obtained by removing the interstitial atom X from X-doped CsPbI_{2}Br and were not relaxed.

3. Results and discussions

3.1. Interstitial doping induced structural distortions of CsPbI_{2}Br

As shown in figure 1 (a), the ideal PbI_{4}Br_{2} octahedrons contained in the undoped CsPbI_{2}Br supercell keep highly symmetric and the same with each other. By contrast, the interstitial doping of K or Mn atom deforms the PbI_{4}Br_{2} octahedrons adjacent to dopant by breaking their symmetry, as shown in figures 1 (b) and (c). The local structures of octahedral interstices containing K and Mn atoms are displayed in figues 1 (d) and (e), respectively. In order to have a deep-going understanding on the interstitial doping induced structural changes in CsPbI_{2}Br supercell, not only the volume of doped and undoped CsPbI_{2}Br supercells and interstices therein, but also some structural parameters, including bond lengths and angles, magnitudes of distortion (i.e., standard deviations of bond lengths and angles) \cite{37, 38} and volumes, for the PbI_{4}Br_{2} octahedrons adjacent to interstitial dopants and the dopant-occupied octahedral interstices were determined after structural relaxations.

As shown in figure 2, the volume of K- and Mn-doped CsPbI_{2}Br supercells is larger than that of the undoped one, meaning that the interstitial doping of K and Mn atoms leads to the expansion of CsPbI_{2}Br lattice, which agrees well with the experimental results \cite{20, 39}. Besides this, the K-doped CsPbI_{2}Br supercell has a larger volume than the Mn-doped one, due to the larger radius of K atom than that of Mn atom. By using the Crystal Explorer 3.1 software (isovalue: 0.002, quality: high), the interstice volume of doped and undoped CsPbI_{2}Br supercells and interstices therein, but also some structural parameters, including bond lengths and angles, magnitudes of distortion (i.e., standard deviations of bond lengths and angles) \cite{37, 38} and volumes, for the PbI_{4}Br_{2} octahedrons adjacent to interstitial dopants and the dopant-occupied octahedral interstices were determined after structural relaxations.

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As the ideal PbI_{4}Br_{2} octahedrons in the undoped CsPbI_{2}Br supercell are totally the same with each other, so the measured volumes of such high-symmetric PbI_{4}Br_{2} octahedrons are equal to 41.62 Å³, as shown in table 1. Both the Pb-I/Br bond lengths and the I-Pb-Br bond angles in each ideal PbI_{4}Br_{2} octahedron are the same with each other. By contrast, in the interstitially K- and Mn-doped CsPbI_{2}Br supercells, the structure of PbI_{4}Br_{2}...
octahedrons adjacent to K and Mn atoms is significantly distorted with asymmetric bond lengths and angles. That is, both the bond lengths and angles of the PbI$_4$Br$_2$ octahedrons adjacent to K and Mn dopants are no longer equal with each other, signaling that the interstitial doping of K and Mn dopants in the K- and Mn-doped CsPbI$_2$Br supercells, as compared with those of PbI$_4$Br$_2$ octahedrons in the undoped CsPbI$_2$Br.

From table 1, we can also see that the volume of these PbI$_4$Br$_2$ octahedrons in the K- and Mn-doped CsPbI$_2$Br supercells is 42.58 Å$^3$ and 42.36 Å$^3$, increasing by about 2.31% and 1.78% as compared with the distortion-free octahedrons in the undoped CsPbI$_2$Br supercell, respectively. The volume expansion of PbI$_4$Br$_2$ octahedrons adjacent to the dopants should be attributed to the extension of average bond length caused by the interstitial doping. Although the average bond length of PbI$_4$Br$_2$ octahedrons neighboring to the K atom is shorter than the Mn atom, the volume and its expansion of PbI$_4$Br$_2$ octahedrons neighboring to the K atom are larger, which should be related to the interstitial doping induced distinct changes in the bond angles of PbI$_4$Br$_2$ octahedrons.

