Computational Investigation of the Folded and Unfolded Band Structure and Structural and Optical Properties of CsPb(I$_{1-x}$Br$_x$)$_3$ Perovskites

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Abstract: The structural, electronic, and optical properties of inorganic CsPb(I$_{1-x}$Br$_x$)$_3$ compounds were investigated using the full-potential linear augmented-plane wave (FP-LAPW) scheme with a generalized gradient approximation (GGA). Perdew–Burke–Ernzerhof generalized gradient approximation (PBE-GGA) and modified Becke–Johnson GGA (mBJ-GGA) potentials were used to study the electronic and optical properties. The band gaps calculated using the mBJ-GGA method gave the best agreement with experimentally reported values. CsPb(I$_{1-x}$Br$_x$)$_3$ compounds were wide and direct band gap semiconductors, with a band gap located at the M point. The spectral weight (SW) approach was used to unfold the band structure. By substituting iodide with bromide, an increase in the band gap energy ($E_g$) values of 0.30 and 0.55 eV, using PBE-GGA and mBJ-GGA potentials, respectively, was observed, whereas the optical property parameters, which were also investigated, demonstrated the reverse effect. The high absorption spectra in the ultraviolet–visible energy range demonstrated that CsPb(I$_{1-x}$Br$_x$)$_3$ perovskite could be used in optical and optoelectronic devices by partly replacing iodide with bromide.

Keywords: CsPb(I$_{1-x}$Br$_x$)$_3$ perovskite; PBE-GGA and mBJ-GGA; fold2Bloch; electronic and optical properties

1. Introduction

Halide perovskite ABX$_3$ has attracted increasing interest as a potential solar cell material because of its simple fabrication techniques and outstanding optoelectronic properties. ABX$_3$ perovskite materials have a high absorption coefficient, appropriate band gap ($E_g$), and balanced electron and hole mobility [1–6]. In recent years, numerous researchers have focused on methylammonium lead trihalide perovskite (CH$_3$NH$_3$PbX$_3$), metal halide perovskite (ABX$_3$, A = Cs, Rb; B = Pb, Sn; X = Cl, Br, I), and CsPbI$_3$, which have shown great potential [7,8].

Most of the researchers have studied the structural, electronic, and optical properties of CsPbX$_3$ (X = Cl, Br, I) using the density functional theory (DFT) and the WIEN2k package [8–11]. The $E_g$ tenability for CsPbX$_3$ was studied experimentally [12], and the lattice modulation of Cs$_{1-x}$R$_x$PbBr$_3$ (R = Li, Na, K, Rb, x = 0–1) was also investigated [13]. By doping the perovskite, the efficiency can be increased, as this can affect numerous electronic and optical properties [7]. The structural and electronic properties of all of the...
inorganic mixed-halide perovskites, CsPb(Br₁₋ₓIx₃)₃ and CsPb(Cl₁₋ₓBrₓ)₃, were investigated according to their halide composition using the Vienna ab initio simulation package (VASP) [14]. The accuracy of DFT calculations, i.e., how close they are to experimentally measured values, has been a concern for DFT calculations on perovskite since their recent introduction into solar cell and LED applications [15–21]. The accuracy of DFT calculations proved to be highly dependent on the exchange potential used in the calculations, such as local density approximation (LDA) [22], Perdew–Burke–Ernzerhof generalized gradient approximation (PBE-GGA) [23], modified Becke–Johnson GGA (mBJ-GGA) [24,25], Green function for the wave equation approximation (GW) [26,27], and hybrid functionals (HF) [27,28]. The HF and GW potentials have shown higher accuracy of the calculated band gap [26–28], but these functionals were more computationally expensive than LDA or PBE-GGA. The calculated band gap using LDA or PBE-GGA potentials was strongly underestimated because these functions contain a self-interaction error [29,30]. For example, calculation of the E₉ has varied greatly among many recent DFT reports, occasionally with considerable deviations from experimental values (band gap reported between 1.359–1.75 eV [8,9,31,32] compared to experimental values of ~1.791 eV [33,34] for CsPbI₃ and 1.7–4.53 eV [1,8,10,35–38] compared to experimental values of ~2.3 eV [13,39–44] for CsPbBr₃). However, very accurate measurements of the band gaps of semiconductors and insulators were obtained when an orbital-independent exchange-correlation potential, mBJ-GGA, was used. This depended solely on semilocal quantities and was competitive in accuracy with the expensive HF and GW methods [24,45]. The supercell calculations are usually performed to allow minor modification of the crystal structure by replacing one atom with another atom. The most successful approach, spectral weight (SW), which links the supercell band structure with the primitive basis representation, is based on a Bloch spectral density [46]. One of the main challenges of supercell electronic structure calculations is to recover the Bloch character of electronic eigenstates [46]. To our knowledge, there have been no studies so far for a spectral weight (SW) approach which can be used to unfold the band structure of inorganic perovskite compounds by fold2Bloch package [46]. The fold2Bloch package was used in the past to unfold the band structure for other compounds such as GaAsBi [47], group (III–V and II–VI) semiconductor solid solutions [46], and graphene [48].

