Density Functional Theory Analysis of Structural, Electronic, and Optical Properties of Mixed-Halide Orthorhombic Inorganic Perovskites

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ABSTRACT: Inorganic metal-halide perovskites hold a lot of promise for solar cells, light-emitting diodes, and lasers. A thorough investigation of their optoelectronic properties is ongoing. In this study, the accurate modified Becke Johnson generalized gradient approximation (mBJ-GGA) method without/with spin orbital coupling (SOC) implemented in the WIEN2k code was used to investigate the effect of mixed I/Br and Br/Cl on the electronic and optical properties of orthorhombic CsPb-(I1−xBrx)3 and CsPb(Br1−xClex)3 perovskites, while the Perdew–Burke–Ernzerhof generalized gradient approximation (PBE-GGA) method was used to investigate their structural properties. The calculated band gap \(E_g\) using the mBJ-GGA method was in good agreement with the experimental values reported, and it increased clearly from 1.983 eV for CsPbI3 to 2.420 and 3.325 eV for CsPbBr3 and CsPbCl3, respectively. The corrected mBJ + SOC \(E_g\) value is 1.850 eV for CsPbI3, which increased to 2.480 and 3.130 eV for CsPbBr3 and CsPbCl3, respectively. The calculated photoabsorption coefficients show a blue shift in absorption, indicating that these perovskites are suitable for optical and optoelectronic devices.

1. INTRODUCTION

Because of their superior thermal stability compared to their organic–inorganic hybrid counterparts, inorganic perovskites have emerged as one of the most appealing research hotspots in the field of perovskite photovoltaics over the last 5 years.1–3 Perovskite compounds have the chemical formula ABX3, where A is a monovalent cation such as CH3NH3 (MA), HC(NH2)2 (FA), or Cs, B is a divalent cation such as Pb or Sn, and X is an anion such as I, Br, or Cl.4 Inorganic mixed halides have recently been used to create various nanophotonic components due to their electroluminescence in the green5,6 to blue7 optical ranges. The broad tunability of halide perovskites has emerged as promising demonstrations for appealing solar cells, light-emitting diodes (LEDs), and laser applications, with the promising demonstrations for appealing solar cells, light-emitting diodes, and laser applications, with the possibility of manipulating energy-e10
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Castelli et al. investigated the trends over band gaps for 240 perovskites composed of organic−inorganic cations, Sn and Pb as B-ion, and halides as anions. The optoelectronic properties of mixed inorganic perovskites at the orthorhombic phase (Pnma) have not yet been investigated in detail, particularly the mixed halide from I to Br and Cl. It is advantageous to investigate the optoelectronic properties of mixed orthorhombic (Pnma) inorganic perovskites, which are available at room
temperature and have applications in solar cells, LEDs, and lasers, using the most accurate DFT calculation methods.

Table 1. Theoretical Lattice Parameters \((a, b, \text{ and } c)\), Unit-Cell Volume \(V (\text{Å}^3)\), Pressure Derivatives \(B'\), Bulk Modulus \(B\) (GPa), and Total Energy \(E\) for Mixed-Halide Perovskites. Note: The lattice Parameter, \(c\) has been doubled.

| Mixed halide perovskites | \(a\) (Å) | \(b\) (Å) | \(c\) (Å) | \(V(\text{Å}^3)\) | \(B'\) | \(B\) (GPa) | Total energy \(E\) (eV) |
|--------------------------|-----------|-----------|-----------|-----------------|-------|-------------|------------------------|
| CsPbI\(_3\) | 8.93 | 12.76 | 17.71 | 2017.394 | 4.357 | 17.85 | -800964.3712 |
| Previous work | 8.906\(^{50}\) \((8.8561)\) | 12.665\(^{50}\) \((8.577)\) | 1903.098 | 5.448 | 19.52 | -746912.3966 |
| CsPbI\(_{1.25}\)Br\(_{0.75}\) | 8.76 | 12.50 | 17.53 | 1793.199 | 5.441 | 20.10 | -602776.4668 |
| CsPbI\(_{1.15}\)Br\(_{0.85}\) | 8.58 | 12.25 | 17.05 | 1687.614 | 6.096 | 21.35 | -638692.1949 |
| CsPbI\(_{1.05}\)Br\(_{0.95}\) | 8.42 | 12.00 | 16.72 | 1586.254 | 5.799 | 22.65 | -584536.6893 |
| CsPbBr\(_3\) | 8.24 | 11.74 | 16.39 | 8.244\(^{55}\) \((8.208)\) | 11.735\(^{55}\) \((11.763)\) | 8.1982\(^{55}\) \((8.257)\) | -558781.0674 |
| Previous work | 8.244\(^{55}\) \((8.208)\) | 11.735\(^{55}\) \((11.763)\) | 1547.011 | 5.427 | 23.44 | -553010.0061 |
| CsPbBr\(_{1.75}\)Cl\(_{0.25}\) | 8.18 | 11.64 | 16.25 | 8.03 | 15.87 | 1482.081 | 4.866 | 24.21 | -507337.2300 |
| CsPbBr\(_{1.65}\)Cl\(_{0.35}\) | 8.02 | 11.45 | 15.77 | 1448.388 | 5.581 | 25.66 | -481486.4912 |
| CsPbCl\(_3\) | 7.97 | 11.36 | 15.83 | 7.97 | 15.36 | 1433.32 | 5.654 | 25.62 | -481486.4912 |