From table 2, it is clear that the octahedral interstices in which the dopant atoms are occupying, also undergo structural distortions as characterized by the standard deviations of bond lengths and angles, in comparison with the undistorted octahedral interstices in the undoped CsPbI$_2$Br supercell. Moreover, the structural distortion of Mn-occupied octahedral interstice is more significant than that of K-occupied octahedral interstice, due to the

![Figure 2. Supercell and interstice volumes of undoped and interstitially K-and Mn-doped CsPbI$_2$Br.](image)

**Table 1.** Bond lengths ($d$ (Å)) and angles ($\alpha$ (°)) and their average values $\bar{d}$ (Å) and $\bar{\alpha}$ (°), standard deviations $\sigma(d)$ and $\sigma(\alpha)$, volume $V_i$ (Å$^3$) as well as the interstitial doping induced change in volume $\Delta V_i$ (Å$^3$) of PbI$_4$Br$_2$ octahedrons adjacent to K and Mn dopants in the K- and Mn-doped CsPbI$_2$Br supercells, as compared with those of PbI$_4$Br$_2$ octahedrons in the undoped CsPbI$_2$Br.

| CsPbI$_2$Br    | $d$   | $\bar{d}$ | $\sigma(d)$ | $\alpha$ | $\bar{\alpha}$ | $\sigma(\alpha)$ | $V_i$  | $\Delta V_i$ |
|----------------|-------|-----------|-------------|----------|---------------|-----------------|--------|--------------|
| Undoped        | $d_{\text{Pb-I}} = 3.15$ | 3.15 | 0.00 | $\alpha_{\text{Pb-Br}} = 90.00$ | 90.00 | 0.00 | 41.62 | — |
| K-doped        | $d_{\text{Pb-I}} = 3.14$ | 3.15 | 0.05 | $\alpha_{\text{Pb-Br}} = 82.50$ | 90.46 | 3.40 | 42.58 | 2.31% |
| Mn-doped       | $d_{\text{Pb-I}} = 3.21$ | 3.19 | 0.08 | $\alpha_{\text{Pb-Br}} = 87.98$ | 89.90 | 9.31 | 42.36 | 1.78% |
Table 2. Bond lengths $d$ (Å) and angles $\alpha$ (°) and their average values $\bar{d}$ (Å) and $\bar{\alpha}$ (°), standard deviations $\sigma(d)$ and $\sigma(\alpha)$, volume $V_2$ (Å$^3$) as well as the interstitial doping induced change in volume $\Delta V_2$ (Å$^3$) of dopant-occupied octahedral interstices in the K- and Mn-doped CsPbI$_2$Br supercells, as compared with those of octahedral interstices in the undoped CsPbI$_2$Br supercell.

| Structural parameters | CsPbI$_2$Br | K-doped | Mn-doped |
|-----------------------|------------|---------|----------|
| $d_{Cs-Br}$          | 4.45       | 5.13    | 4.58     |
| $d_{Cs-I}$           | 4.45       | 5.42    | 4.84     |
| $d_{Br-I}$           | 4.45       | 4.72    | 3.87     |
| $\sigma(d)$          | 0.00       | 0.28    | 0.41     |
| $\sigma(\alpha)$     | 0.00       | 0.00    | 0.00     |
| $V_2$ (Å$^3$)        | 41.62      | 60.26   | 60.00    |
| $\Delta V_2$ (Å$^3$) | —          | 44.43%  | 44.35%   |

larger $\sigma(d)$ and $\sigma(\alpha)$ of Mn-occupied octahedral interstice. The doping of K atom increases the volume of the occupied octahedral interstice from 41.62 Å$^3$ to 60.11 Å$^3$, with a percentage increase of 44.43%. Comparing the bond lengths and angles of K-doped octahedral interstice with those of undoped octahedral interstice, we can see that the K doping elongates all of the bonds or atomic distances of the octahedral interstice, as shown in table 2. This is because that K and Cs are from the same group of elemental periodic table and the repulsive interaction between them may force the K and Cs atoms to part from each other, resulting in the increase of Cs-Cs interatomic distance in the octahedral interstice. Hence, both Cs-Br and Cs-I bond lengths are increased after the K atom is doped into the octahedral interstice. Moreover, the increase in these two kinds of bond lengths is larger than the increase in the Br-I distances, as shown in table 2. The increase in the Br-I distances also indicates the expansion of K-Br-I atomic plane of the octahedral interstice. As a result, the increase of Cs-Cs interatomic distance and the expansion of K-Br-I atomic plane should be the main reasons for the volume expansion of K-doped octahedral interstice.