In this study, a combination of CsPbI₃ and CsPbBr₃ was proposed to tune the electronic and optical properties, using the full-potential linear-augmented plane wave (FP-LAPW) method [49,50] within the framework of the DFT [22], as implemented in the WIEN2K code [51]. Here, an investigation into CsPb(I₁₋ₓBrₓ)₃ (where x = 0.00, 0.25, 0.50, 0.75, 1.00) was performed to calculate the electronic and optical properties using PBE-GGA [23] and mBJ-GGA [24] methods. The structural properties were calculated using PBE-GGA potential. Unfolding the band structure of CsPb(I₁₋ₓBrₓ)₃ compounds for a number of Br fractions was performed by calculating the Bloch SW, using the fold2Bloch package [46] implemented in WIEN2k, in order to observe how the electronic properties of these compounds develop [47]. The visualization for electronic and structural analysis (VESTA) program was used for atomic structure visualization [52].

2. Computational Method

The ground state properties of CsPb(I₁₋ₓBrₓ)₃ were calculated by the FP-LAPW method [50] within the framework of the DFT [22,49], as implemented in the WIEN2K code [51]. The PBE-GGA and mBJ-GGA potentials were used to calculate the electronic properties of CsPb(I₁₋ₓBrₓ)₃ perovskite [23,24]. To simulate CsPb(I₁₋ₓBrₓ)₃ (x = 0.00, 0.25, 0.50, 0.75, 1.00), a 1 × 1 × 4 supercell with 20 atoms was used. For x = 0.25, three atoms of iodide were substituted with three atoms of bromide. For x = 0.50, six atoms of iodide were substituted with six atoms of bromide. For x = 0.75, nine atoms of iodide were substituted with nine atoms of bromide. For x = 1.00, twelve atoms of iodide were substituted with twelve atoms of bromide.

The muffin-tin radius R_MT was chosen with no charge leakage from the core, and total energy convergence was ensured. The convergence of the basis set was controlled by the cutoff parameter, R_MT-K_max = 9, where K_max is the largest reciprocal lattice vector used in the plane wave expansion.
within the interstitial region. The magnitude of the largest vector in the charge density Fourier expansion was $G_{\text{max}} = 12$ (a.u)$^{-1}$. The Brillouin zones were sampled with a $12 \times 12 \times 12$ k-point mesh for the unit cell and a $15 \times 15 \times 3$ k-point mesh for the supercell. The energy cutoff was chosen as $-6.0$ Ry, which defines the separation of the valence and core states. The charge convergence was selected as 0.0001e during the self-consistency cycles. The unfolded band structure of CsPb(I$_{1-x}$Br$_x$)$_3$ compounds was determined by calculating the Bloch SW, using fold2Bloch package [46] implemented in WIEN2k, which is available from GitHub [46]. See the Supplementary Materials for more details about fold2Bloch package.

3. Results and Discussions

3.1. Structural Properties

The crystal structures of cubic CsPbX$_3$ with the atomic positions of Cs at (0, 0, 0), Pb at (0.5, 0.5, 0.5), and X at (0.5, 0.5, 0) within the Pm3m space group were evaluated through these calculations. The CsPb(I$_{1-x}$Br$_x$)$_3$ semiconductor compounds were modeled at the selected compositions with ordered structures of periodically repeating supercells $1 \times 1 \times 4$ with 20 atoms per unit cell for $x = 0.00, 0.25, 0.50, 0.75, \text{ and } 1.00$, as shown in Figure 1. See the Supplementary Materials, Tables S1–S5 for more details.