Figure 3. Band structure of (a) CsPbI\(_3\), (b) CsPbI\(_{1.25}\)Br\(_{0.75}\), (c) CsPbI\(_{1.15}\)Br\(_{0.85}\), (d) CsPbI\(_{0.75}\)Br\(_{2.25}\), (e) CsPbBr\(_3\), (f) CsPbBr\(_{1.75}\)Cl\(_{0.25}\), (g) CsPbBr\(_{1.65}\)Cl\(_{0.35}\), and (i) CsPbCl\(_3\) obtained using mBJ-GGA potential without/with SOC. The band gap values versus the concentration of Br and then Cl calculated using mBJ, mBJ + SOC, and the corrected mBJ + SOC (j). The black dashed line represents the band structure calculated with mBJ + SOC. The VBM is set as zero.

In this study, the mBJ-GGA method without/with spin orbital coupling (SOC)\(^{57–59}\) was used to look into the impact of halide composition on the electronic and optical properties of mixed...
orthorhombic perovskites $1 \times 1 \times 2 \text{CsPb}(I_{1-x}B_x)_{3}$ and 
$
\text{CsPb}(\text{Br}_{1-x}\text{Cl}_x)_{3} \quad (x = 0.00, 0.25, 0.50, 0.75, 1.00), \n$ while the 
PBE-GGA method was used to investigate their structural 
properties. The mBJ-GGA method demonstrated the evolution 
of band structure, optical absorption, and energy band gap ($E_g$) 
with increasing $x$ in CsPb(I$_{1-x}$Br$_x$)$_3$ and 
CsPb(\text{Br}_{1-x}\text{Cl}_x)_{3}$. The 
lattice constants and $E_g$ were computed and found to be 
consistent with previous research.

Furthermore, the effective masses of charge carriers, absorption, 
optical dielectric, and reflectivity were precisely calculated.

2. RESULTS AND DISCUSSION

2.1. Optimized Structures. At room temperature, CsPb$_3$ 
($X = I, Br, Cl$) perovskites have orthorhombic structures with 
space group $Pnma$. Using VESTA software, a supercell 
$1 \times 1 \times 2$ with 40 atoms was used to simulate 
CsPb(I$_{1-x}$Br$_x$)$_3$ and CsPb(\text{Br}_{1-x}\text{Cl}_x)_{3}$. The 
starting with an orthorhombic inorganic CsPb$_3$ structure, a supercell 
of CsPb(I$_{1-x}$Br$_x$)$_3$ and 
CsPb(\text{Br}_{1-x}\text{Cl}_x)_{3}$. As the iodide was gradually replaced 
with an appropriate concentration of Br and Cl, the structure of the 
perovskite is presented in Tables S1—S9, Supporting 
Information. 

Figure 1. The structural properties of mixed-halide perovskites 
are investigated using first-principles DFT with the PBE-GGA 
method, which is implemented in the WIEN2k code. The 
structural information is presented in Tables S1—S9, Supporting 
Figure 2a–i shows the fitting of total energy as a function of volume using the 
Murnaghan equation of state. a supercell 
$1 \times 1 \times 2$ with 40 atoms was used to simulate 
CsPb(I$_{1-x}$Br$_x$)$_3$ and CsPb(\text{Br}_{1-x}\text{Cl}_x)_{3}$. The 
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with an appropriate concentration of Br and Cl, the structure of the 
perovskite is presented in Tables S1—S9, Supporting 
Information. The VBM is primarily derived from 
the iodide, whereas there was no signiﬁcant change in the 
valence band (VB) for pure CsPb$_3$/CsPbBr$_3$, but the VBM or CBM but only maintains overall load neutrality and 
is the change in band gap for the mixed 
$\text{CsPb}(I_{1-x}B_x)_{3}$ and $\text{CsPb}(\text{Br}_{1-x}\text{Cl}_x)_{3}$ perovskites, $DE(A)$ is the change in band gap for pure CsPb$_3$/CsPbBr$_3$ and $DE(B)$ is the change in band gap for pure CsPb$_3$/CsPbCl$_3$. 

