

Article

Computational Investigation of the Folded and Unfolded Band Structure and Structural and Optical Properties of CsPb(I_{1-x}Br_x)₃ Perovskites

Hamid M. Ghaithan ^{1,2,*}, Zeyad A. Alahmed ^{1,*}, Andreas Lyras ¹, Saif M. H. Qaid ¹, and Abdullah S. Aldwayyan ^{1,3,4,*}

- ¹ Physics and Astronomy Department, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia; alyras@ksu.edu.sa (A.L.); sqaid@ksu.edu.sa (S.M.H.Q.)
- ² Physics Department, College of Education and linguistic, Amran University, Amran 2915, Yemen
- ³ King Abdullah Institute for Nanotechnology, King Saud University, P.O. Box 2454, Riyadh 11451, Saudi Arabia
- ⁴ K.A.CARE Energy Research and Innovation Center at Riyadh, P.O. Box 2022, Riyadh 11454, Saudi Arabia
- * Correspondence: hghaithan@ksu.edu.sa (H.M.G.); zalahmed@ksu.edu.sa (Z.A.A.); dwayyan@ksu.edu.sa (A.S.A.)

Received: 13 March 2020; Accepted: 20 April 2020; Published: 27 April 2020



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 ABX₃ has attracted increasing interest as a potential solar cell material because of its simple fabrication techniques and outstanding optoelectronic properties. ABX₃ 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 (CH₃NH₃PbX₃), metal halide perovskite (ABX₃, A = Cs, Rb; B = Pb, Sn; X = Cl, Br, I), and CsPbI₃, which have shown great potential [7,8].

Most of the researchers have studied the structural, electronic, and optical properties of CsPbX₃ (X = Cl, Br, I) using the density functional theory (DFT) and the WIEN2k package [8–11]. The E_g tenability for CsPbX₃ was studied experimentally [12], and the lattice modulation of Cs_{1-x}R_xPbBr₃ (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, $CsPb(Br_{1-x}I_x)_3$ and $CsPb(Cl_{1-x}Br_x)_3$, 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 E_g 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(I_{1-x}Br_x)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(I_{1-x}Br_x)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($I_{1-x}Br_x$)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($I_{1-x}Br_x$)₃ perovskite [23,24]. To simulate CsPb($I_{1-x}Br_x$)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, $R_{MT}\cdot K_{max} = 9$, 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 $G_{max} = 12 \cdot (a.u)^{-1}$. 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 CsPbX₃ 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 Pm $\overline{3}$ m 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, 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, and 1.00 for the different mixed ratios of x.

The computed lattice parameters for cubic CsPbBr₃, CsPbI₃, 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].

$CsPb(I_{1-x}Br_x)_3$	Lattice Constants (Å)		Unit-Cell Volume V(Å) ³	B (GPa)		B
	This Study	Previous Studies (Exp.)	This Study	This Study	Previous Studies	This Study
CsPbI ₃	6.28	6.40 [9] (PBE-GGA) 6.4004 [53] (PBE-GGA) 6.14 [9] (LDA) 6.25 [9] (PBEsol-GGA) 6.39 [14] (PBE-GGA) (6.29) [54] (6.18) [55]	990.69	14.5770	14.3971 [9] (PBE-GGA) 20.220 [9] (LDA) 16.910 [9] (PBEsol-GGA)	4.502
CsPb(I _{0.75} Br _{0.25}) ₃	6.1775	6.395 [14] (PBE-GGA)	942.97	-	_	-
CsPb(I _{0.5} Br _{0.5}) ₃	6.075	5.990 [14] (PBE-GGA)	896.81	-	_	-
CsPb(I _{0.25} Br _{0.75}) ₃	5.9725	5.997 [14] (PBE-GGA)	852.17	_	-	-
CsPbBr ₃	5.87	6.0051 [8] (PBE-GGA) 6.00549 [53] (PBE-GGA) 6.009 [31] (PBE-GGA) 5.875 [56] (PBEsol-GGA) 6.046 [31] (HSE) 5.999 [14] (PBE-GGA) 5.84 [57] (WC-GGA) (5.874) [58]	809.05	18.7612	-	4.2192

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.



Figure 2. The unit-cell volumes vary linearly as a function of Br content (x).

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 Γ 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 CsPbI₃ 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 CsPbI₃, 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 CsPbBr₃ 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].

	Eg(eV)					
$CsPb(I_{1-x}Br_x)_3$	This Study		Other Calculations			
X =	PBE-GGA	mBJ-GGA	Theoretical	Experimental		
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) 1.879 [9] (mBJ-GGA) 1.478 [8] (PBE-GGA) 1.75 [8] (nTmBJ) 1.90 [53] (PBE-GGA)	1.791 [33] 1.73 [34]		
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)	2.30 [66] 2.36 [67] 2.32 [13] 2.282 [68]		

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.