![Figure 1. Atomic structures of CsPb(I$_{1-x}$Br$_x$)$_3$, with $x = 0.00, 0.25, 0.50, 0.75, \text{ and } 1.00$ for the different mixed ratios of $x$.](image)

The computed lattice parameters for cubic CsPbBr$_3$, CsPbI$_3$, and their compounds using PBE-GGA potential were in good agreement with previous experimental and theoretical values, as listed in Table 1. Figure 2 shows that the unit-cell volume varies linearly as a function of the ratio $x$, which is in agreement with Vegard’s law [14].

| Table 1. Calculated lattice constants (Å), bulk moduli $B$ (GPa), and the pressure derivatives $B'$ using Perdew–Burke–Ernzerhof generalized gradient approximation (PBE-GGA) potential compared with previous results. |
|---|---|---|---|---|
| CsPb(I$_{1-x}$Br$_x$)$_3$ | Lattice Constants (Å) | Unit-Cell Volume V(Å$^3$) | $B$ (GPa) | $B'$
| This Study | Previous Studies (Exp.) | This Study | This Study | This Study | Previous Studies | This Study |
| CsPbI$_3$ | 6.28 | 6.40 [9] (PBE-GGA) 6.404 [531] (PBE-GGA) 6.14 [9] (LDA) | 990.69 | 14.5770 | 14.3971 [9] (PBE-GGA) 20.220 [9] (LDA) 16.910 [9] (PBEsol-GGA) 14.593 [9] (PBEsol-GGA) | 4.502 |
| CsPbI$_{0.75}$Br$_{0.25}$ | 6.1775 | 6.395 [14] (PBE-GGA) | 942.97 | – | – | – |
| CsPbI$_{0.5}$Br$_{0.5}$ | 6.075 | 5.990 [14] (PBE-GGA) | 896.81 | – | – | – |
| CsPbI$_{0.25}$Br$_{0.75}$ | 5.9725 | 5.997 [14] (PBE-GGA) | 852.17 | – | – | – |
| CsPbBr$_3$ | 5.87 | 6.0055 [5] (PBE-GGA) 6.00549 [53] (PBE-GGA) 6.009 [53] (PBE-GGA) 5.975 [56] (PBEsol-GGA) 6.046 [51] (HSE) 5.999 [14] (PBE-GGA) 5.84 [57] (WC-GGA) (5.874) [58] | 809.05 | 18.7612 | – | 4.2192 |

| CsPbI$_3$ | 6.28 | 6.40 [9] (PBE-GGA) 6.404 [531] (PBE-GGA) 6.14 [9] (LDA) | 990.69 | 14.5770 | 14.3971 [9] (PBE-GGA) 20.220 [9] (LDA) 16.910 [9] (PBEsol-GGA) 14.593 [9] (PBEsol-GGA) | 4.502 |
| CsPbI$_{0.75}$Br$_{0.25}$ | 6.1775 | 6.395 [14] (PBE-GGA) | 942.97 | – | – | – |
| CsPbI$_{0.5}$Br$_{0.5}$ | 6.075 | 5.990 [14] (PBE-GGA) | 896.81 | – | – | – |
| CsPbI$_{0.25}$Br$_{0.75}$ | 5.9725 | 5.997 [14] (PBE-GGA) | 852.17 | – | – | – |
| CsPbBr$_3$ | 5.87 | 6.0055 [5] (PBE-GGA) 6.00549 [53] (PBE-GGA) 6.009 [53] (PBE-GGA) 5.975 [56] (PBEsol-GGA) 6.046 [51] (HSE) 5.999 [14] (PBE-GGA) 5.84 [57] (WC-GGA) (5.874) [58] | 809.05 | 18.7612 | – | 4.2192 |
3.2. Electronic Properties

The electronic properties of CsPb(I$_{1-x}$Br$_x$)$_3$ were studied by calculating the energy band structure. The folded band structure calculations at $x = 0.00, 0.25, 0.50, 0.75,$ and 1.00 were performed using both PBE-GGA and mBJ-GGA methods. The calculated folded band structures along the wave vectors $X$, $M$, and $\Gamma$ in the Brillouin zone, using mBJ-GGA potential, are shown in Figure 3a–e. In order to study the behavior of $E_g$ with the composition $x$ of Br, the variation of $E_g$ versus the concentration obtained using the PBE-GGA and mBJ-GGA methods was calculated. Here, $E_g$ increased with an increasing Br concentration, as shown in Figure 4. The folded band structures using PBE-GGA are available in the Supplementary Materials, Figure S1.