2.2. Electronic Properties. The electronic properties of 
mixed-halide perovskites are investigated using the mBJ-GGA 
method without/with SOC, which is implemented in the 
WIEN2k code. The electronic band structures without/with SOC 
follow the high-symmetry $\Gamma$-point path $R \rightarrow \Gamma \rightarrow X \rightarrow M$ and $\Gamma$ as shown in 
Figure 3a–i. The SOC had a significant effect on the conduction band (CB) region, with a sharp reduction in 
the CBM in CsPb$_3$ to 3.130 eV for CsPbCl$_3$. Figure 3j shows the 
Table 2. Band gap $E_g$ (eV) Values for Mixed-Halide Inorganic Perovskites Compared With Previous Experimental and Theoretical Studies

| mixed-halide perovskites | mBJ | mBJ + SOC | corrected mBJ + SOC | other DFT (exp.) |
|--------------------------|-----|----------|---------------------|-----------------|
| CsPbI$_3$                | 1.983 | 1.066 | 1.850 | 1.831,79(1.75),97,100,101 |
| CsPbI$_{0.75}$Br$_{0.25}$ | 2.029 | 1.123 | 2.064 | (2.010)$^{11}$ |
| CsPbI$_{0.50}$Br$_{0.50}$ | 2.112 | 1.151 | 2.079 | 1.93,$^{10}$ (1.97),76,95 |
| CsPbI$_{0.25}$Br$_{0.75}$ | 2.281 | 1.343 | 2.276 | (2.17),86 (2.23)$^{11}$ |
| CsPbBr$_3$              | 2.420 | 1.482 | 2.480 | 2.32,$^{10}$ (2.40),40 |
| CsPbBr$_{0.75}$Cl$_{0.25}$ | 2.623 | 1.602 | 2.593 | 2.670,$^{10}$ |
| CsPbBr$_{0.50}$Cl$_{0.50}$ | 2.841 | 1.815 | 2.791 | 2.720,$^{10}$ (2.800)$^{11}$ |
| CsPbBr$_{0.25}$Cl$_{0.75}$ | 3.033 | 1.973 | 2.933 | (2.940)$^{11}$ |
| CsPbCl$_3$              | 3.325 | 2.182 | 3.130 | 3.05,$^{10}$ (2.91)$^{10}$,16 (2.78),16 (3.132)$^{11}$ |

where $DE(A)_{I_{1-x}B_x}$ is the change in band gap for the mixed 
$\text{CsPb}(I_{1-x}B_x)_{3}$ and $\text{CsPb}(\text{Br}_{1-x}\text{Cl}_x)_{3}$ perovskites, $DE(A)$ is the change in band gap for pure CsPb$_3$/CsPbBr$_3$ and $DE(B)$ is the change in band gap for pure CsPb$_3$/CsPbCl$_3$. Table 2 shows that the corrected mBJ-GGA + SOC $E_g$ ranges from 1.850 eV for CsPb$_3$ to 3.130 eV for CsPbCl$_3$. Figure 3j shows the dramatic increase in $E_g$ caused by replacing I with Br, followed by Cl. 

The effective masses, $m^*_e$ and $m^*_h$, were calculated using the equation $m^*_i = \frac{\hbar^2}{\epsilon_i^{\text{eff}}}$ where $\epsilon_i^{\text{eff}}$ is the effective mass of the electron or hole, $i = e$ or $h$, and $\epsilon_i^{\text{eff}}(k \rightarrow)$ is the energy dispersion function of the nth band, and $k \rightarrow$ represents the wave vector. The effective masses, $m^*_e$ and $m^*_h$, without SOC ranged from 0.13579 to 0.23119$\hbar$m$^2$/eV$^2$ and from 0.07099 to 0.09354$\hbar$m$^2$/eV$^2$, respectively, and those with SOC ranged from 0.06019 to 0.08938$\hbar$m$^2$/eV$^2$ and from 0.06828 to 0.08354$\hbar$m$^2$/eV$^2$, respectively. As indicated by Figure 4, the calculated reduced effective mass $\mu = \frac{m^*_e}{m^*_e + m^*_h}$ without/with SOC increased significantly with increasing Br and Cl concentration in CsPb(I$_{1-x}$Br$_x$)$_3$ and CsPb(\text{Br$_1$Cl$_2$})$_3$ perovskites, but the edges were shifted up, when the VBM was shifted to 0 eV. The partial DOS (PDOS) for the mixed perovskite demonstrates that Cs$^+$ has no effect on the VBM or CBM but only maintains overall load neutrality and structural stability.