By contrast, the doping of Mn atom decreases the volume of the octahedral interstice from 41.62 Å$^3$ to 37.73 Å$^3$ and the percentage decrease in volume is about 9.35%, as shown in table 2. The doping of Mn atom shrinks the Mn-Br-I atomic plane and elongates the Cs-Cs interatomic distance of the octahedral interstice, as proved by the obvious decrease in the Br-I interatomic distances and the slight increase in the Cs-Br and Cs-I bond lengths. Therefore, it is concluded that the Mn atom in the octahedral interstice may play a role in attracting its I and Br neighbors and repelling the Cs atoms and thus decreases the volume of the octahedral interstice. Here, the shrinkage of Mn-Br-I atomic plane and the elongation of Cs-Cs interatomic distance of the Mn-occupied octahedral interstice are highly considered to be the typical characters of Q3 Jahn-Teller distortion, which is caused by the 3d electrons of transition metals (e.g., Mn and Cu) and found in many perovskite materials such as Sr$_2$CuWO$_6$.[37, 40, 41]

From figure 2, tables 1 and 2, we can further conclude that the bigger volume of interstitially K-doped CsPbI$_2$Br supercell as compared with the Mn-doped one can be attributed to the larger increase in the volume of PbI$_2$Br$_2$ octahedrons adjacent to the K atom and K-occupied octahedral interstice. The volume expansion of interstitially Mn-doped CsPbI$_2$Br supercell mainly originates from the increase in the volume of PbI$_2$Br$_2$ octahedrons adjacent to the Mn atom, while the decrease in the volume of Mn-occupied octahedral interstice has a negative contribution to the volume expansion.

3.2. Solution energy of interstitial K and Mn atoms in CsPbI$_2$Br supercell

As shown in figure 3, the solution energy of interstitial K and Mn atoms in the CsPbI$_2$Br supercell is $-0.87$ eV and $2.25$ eV, indicating that the process of K- and Mn-doping is exothermic and endothermic, respectively. Due to the negative $E_{sol}$ or $E_M$ it is thermodynamically easier for the K atom to enter into an octahedral interstice of CsPbI$_2$Br than the Mn atom. The solubility of Mn atom should be lower than that of K atom in the octahedral interstices of CsPbI$_2$Br lattice.

To gain more physical insight, the solution energies were further split into the mechanical ($E_{M}$) and chemical ($E_C$) contributions displayed in figure 3. It can be seen that the solution energies are mainly determined by the chemical contributions, as compared with the slight mechanical contributions. For the interstitial doping of K atom, the negative $E_C$ and positive $E_M$ mean that the chemical contribution enhances the binding interaction between K atom and CsPbI$_2$Br host lattice, while the mechanical contribution caused by the K-doping induced relaxation of host lattice weakens the binding interaction. As the negative $E_C$ overcompensates the positive $E_M$, so negative solution energy for the interstitial K atom was obtained. It is obvious that the $E_C$ is conducive to lower...
the solution energy and thus facilitates the doping of K atom into CsPbI2Br with the formation of chemical bonds between K atom and its surrounding host atoms, while the size-mismatch induced lattice relaxation or structural distortion ($E_{M}$) obstructs the entry of K atom into CsPbI2Br.

By contrast, both $E_{C}$ and $E_{M}$ are positive for the interstitial doping of Mn atom, which leads to a positive solution energy finally. Although the atomic size of K and Mn atoms is smaller than that of Cs atom, the size of K atom is quite close to the Cs atom while the size of Mn atom is significantly smaller than that of Cs or K atom. That is, the Mn atom cannot fit well into the octahedral interstice with respect to the K-occupied interstice and Cs-occupied PbI$_4$Br$_2$ octahedrons, which is completely consistent with the aforementioned results that the Mn-doping caused a more pronounced structural distortion of PbI$_4$Br$_2$ octahedrons and octahedral interstice, as presented in tables 1 and 2. Therefore, the $E_{M}$ part of the solution energy of Mn atom is obviously larger than that of K atom. Moreover, some bonds between Mn and host atoms would be too expanded, which would inevitably lead to weakened binding interactions between Mn and host atoms and thus a positive $E_{C}$.