The substitution of bromide atoms at the iodide sites in the CsPbI$_3$ compound provided a direct band gap character ($M \rightarrow M$). The overall behavior of the folded band structures calculated by these two approximations was similar, except for the value of $E_g$, which was higher for the mBJ-GGA method, as listed in Table 2. The calculated $E_g$ of CsPb(I$_{1-x}$Br$_x$)$_3$ using the mBJ-GGA method, agreed with the experimental values, as listed in Table 2 and shown in Figure 4. Therefore, it could be concluded that the mBJ-GGA potential presents a good approach for calculating the electronic properties for a wide range of materials, such as wide-band-gap insulators, semiconductors, and three-dimensional transition-metal oxides, particularly their band gaps [24,45,59–61].

The folded band structure calculation for a 20-atom supercell of CsPb(I$_{1-x}$Br$_x$)$_3$ represents a zone folding that hinders the analysis of the band structure of supercells, and the direct character of the folded band gap is obscured [46]. In order to recover the CsPb(I$_{1-x}$Br$_x$)$_3$ band structure in its conventional Bloch representation, the SW approach was applied to unfold the electronic structure obtained from the framework of density functional theory, using the all-electron Wien2k package. The calculation of the SW is based on remapping the supercell reciprocal space with a mesh that is compatible with the translational symmetry of a primitive cell [46]. The unfolded band structure calculation for a 20-atom supercell $1 \times 1 \times 4$ was calculated as shown in Figure 3f–j and can be directly compared to that in Figure 3a–e. The unfolded band structure for the pure supercell CsPbI$_3$ is shown in Figure 3f. Due to the increases in the doping level of Br, the unfolded band structure becomes more obvious (Figure 3g–j). In another words, the colors in the conduction band minimum (CBM) and valence band maximum (VBM) change, which indicate the Bloch spectral weights as shown in the right axis of Figure 3. The SW is determined by both degeneracy and magnitude of the corresponding Bloch character [46,62–64].
Figure 3. (a–e) Calculated folded band structures of CsPbI$_3$, CsPb(I$_{0.75}$Br$_{0.25}$)$_3$, CsPb(I$_{0.5}$Br$_{0.5}$)$_3$, CsPb(I$_{0.25}$Br$_{0.75}$)$_3$, and CsPbBr$_3$ using the (most accurate) modified Becke–Johnson generalized gradient approximation (mBJ-GGA) method. (f–j) Band structures obtained by the first-principle simulations equipped with fold2Bloch function at Br fractions of 0%, 25%, 50%, 75%, and 100% respectively. The color scale at the bottom right indicates the Bloch spectral weights.

Figure 4. Compositional dependence of the $E_g$ calculated using the PBE-GGA and mBJ-GGA methods, compared with experimental values [12,13,33].
Table 2. Calculated $E_g$ (in eV) of CsPb$(I_{1-x}Br_x)_3$ compared to the experimental and density functional theory (DFT) calculated values.

| CsPb$(I_{1-x}Br_x)_3$ $x$ | This Study | Other Calculations | 
|---------------------------|-------------|---------------------|
|                           | $E_g$(eV)   | Theoretical         | Experimental       |
|                           | PBE-GGA     | mBJ-GGA             |                   |
| 0.00                      | 1.52        | 1.83                | 1.485 [32] (PBE-GGA) |
|                           |             |                     | 1.938 [32] (HSE06)  |
|                           |             |                     | 1.359 [31] (PBE-GGA) |
|                           | 1.56 [9] (PBE-GGA) | 1.791 [33] (PBE-GGA) | 1.879 [9] (mBJ-GGA) |
|                           | 1.478 [8] (PBE-GGA) | 1.73 [34] (mBJ-GGA) | 1.75 [8] (nTmBJ) |
|                           | 1.90 [53] (PBE-GGA) | 1.791 [33] (PBE-GGA) |                   |
| 0.25                      | 1.58        | 1.92                | 1.92 [12]          |
| 0.50                      | 1.74        | 2.14                | 2.167 [33]         |
| 0.75                      | 1.81        | 2.34                |                   |
| 1.00                      | 1.82        | 2.38                | 1.60 [57] (WC-GGA) |
|                           |             |                     | 2.41 [65] (HSE)    |
|                           |             |                     | 1.482 [14] (PBE-GGA) |
|                           |             |                     | 1.764 [31] (PBE-GGA) |
|                           |             |                     | 2.50 [53] (PBE-GGA) |