3.3. Density of States. Figure 5 shows that the total density of states (TDOS) remained unchanged as the concentration ($x$) increased from 0.00 to 1.00 of Br and Cl in CsPb(I$_{1-x}$Br$_x$)$_3$ and 
CsPb(\text{Br$_1$Cl$_2$})$_3$ perovskites, but the edges were shifted up, when the VBM was shifted to 0 eV. The partial DOS (PDOS) for the mixed perovskite demonstrates that Cs$^+$ has no effect on the VBM or CBM but only maintains overall load neutrality and structural stability.
The CBM was formed mostly by the p states of Pb and minor contribution by the s and p states of I, Cl, and Br. An in-depth look at the band structure of CsPbI3, CsPbI1.50Br1.50, CsPbBr3, CsPbBr1.50Cl1.50, and CsPbCl3 with respect to PDOS is shown in Figure S4, Supporting Information.

### 3.4. Electron Density

To visualize the charge distribution and bonding nature of CsPbI3, CsPbI2.25Br0.75, CsPbI1.50Br1.50, CsPbI0.75Br2.25, CsPbBr3, CsPbBr2.25Cl0.75, CsPbBr1.50Cl1.50, CsPbBr0.75Cl2.25, and CsPbCl3 perovskites, the electron density distribution is investigated and presented in Figure 6. The atoms Cs, Pb, I, Br, and Cl have electronegativity values of 0.79, 2.33, 2.66, 2.96, and 3.16 on the Pauling scale, respectively. The difference in electronegativity (X1 − X2) is critical for describing the bonding character.98 The following equation is used to calculate the percentage of ionic character (IC) of the bonding obtained31,98,99

$$\% \text{ IC} = [1 - e^{-(0.25)(X_1-X_2)^2}] \times 100$$

The electronegativities of the 1 and 2 atoms are represented by X1 and X2, respectively. The % IC of Cs−Br, Cs−I, and Cs−Cl was 69.18, 58.28, and 75.44, whereas for Pb−Br, Pb−I, and Pb−Cl, was 9.45, 2.66, and 15.82, respectively. The electron clouds surrounding Cs atoms are spherical and free of distortion, indicating that they are mostly ionic and partially covalent with the surrounding atoms.21,31,100 In contrast, the bond between Pb and I, Br, or Cl is mostly covalent and partially ionic, with electron clouds around these atoms distorted and overlapping significantly.

### 3.5. Optical Properties

We investigate the optical properties of mixed-halide perovskites, including dielectric function, refractive index, extinction coefficient, reflectivity, and optical absorption for energy ranging from 0 to 10 eV. The calculated dielectric functions $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are shown in Figure 7a,b. The dielectric function describes how a material responds to incident photons as a function of energy. The real part of the dielectric function $\varepsilon_1(\omega)$ value at zero frequency is known as the static frequency $\varepsilon_1(0)$, and it varies between 4.72 and 3.12 as shown in Figure 8. Figure 7b shows the behavior of the imaginary part of the dielectric function $\varepsilon_2(\omega)$, where it represents the radiation absorbed by the compound,31,101 with main peaks between 3.42 and 6.68 eV. It is worth noting that $\varepsilon_2(\omega)$ has a zero value until absorption begins after the photon energy reaches the band gap energy, which establishes the threshold for a direct optical transition between the VBM and the CBM.

The refractive index $n(\omega)$ and extinction coefficient $k(\omega)$ were calculated, as shown in Figure S5a,b, Supporting Information. $n(\omega)$ is a critical feature of semiconductors that indicates how much light is bent or refracted.101 The value of $n(\omega)$ increases as the energy increases up to 2.87 and 2.14 for CsPbI3 and CsPbCl3, and then it begins to decrease to 1.27 and 1.44 showing a nonlinear behavior as shown in Figure S5a. For CsPbI3, CsPbBr3, and CsPbCl3, the calculated $n(0)$ values were 2.17, 1.95, and 1.77 which agree well with the previous theoretical and experimental values31,55,102 as shown in Figure 8. Figure S5b shows that $k(\omega)$ is proportional to Br/Cl concentration, similar to $\varepsilon_2(\omega)$, with the local maximum...
occurring between 3.89 and 6.72 eV when moving from CsPbI3 to CsPbCl3.