3.3. Interstitial doping induced changes in electronic properties of CsPbI$_2$Br

To better understand the effects of interstitial doping of alkali metal and transition metal elements on the electronic properties of CsPbI$_2$Br, both the electronic densities of states (DOS) and the crystal orbital Hamilton population (COHP) of CsPbI$_2$Br supercells with and without interstitial K and Mn atoms were analyzed comparatively. For the undoped CsPbI$_2$Br, the main peaks of total density of states (TDOS) are temporally denoted as P1 to P9 from the lower energy side, as displayed in figure 4(a). The TDOS clearly indicates that the pristine CsPbI$_2$Br is a semiconductor with a band gap of about 1.4 eV, which is in good agreement with our previous calculation result (1.42 eV) [30].

From the partial densities of states (PDOS), it can be seen that the valence band maximum (VBM) of pristine CsPbI$_2$Br is mainly contributed from a mixture of I-5$p$, Br-4$p$ and Pb-6$s$ states, and the conduction band minimum (CBM) is almost contributed by Pb-6$p$ states, which are quite similar with the characters of VBM and CBM of the organic-inorganic perovskite CH$_3$NH$_3$PbI$_3$ [42]. The inorganic Cs$^+$ cations have little contribution to the VBM and CBM, which is also similar with the electronic behavior of organic CH$_3$NH$_3$PbI$_3$ cations contained in the organic-inorganic perovskite [43]. The highly localized peaks named P1, P2, P3 and P5 are separately from the contribution of Cs-5$s$, Pb-5$d$, Br-4$s$ and Cs-5$p$ states, indicating the non-bonding character of these states. The peak named P4 (around $-12.2$ eV) is composed predominantly of I-5$s$ orbitals with some hybridization with Pb-6$s$ states. On the contrary, the peak named P6 (around $-8.1$ eV) is made up mainly of Pb-6$s$ orbitals with some hybridization with I-5$s$ and 5$p$ states. As shown in figure 4(b), the states in the vicinity of $-12.2$ eV (P4) and $-8.1$ eV (P6) arise primarily from the bonding interactions between Pb-6$s$ and I-5$s$, 5$p$ states, due to the positive value of COHP. From figures 4(a) and (b), we can also see that the peak named P7 with a bonding character (around $-3.5$ eV) consists mainly of I-5$p$ and Br-4$p$ states hybridized with Pb-6$p$ states. The peak named P8 arises mainly from the mixing of I-5$p$ and Br-4$p$ states. Notice that the VBM manifests an antibonding characteristic (negative value of COHP) derived from the hybridization between I-5$p$, Br-4$p$ and Pb-6$s$ states as

![Figure 3. Solution energy ($E_{sol}$) and its mechanical ($E_{M}$) and chemical ($E_{C}$) parts for interstitial K and Mn atoms as incorporated into CsPbI$_2$Br supercell.](image-url)
shown in figures 4(a) and (b), which is consistent with the strong antibonding coupling of Pb $s$ and I $p$ in the VBM of CH$_3$NH$_3$PbI$_3$ perovskite as indicated by Yin et al [42].

As shown in figures 5(a) and (b), the VBM of K-doped CsPbI$_2$Br with an antibonding characteristic still arises mainly from the mixing of I-5$p$ and Br-4$p$ states hybridized with Pb-6$p$ states, indicating that the interstitial K-doping has little effect on the VBM of CsPbI$_2$Br. Similarly, the orbital contributions to the CBM and the peak named P9 of the K-doped CsPbI$_2$Br and their antibonding characters are unchanged in comparison with the pristine CsPbI$_2$Br, which mainly consist of Pb-6$p$ states with minor contributions from I-5$p$ and Br-4$p$ states. As the 5$s$ core orbitals of Cs atoms always keep localized and do not contact with other atoms in both undoped and doped systems, so we further studied the shift of band edges for the K-doped CsPbI$_2$Br with reference to the position of VBM and CBM of the pristine CsPbI$_2$Br by aligning Cs-5$s$ core levels, as shown in figure 5(c). It can be seen that the position of VBM and CBM of K-doped CsPbI$_2$Br is almost unshifted with respect to the undoped case. Notice that an upshift of both VBM and CBM for the K-doped perovskite with a K $^+$ content of 5% has been reported experimentally by Tang et al [44] and Yao et al [27], who held the opinion that the interstitial K-doping into perovskite lattice could be an effective method to promote energy band alignment with electron transport materials and thus to enhance charge carrier transport and device performance. As the band edge shifts were usually found to relate with the dopant concentration [27, 45, 46], so the nearly unchanged VBM and CBM positions of the K-doped CsPbI$_2$Br herein should be attributed to the relatively lower K-doping concentration (2.5%), which has no appreciable effect on the position and component of VBM and CBM of CsPbI$_2$Br.