3.3. Density of States

The total density of states (TDOS) and partial density of states (PDOS) based on the variable control approach were determined to further reveal the factors controlling the $E_g$ trends. In order to study the effect of replacing iodide by bromide on $E_g$ trend, the TDOS were calculated using PBE-GGA and mBJ-GGA methods shown in Figure 5a,b. The overall feature of the TDOS remains the same in CsPb$(I_{1-x}Br_x)_3$ compounds. However, by increasing the concentration of $x$ from 0.00 to 1.00, the edges of TDOS show upshifts. Figure 6 shows the calculated PDOS with various doping concentrations, using mBJ-GGA potential. For all concentrations, the Cs atom makes a negligible contribution to the valence band maximum (VBM) or conduction band minimum (CBM).

Figure 5. Calculated total density of states (TDOS) of CsPb$(I_{1-x}Br_x)_3$ with various doping concentrations by (a) PBE-GGA and (b) mBJ-GGA potentials where the valence band maximum (VBM) is shifted to 0 eV.
The optical properties of a material, according to Maxwell’s equations, are based on characteristic constants of matter, such as the dielectric constant, magnetic permeability, and electrical conductivity, which are functions of the frequency (\(\omega\)) of the incident photon [9].

The incident photon interacts with the constituent atoms, and subsequently, the dielectric function \(\varepsilon(\omega)\) describes the optical response of a material. In Figure 7, the imaginary parts \(\varepsilon_2(\omega)\) of the calculated dielectric functions are shown using the results of the mBJ-GGA method. The optical parameters, including refraction, reflection, and absorption, can be derived from the real and imaginary parts of the dielectric function [9,69]. The complete response of a material to the disturbances caused by electromagnetic radiation is described by the complex dielectric function [57]. The imaginary part of the function \(\varepsilon_2(\omega)\) is related to the band structure and describes its absorptive behavior [57]. The critical (start) points in the spectra of \(\varepsilon_2(\omega)\) were at 1.79, 1.945, 2.11, 2.26, and 2.33 eV for CsPbI\(_3\), CsPb(I\(_{0.75}\)Br\(_{0.25}\))\(_3\), CsPb(I\(_{0.5}\)Br\(_{0.5}\))\(_3\), CsPb(I\(_{0.25}\)Br\(_{0.75}\))\(_3\), and CsPbBr\(_3\), respectively, which are closely related to the band gaps of 1.78, 1.89, 2.21, 2.23, and 2.34 eV, respectively.

![Figure 6](image-url)  
**Figure 6.** Calculated partial density of states (PDOS) of CsPb(I\(_{1-x}\)Br\(_x\))\(_3\) using the mBJ-GGA potential.

3.4. Optical Properties

The optical properties of a material, according to Maxwell’s equations, are based on characteristic constants of matter, such as the dielectric constant, magnetic permeability, and electrical conductivity, which are functions of the frequency (\(\omega\)) of the incident photon [9].

The incident photon interacts with the constituent atoms, and subsequently, the dielectric function \(\varepsilon(\omega)\) describes the optical response of a material. In Figure 7, the imaginary parts \(\varepsilon_2(\omega)\) of the calculated dielectric functions are shown using the results of the mBJ-GGA method. The optical parameters, including refraction, reflection, and absorption, can be derived from the real and imaginary parts of the dielectric function [9,69]. The complete response of a material to the disturbances caused by electromagnetic radiation is described by the complex dielectric function [57]. The imaginary part of the function \(\varepsilon_2(\omega)\) is related to the band structure and describes its absorptive behavior [57]. The critical (start) points in the spectra of \(\varepsilon_2(\omega)\) were at 1.79, 1.945, 2.11, 2.26, and 2.33 eV for CsPbI\(_3\), CsPb(I\(_{0.75}\)Br\(_{0.25}\))\(_3\), CsPb(I\(_{0.5}\)Br\(_{0.5}\))\(_3\), CsPb(I\(_{0.25}\)Br\(_{0.75}\))\(_3\), and CsPbBr\(_3\), respectively, which are closely related to the band gaps of 1.78, 1.89, 2.21, 2.23, and 2.34 eV, respectively.