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.



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 (ω) 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 CsPbI₃, CsPb(I_{0.75}Br_{0.25})₃, CsPb(I_{0.25}Br_{0.75})₃, and CsPbBr₃, 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. Calculated $\varepsilon_2(\omega)$ for CsPbI₃, 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 CsPbBr₃ 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(ω) (**c**) as functions of photon energy for CsPbI₃, 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 CsPbBr₃.

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.



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

Parameters	x = 0.00	x = 0.25	x = 0.50	x = 0.75	x = 1.00
ε ₁ (0)	4.82 6.003 [57]	4.60	3.87	3.73	3.08 4.631 [57]
R(0)	0.14 0.177 [57]	0.13	0.11	0.10	0.07 0.134 [57]
n(0)	2.19 2.45 [57]	2.14	1.96 _	1.93 _	1.75 1.928 [57]



Figure 10. Zero frequency limit of $\varepsilon_1(0)$, n(0), and R(0) vs. Br content (x).

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 CsPbI₃; for CsPb(I_{0.75}Br_{0.25})₃, $R(\omega)$ was initially 13.1% and increased to 28.7%; for CsPb(I_{0.5}Br_{0.5})₃, $R(\omega)$ was initially 10.7% and reached a maximum value of 38.5%; for CsPb(I_{0.25}Br_{0.75})₃, $R(\omega)$ was initially 7.6% and reached a maximum value of 52.2%; and for CsPbBr₃, $R(\omega)$ 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 9c 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 CsPbI₃ from the zero frequency limits and reached the maximum values of 2.8, 2.85, 2.57, 2.234, and 2.38 for CsPbI₃, 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 CsPbBr₃, respectively. After $n(\omega)$ reached the maximum value, it decreased to below unity in certain energy ranges; thus, the group velocity (V_g = c/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 $CsPb(I_{1-x}Br_x)_3$ (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 $CsPb(I_{1-x}Br_x)_3$ 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. $CsPb(I_{1-x}Br_x)_3$ 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 $CsPbI_3$, $CsPb(I_{0.75}Br_{0.25})_3$, $CsPb(I_{0.5}Br_{0.5})_3$, $CsPb(I_{0.25}Br_{0.75})_3$, and $CsPbBr_3$ using the PBE-GGA method, fold2Bloch package.

Author Contributions: Conceptualization, H.M.G., Z.A.A., and A.S.A.; methodology, H.M.G. and Z.A.A.; software, H.M.G. and Z.A.A.; validation, Z.A.A., A.S.A. and S.M.H.Q.; formal analysis, H.M.G. and Z.A.A.; investigation, H.M.G., Z.A.A. and A.S.A.; data curation, H.M.G. and Z.A.A.; writing—original draft preparation, H.M.G.; writing—review and editing, Z.A.A., A.S.A., S.M.H.Q. and A.L.; supervision, A.S.A. and Z.A.A.; funding acquisition, A.S.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: The authors would like to thank Deanship of scientific research at King Saud University for funding and supporting this research through the initiative of DSR Graduate Students Research Support (GSR).