Although the orbital contributions to the characteristic peaks (P1 to P9) of TDOS of K-doped CsPbI$_2$Br almost keep unchanged, there are two observable differences in TDOS between K-doped and undoped systems, as shown in figures 5(a) and (b). First, the peak named P3 becomes delocalized with the formation of shorter peak (~ $-15$ eV) adjacent to P3 due to the hybridization between Br-4$s$ and K-3$p$ states, suggesting the bonding interactions between K and Br atoms. The shorter peak with an antibonding character is mainly composed of K-3$p$ states hybridized with Br-4$s$ states. Second, the new peak named P$^*$ does not appear in the TDOS of undoped CsPbI$_2$Br and is from the contribution of K-3$s$ states which are even lower in energy than Cs-5$s$ levels and also highly localized in the valance bands of CsPbI$_2$Br crystal.

Upon Mn doping, both the overall profile of spin-down TDOS and the orbital contributions to the nine characteristic peaks remain similar to those of undoped CsPbI$_2$Br, except for the unoccupied DOS peak from Mn-3$d$ states (at the Fermi level and close to the CBM) and the broadening peaks named P3 and P4, as shown in figure 6(a). From figures 6(a) and (b), it can be seen that both the VBM and CBM of spin-down TDOS have similar antibonding characteristic and orbital contributions with those of the undoped case. Moreover, an appreciable difference between the spin-down TDOS of Mn-doped case and the TDOS of undoped case is the unoccupied gap states newly-generated at the CB edge, which are mainly contributed by the Mn-3$d$ states (at the Fermi level) and showing an antibonding interaction with I-5$p$ states. As the gap states crossing the Fermi level are close to the CBM, so the interstitially Mn-doped CsPbI$_2$Br is a n-type semiconductor, which is in line with our previous result [30].

For the spin-up TDOS of Mn-doped CsPbI$_2$Br, the orbital contributions from atoms to the nine characteristic peaks are almost unchanged with respect to the undoped case. Besides these characteristic peaks, there are three additional DOS peaks caused by the Mn doping, which were named separately by P$^*$, P$^{**}$ and P$^{***}$,
as displayed in figure 6(a). It is obvious that these three occupied DOS peaks are related with Mn-3d states which are strongly hybridized with Br-4p orbitals. From figures 6(a) and (c), we can see that the peak named P*1 (around $-5.75$ eV) with a bonding character is mainly derived from Br-4p orbitals with some hybridization with Mn-3d states. By contrast, both P*2 and P*3 peaks (around $-2.2$ eV and $-1.3$ eV) show an antibonding characteristic and arise primarily from the contribution of Mn-3d states with some hybridization with I-5p and Br-4p states. Besides this, the VBM of spin-up TDOS shifts upward by 0.41 eV with respect to the pure case due to the emergence of P*3 peak, whereas the CBM remains at the same position as for the pure case, as shown in figure 6(d). Thus, the orbital contributions to the VBM change from the hybridization between I-5p, Br-4p and Pb-6s states as displayed in the pure case to the hybridization between Mn-3d states and I-5p, Br-4p states in the Mn-doped CsPbI$_2$Br. To summarize, the interstitial doping of Mn atom into the CsPbI$_2$Br lattice can not only shift up the VB edge and thus reduce the band gap of CsPbI$_2$Br, but can also introduce new unoccupied gap states (Mn-3d states) at the CB edge which may serve as recombination centers of photogenerated carriers.