![Figure 7](image-url)  
**Figure 7.** Calculated \(\varepsilon_2(\omega)\) for CsPbI\(_3\), CsPb(I\(_{0.75}\)Br\(_{0.25}\))\(_3\), CsPb(I\(_{0.5}\)Br\(_{0.5}\))\(_3\), CsPb(I\(_{0.25}\)Br\(_{0.75}\))\(_3\), and CsPbBr\(_3\) as a function of photon energy.

The optical conductivity spectra, \(\sigma(\omega)\), shown in Figure 8a, demonstrate that optical conductance started at approximately 1.728, 1.864, 2.13, 2.48, and 2.54 eV for \(x = 0.00, 0.25, 0.50, 0.75,\) and 1.00, respectively; the \(\sigma(\omega)\) values reached their maxima and then decreased with small variations [57,70]. Similar features were also observed for the absorption coefficients \(\alpha(\omega)\) (Figure 8b) and extinction
coefficients $k(\omega)$ (Figure 8c). The wide absorption range suggests that these compounds could be used for various optical and optoelectronic devices in this range of the EM spectrum. Moreover, the absorption range could be tuned by varying the composition fraction with values for $x$ between 0.00 and 1.00.

Figure 8. Calculated optical conductivity $\sigma(\omega)$ (a), absorption coefficient $\alpha(\omega)$ (inset: absorption spectra in the range from 1.0 to 3.5 eV) (b), and extinction coefficient $k(\omega)$ (c) as functions of photon energy for CsPbI$_3$, CsPb(I$_{0.75}$Br$_{0.25}$)$_3$, CsPb(I$_{0.5}$Br$_{0.5}$)$_3$, CsPb(I$_{0.25}$Br$_{0.75}$)$_3$, and CsPbBr$_3$.

Figure 9a shows the variation of the real dielectric function $\varepsilon_1(\omega)$ with energy. In this spectra, the zero frequency limit $\varepsilon_1(0)$ was the most important quantity that represented the electronic part of the static dielectric constant [57]. Here, $\varepsilon_1(\omega)$ increased from the zero frequency limit to the maximum...
value and then decreased to below zero. The calculated \( \varepsilon_1(0) \) is shown in Table 3. As seen in Table 3, \( \varepsilon_1(0) \) decreased as \( x \) increased from 0.00 to 1.00, demonstrating an inverse relation between Br content \( (x) \) and \( \varepsilon_1(0) \), see Figure 10.

![Graphs showing \( \varepsilon_1(\omega) \), R(\( \omega \)), and n(\( \omega \)) as a function of photon energy.](image)

**Figure 9.** Calculated \( \varepsilon_1(\omega) \) (a), R(\( \omega \)) (b), and n(\( \omega \)) (c) as a function of photon energy.

| Parameters | \( x = 0.00 \) | \( x = 0.25 \) | \( x = 0.50 \) | \( x = 0.75 \) | \( x = 1.00 \) |
|------------|----------------|----------------|----------------|----------------|----------------|
| \( \varepsilon_1(0) \) | 4.82 [57] | 4.60 | 3.87 | 3.73 | 3.08 |
| \( R(0) \) | 0.14 | 0.13 | 0.11 | 0.10 | 0.07 |
| \( n(0) \) | 2.19 | 2.14 | 1.96 | 1.93 | 1.75 |