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Mao, X.; Sun, L.; Wu, T.; Chu, T.; Deng, W.; Han, K. First-Principles Screening of All-Inorganic Lead-Free ABX₃ Perovskites. *J. Phys. Chem. C* 2018, 122, 7670–7675. [CrossRef]
- Im, J.H.; Lee, C.R.; Lee, J.W.; Park, S.W.; Park, N.G. 6.5% Efficient Perovskite Quantum-Dot-Sensitized Solar Cell. *Nanoscale* 2011, *3*, 4088–4093. [CrossRef]
- 3. Gao, P.; Gratzel, M.; Nazeeruddin, M.K.; Online, V.A.; Gao, P.; Nazeeruddin, M.K. Environmental Science Organohalide lead perovskites for photovoltaic applications. *Energy Environ. Sci.* **2014**, *7*, 2448–2463. [CrossRef]
- 4. Correa-Baena, J.P.; Abate, A.; Saliba, M.; Tress, W.; Jesper Jacobsson, T.; Grätzel, M.; Hagfeldt, A. The rapid evolution of highly efficient perovskite solar cells. *Energy Environ. Sci.* **2017**, *10*, 710–727. [CrossRef]
- 5. Zhao, Y.; Zhu, K. Organic-inorganic hybrid lead halide perovskites for optoelectronic and electronic applications. *Chem. Soc. Rev.* **2016**, *45*, 655–689. [CrossRef] [PubMed]
- 6. Sum, T.C.; Mathews, N. Advancements in perovskite solar cells: Photophysics behind the photovoltaics. *Energy Environ. Sci.* **2014**, *7*, 2518–2534. [CrossRef]
- 7. Eidsvåg, H.; Rasukkannu, M.; Vajeeston, P.; Velauthapillai, D. Bandgap engineering in CsSn_xPb_(1-x)I₃ and their influence on light absorption. *Mater. Lett.* **2018**, 218, 253–256. [CrossRef]
- Maqbool, M.; Rehman, G.; Ali, L.; Shafiq, M.; Iqbal, R.; Ahmad, R.; Khan, T.; Jalali-Asadabadi, S.; Maqbool, M.; Ahmad, I. Structural, electronic and optical properties of CsPbX₃ (X = Cl, Br, I) for energy storage and hybrid solar cell applications. *J. Alloys Compd.* 2017, 705, 828–839.
- 9. Afsari, M.; Boochani, A.; Hantezadeh, M. Electronic, optical and elastic properties of cubic perovskite CsPbI₃: Using first principles study. *Optik (Stuttg).* **2016**, *127*, 11433–11443. [CrossRef]
- 10. Jishi, R.A.; Ta, O.B.; Sharif, A.A. Modeling of lead halide perovskites for photovoltaic applications. *J. Phys. Chem. C* 2014, *118*, 28344–28349. [CrossRef]
- 11. Ilyas, B.M.; Elias, B.H. A theoretical study of perovskite CsXCl₃ (X = Pb, Cd) within first principles calculations. *Phys. B Condens. Matter* **2017**, *510*, 60–73. [CrossRef]
- 12. Moore, D.T.; Kamino, B.A.; Patel, J.B.; Miranda, L.; Johnston, M.B.; Parrott, E.S.; Haghighirad, A.A.; Hörantner, M.T.; Sutton, R.J.; Snaith, H.J.; et al. Bandgap-Tunable Cesium Lead Halide Perovskites with High Thermal Stability for Efficient Solar Cells. *Adv. Energy Mater.* **2016**, *6*, 1502458.
- 13. Duan, J.; He, B.; Li, Y.; Tang, Q.; Zhao, Y.; Yuan, H. Lattice Modulation of Alkali Metal Cations Doped Cs_{1-x}R_xPbBr₃ Halides for Inorganic Perovskite Solar Cells. *Sol. RRL* **2018**, *2*, 1800164.
- 14. Chen, X.; Han, D.; Su, Y.; Zeng, Q.; Liu, L.; Shen, D. Structural and Electronic Properties of Inorganic Mixed Halide Perovskites. *Phys. Status Solidi Rapid Res. Lett.* **2018**, *12*, 1800193. [CrossRef]
- 15. Shi, J.; Yun, S. First-Principles DFT Calculations for Perovskite Solar Cells. In *Counter Electrodes for Dye— Sensitized and Perovskite Solar Cells, II*; Yun, S., Hagfeldt, A., Eds.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2018; pp. 487–509.
- 16. Umari, P.; Mosconi, E.; De Angelis, F. Relativistic GW calculations on CH₃NH₃PbI₃ and CH₃NH₃SnI₃ Perovskites for Solar Cell Applications. *Sci. Rep.* **2014**, *4*, 4467. [CrossRef]