Due to the limitation of semi-local functional (GGA-PBE) and the presence of heavy elements (e.g., Pb) in CsPbI$_2$Br perovskite, both the electron’s self interaction error and the spin–orbit coupling (SOC) effect, which may change the current PBE calculation results, should be considered carefully in future work [47, 48]. As demonstrated by Basera et al, both the advanced hybrid functional HSE06 which includes a fraction of exact Hartree–Fock exchange to capture the electron’s self-interaction error, and the SOC effect play a crucial role in modulating electronic band energy levels of MAPb$_{1-x}$Sn$_x$I$_3$ perovskite, where the positioning of VBM and CBM was corrected by HSE06 functional and SOC effect, respectively [47]. Moreover, Basera et al have also found that using advanced functional HSE06 is extremely important for predicting the thermodynamic stability
(formation energy) of MAPb$_{1-X}$Sn$_X$I$_3$ perovskite, as the semi-local functional GGA-PBE gives an opposite trend [47]. Therefore, the calculation results depend on the kind of functionals that people employ and the consideration of SOC effect. Further investigations of the effect of advanced hybrid functions and SOC on the formation energy, structural and electronic properties of pristine, substitutionally and interstitially
K/Mn-doped CsPbI₂Br are desired for more accurate and reliable predictions and also worthwhile for providing theoretical guidance to experiment, in which the present PBE results could serve as a basis for elevating accuracy.

4. Conclusions

In summary, the effects of interstitial doping of alkali metal element K and transition metal element Mn on the structural and electronic properties of CsPbI₂Br perovskite were investigated comparatively by using the first-principles density functional calculation method. The main results obtained are as follows:

(I) The interstitial doping of K and Mn atoms leads to the volume expansion of CsPbI₂Br lattice, but renders the lattice more compact by decreasing the interstice volume. The bigger supercell volume of K-doped CsPbI₂Br than the Mn-doped case is related to the larger increase in both the volume of PbI₄Br₂ octahedrons adjacent to K atom and the volume of K-occupied octahedral interstice.

(II) The structural distortion of both the PbI₄Br₂ octahedrons neighboring to Mn atom and the Mn-occupied octahedral interstice is more significant than those in the K-doped CsPbI₂Br. Unlike the K doping, the Mn doping is an endothermic process and it shrinks the Mn-Br-I atomic plane and elongates the Cs-Cs interatomic distance of the octahedral interstice, which are considered to be the typical characters of Q3 Jahn–Teller distortion.

(III) The interstitial K-doping with a relatively lower doping concentration has no appreciable effect on the position and orbital component of valence band maximum (VBM) and conduction band minimum (CBM) of CsPbI₂Br.

(IV) The interstitial Mn-doping leads to some unoccupied gap states (Mn-3d states at the Fermi level) formed at the edge of spin-down conduction bands. Due to the emergence of additionally occupied P⁺⁺ peak in the spin-up total density of states (TDOS), the VBM of spin-up TDOS shifts upward by 0.41 eV with respect to the undoped case. The orbital contributions to the spin-up VBM with an antibonding characteristic change to the hybridization between Mn-3d states and I-5p, Br-4p states. As the calculation results depend on the electron’s self interaction error and the spin–orbit coupling (SOC) effect, so further investigations of their effects on the thermodynamic stability, structural and electronic properties of undoped and K/Mn-doped CsPbI₂Br perovskites are desired, using the advanced hybrid functional HSE06 along with SOC.

Acknowledgments

This work was financially supported by the Ministry of Science and Technology of China (Grant No. 2017YFA0700701), the Natural Science Fund for Distinguished Young Scholars of Gansu Province of China (Grant No. 20JR5RA477), the National Natural Science Foundation of China (Grant No. 11764027), the Joint Fund between Shenyang National Laboratory for Materials Science and State Key Laboratory of Advanced Processing and Recycling of Nonferrous Metals (Grant No. 18LHPY003), and the Hongliu Excellent Young Talents Support Program of Lanzhou University of Technology. This work was performed in the Gansu Supercomputer Center.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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