The calculated reflectivity $R(\omega)$ in relation to incident energy is shown in Figure S6, Supporting Information. The mixed perovskites behaved as semiconductors; the value of $R(\omega)$ was not unity at zero energy. At zero frequency, CsPbI3 has a static reflectivity $R(0)$ value of 13.7%, which then decreases to 10.4 and 7.7% for CsPbBr3 and CsPbCl3, respectively. When moving from CsPbI3 to CsPbBr3 and CsPbCl3, the maximum $R(\omega)$ occurs between 3.22 and 4.71 eV, and it begins to fluctuate and decrease at higher energies. As shown in Figure 8, the calculated $R(0)$ at zero energy was approximately 13.65, 12.78, 12.42, 11.01, 10.43, 9.66, 8.42, 8.33, and 7.67% for mixed perovskite when transitioning from CsPbI3 to CsPbBr3 and CsPbCl3.

Figure 9a exhibits the absorption coefficient, $\alpha(\omega)$, as a function of the energy. $\alpha(\omega)$ peaks shifted to higher energies with increasing Br and Cl concentrations in CsPb(I1−xBrx)3 and CsPb(Br1−xClx)3. The wide absorption coefficient range from visible to ultraviolet indicates that they are useful for a variety of optical and optoelectronic applications. Figure 9b shows the optical conductivity $\sigma(\omega)$ characteristics, which are analogous to $\alpha(\omega)$ and provide information on how external parameters affect the electronic structure. The optical properties of the studied perovskite were consistent with those previously measured and reported.

3. CONCLUSIONS

In this study, the influence of halide composition on the optoelectronic properties of mixed-halide perovskites was investigated. The structural properties were calculated using the PBE-GGA method, and the lattice parameters are well comparable to previous experimental and theoretical work. When iodide (I) was replaced with bromide (Br) and then chloride (Cl), the unit-cell volume decreased linearly. The calculated band gap ($E_g$) using the mBJ-GGA method is in good agreement with the experimental values reported, and it increased clearly from 1.983 eV for CsPbI3 to 2.420 and 3.325 eV for CsPbBr3 and CsPbCl3, respectively, due to the increase in electronegativity of Br and Cl. Because the $E_g$ values with mBJ + SOC are small compared to the experimental results, the alloy formula was used to correct the $E_g$ values. The corrected mBJ + SOC $E_g$ value is 1.850 eV for CsPbI3 and 2.480 and 3.130 eV for CsPbBr3 and CsPbCl3, respectively. The reduced masses ($\mu$) are correlated with the energies of $E_g$, VBM, and CBM. When moving from CsPbI3 to CsPbBr3 and CsPbCl3, $\mu$ ranges from 0.046618 m_o to 0.066595 m_o without SOC and from 0.031569 m_o to 0.043181 m_o with SOC. As the Br and Cl content increases, the calculated photoabsorption coefficients show a blue shift in
the absorption coefficient. According to the calculations, these perovskites can be used in solar cells, LEDs, and laser applications.

3.1. Computational Method. The FP-LAPW method within the framework of DFT as implemented in the WIEN2k code was used to optimize the structure of the mixed inorganic perovskites.33,73 The PBE-GGA method was used to calculate the structural properties of the mixed perovskites. The mixed inorganic perovskite structures were created by building a 1 × 1 × 2 supercell with a binary perovskite’s Pnma space group. Because of the presence of a heavy element (Pb) in the structure, the SOC interaction was described in our previous work.47 To match the experimental values, the calculated band gap with SOC was corrected by using the alloy formula. To match the experimental values, the calculated band gap with SOC was corrected by using the alloy formula.14,69,105 During the calculation, \( K_{\text{max}} = 9 \) and \( k \)-points = 100 were used, and the total energy was converged to \( 10^{-4} \) Ry.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c04806.

Structural parameters; unit-cell volume versus Br and Cl contents; SOC; energy level splitting diagram for the orthorhombic phase of inorganic perovskites; PDOS of mixed inorganic perovskites; band structures; calculated effective mass of the electron and hole and reduced mass for mixed-halide perovskites; and calculated refraction indices and extinction coefficients and reflectivity spectra of mixed-halide perovskites with different dopant concentrations (PDF)

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### Notes

The authors declare no competing financial interest.

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