**Table 3.** Calculated zero frequency limits of \( \varepsilon_1(0) \), R(0), and n(0).
The frequency-dependent reflectivity \( R(\omega) \) for these compounds is shown in Figure 9b, while the zero frequency reflectivities are listed in Table 3. In addition, \( R(0) \) increased in a similar way to \( \varepsilon_1(0) \) as the change of anion concentration \( x \) increases from 0.00 to 1.00. As Figure 9a,b shows, the maximum \( R(\omega) \) occurred when \( \varepsilon_1(\omega) \) reached a negative value; thus, the material exhibited a dielectric behavior (\( \varepsilon_1(\omega) > 0 \)). Below zero, the material demonstrated metallic properties (\( \varepsilon_1(\omega) < 0 \)) [57,71]. The maximum range of \( R(\omega) \) increased with the metallicity when \( \varepsilon_1(\omega) \) was negative [9]. The reflectivity \( R(\omega) \) was initially 14.1% and reached a maximum value of 31.3% for \( \text{CsPbI}_3 \); for \( \text{CsPb}(\text{I}_{0.75}\text{Br}_{0.25})_3 \), \( R(\omega) \) was initially 13.1% and increased to 28.7%; for \( \text{CsPb}(\text{I}_{0.5}\text{Br}_{0.5})_3 \), \( R(\omega) \) was initially 10.7% and reached a maximum value of 38.5%; for \( \text{CsPb}(\text{I}_{0.25}\text{Br}_{0.75})_3 \), \( R(\omega) \) was initially 7.6% and reached a maximum value of 52.2%; and for \( \text{CsPbBr}_3 \), \( R(\omega) \) was initially 10% and reached a maximum value of 47.9%. The maximum reflectivity peak decreased as \( x \) approached 1.00 [66]. The calculated \( R(0) \) is shown in Table 3 and Figure 10 which show that \( R(0) \) decreased as \( x \) increased from 0.00 to 1.00.

Figure 10 shows the refractive indices \( n(\omega) \) as a function of the incident photon energy. The spectrum of \( n(\omega) \) closely followed \( \varepsilon_1(\omega) \) [57,70]. From Figure 9c, \( n(\omega) \) of the material increased with an increasing Br concentration in \( \text{CsPbI}_3 \) from the zero frequency limits and reached the maximum values of 2.8, 2.85, 2.57, 2.234, and 2.38 for \( \text{CsPbI}_3 \), \( \text{CsPb}(\text{I}_{0.75}\text{Br}_{0.25})_3 \), \( \text{CsPb}(\text{I}_{0.5}\text{Br}_{0.5})_3 \), \( \text{CsPb}(\text{I}_{0.25}\text{Br}_{0.75})_3 \), and \( \text{CsPbBr}_3 \), respectively. After \( n(\omega) \) reached the maximum value, it decreased to below unity in certain energy ranges; thus, the group velocity \( (V_g = \omega/n) \) of the incident radiation was greater than \( c \) [57,70]. The group velocity shifted to a negative domain, and the nature of the medium changed from linear to nonlinear or the material became superluminal for high energy photons [57,70]. The calculated \( n(0) \) is shown in Table 3, and Figure 10 shows that \( n(0) \) decreased as \( x \) increased from 0.00 to 1.00.

4. Conclusions

The structural, electronic, and optical properties of \( \text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3 \) (\( x = 0.00, 0.25, 0.50, 0.75 \) and 1.00) were investigated using the FP-LAPW scheme within the framework of the GGA. The two exchange potentials, PBE-GGA and mBJ-GGA, were used to study the electronic and optical properties. In this study, a variation in the \( E_g \) values (1.83, 1.92, 2.14, 2.34, and 2.38 eV) was observed with the increasing concentration of Br atoms in the \( \text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3 \) compounds using the mBJ-GGA potential, while another variation in \( E_g \) values (1.52, 1.58, 1.74, 1.81, and 1.82 eV) was observed using the PBE-GGA potential. \( \text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3 \) compounds were found to be wide and direct band gap semiconductors with \( E_g \) located at the M-symmetry wave vector. The effects of the substitution of I by Br on the electronic structure were studied from first principles. By controlling the portion of Br, the unfolded band structure was obtained by both degeneracy and magnitude of the corresponding Bloch character, leading to color changes in CBM and VBM. The optical properties, such as the optical conductivities, absorption coefficients, real and imaginary parts of the dielectric functions, refractive indices, extinction coefficients, and reflectivities, were also calculated. The direct \( E_g \) and high absorption spectra of these compounds in the ultraviolet–visible energy range demonstrated that the perovskite could be used.
in optical and optoelectronic devices in this range of the spectrum by varying the level of x in the composition of the compound.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2073-4352/10/5/342/s1, Tables S1–S5: Structural properties of CsPb(I$_{1-x}$Br$_x$)$_3$ Perovskite, Figure S1: Calculated the band structures of CsPb$_3$, CsPb$_{0.75}$Br$_{0.25}$, CsPb$_{0.5}$Br$_{0.5}$, CsPb$_{0.25}$Br$_{0.75}$, and CsPbBr$_3$ using the PBE-GGA method, fold2Bloch package.

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