- Li, B.; Zhang, Y.; Fu, L.; Yu, T.; Zhou, S.; Zhang, L.; Yin, L. Surface passivation engineering strategy to fully-inorganic cubic CsPbI₃ perovskites for high-performance solar cells. *Nat. Commun.* 2018, *9*, 1076. [CrossRef]
- Wang, P.; Zhang, X.; Zhou, Y.; Jiang, Q.; Ye, Q.; Chu, Z.; Li, X.; Yang, X.; Yin, Z.; You, J. Solvent-controlled growth of inorganic perovskite films in dry environment for efficient and stable solar cells. *Nat. Commun.* 2018, *9*, 2225. [CrossRef]
- 19. Liu, C.; Hu, M.; Zhou, X.; Wu, J.; Zhang, L.; Kong, W.; Li, X.; Zhao, X.; Dai, S.; Xu, B.; et al. Efficiency and stability enhancement of perovskite solar cells by introducing CsPbI₃ quantum dots as an interface engineering layer. *NPG Asia Mater.* **2018**, *10*, 552–561. [CrossRef]
- 20. Wang, K.; Jin, Z.; Liang, L.; Bian, H.; Bai, D.; Wang, H.; Zhang, J.; Wang, Q.; Liu, S. All-inorganic cesium lead iodide perovskite solar cells with stabilized efficiency beyond 15%. *Nat. Commun.* **2018**, *9*, 4544. [CrossRef]
- 21. Chen, M.; Ju, M.G.; Garces, H.F.; Carl, A.D.; Ono, L.K.; Hawash, Z.; Zhang, Y.; Shen, T.; Qi, Y.; Grimm, R.L.; et al. Highly stable and efficient all-inorganic lead-free perovskite solar cells with native-oxide passivation. *Nat. Commun.* **2019**, *10*, 16. [CrossRef]
- Kohn, W.; SHAM, L.J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* 1965, 140, A1133. [CrossRef]
- Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* 1996, 77, 3865–3868. [CrossRef] [PubMed]
- 24. Tran, F.; Blaha, P. Accurate band gaps of semiconductors and insulators with a semilocal exchange-correlation potential. *Phys. Rev. Lett.* **2009**, *102*, 226401. [CrossRef] [PubMed]
- 25. Bylander, D.M.; Kleinman, L. Good semiconductor band gaps with a modified local-density approximation. *Phys. Rev. B* **1990**, *41*, 7868–7871. [CrossRef]
- 26. Bechstedt, F.; Fuchs, F.; Kresse, G. Ab-initio theory of semiconductor band structures: New developments and progress. *Phys. Status Solidi Basic Res.* **2009**, 246, 1877–1892. [CrossRef]
- 27. Camargo-Martínez, J.A.; Baquero, R. The band gap problem: The accuracy of the wien2k code confronted. *Rev. Mex. Fis.* **2013**, *59*, 453–459.
- 28. Heyd, J.; Peralta, J.E.; Scuseria, G.E.; Martin, R.L. Energy band gaps and lattice parameters evaluated with the Heyd-Scuseria-Ernzerhof screened hybrid functional. *J. Chem. Phys.* **2005**, *123*, 174101. [CrossRef]
- Koller, D.; Tran, F.; Blaha, P. Improving the modified Becke-Johnson exchange potential. *Phys. Rev. B Condens. Matter Mater. Phys.* 2012, *85*, 155109. [CrossRef]
- 30. Perdew, J.P.; Zunger, A. Self-interaction correction to density-functional approximations for many-electron systems. *Phys. Rev. B* **1981**, *23*, 5048–5079. [CrossRef]
- Yuan, Y.; Xu, R.; Xu, H.T.; Hong, F.; Xu, F.; Wang, L.J. Nature of the band gap of halide perovskites ABX₃(A = CH₃NH₃, Cs; B = Sn, Pb; X = Cl, Br, I): First-principles calculations. *Chinese Phys. B* 2015, 24, 116302. [CrossRef]
- Ray, D.; Clark, C.; Pham, H.Q.; Borycz, J.; Holmes, R.J.; Aydil, E.S.; Gagliardi, L. Computational Study of Structural and Electronic Properties of Lead-Free CsMI₃ Perovskites (M = Ge, Sn, Pb, Mg, Ca, Sr, and Ba). J. Phys. Chem. C 2018, 122, 7838–7848. [CrossRef]
- He, M.; Ding, L.; Liu, S.; Shao, G.; Zhang, Z.; Liang, X.; Xiang, W. Superior fluorescence and high stability of B-Si-Zn glasses based on Mn-doped CsPbBr_xI_{3-x} nanocrystals. J. Alloys Compd. 2019, 780, 318–325. [CrossRef]
- Eperon, G.E.; Stranks, S.D.; Menelaou, C.; Johnston, M.B.; Herz, L.M.; Snaith, H.J. Formamidinium lead trihalide: A broadly tunable perovskite for efficient planar heterojunction solar cells. *Energy Environ. Sci.* 2014, 7, 982–988. [CrossRef]
- 35. Castelli, I.E.; García-Lastra, J.M.; Thygesen, K.S.; Jacobsen, K.W. Bandgap calculations and trends of organometal halide perovskites. *APL Mater.* **2014**, *2*, 081514. [CrossRef]
- Goesten, M.G.; Hoffmann, R. Mirrors of Bonding in Metal Halide Perovskites. J. Am. Chem. Soc. 2018, 140, 12996–13010. [CrossRef] [PubMed]
- Kang, B.; Biswas, K. Exploring Polaronic, Excitonic Structures and Luminescence in Cs₄PbBr₆/CsPbBr₃. J. Phys. Chem. Lett. 2018, 9, 830–836. [CrossRef] [PubMed]
- 38. Wolf, C.; Lee, T.W. Exciton and lattice dynamics in low-temperature processable CsPbBr₃ thin-films. *Mater. Today Energy* **2018**, *7*, 199–207. [CrossRef]
- 39. Zhang, M.; Zheng, Z.; Fu, Q.; Chen, Z.; He, J.; Zhang, S.; Chen, C.; Luo, W. Synthesis and single crystal growth of perovskite semiconductor CsPbBr₃. *J. Cryst. Growth* **2018**, *484*, 37–42. [CrossRef]

- 40. Stoumpos, C.C.; Malliakas, C.D.; Peters, J.A.; Liu, Z.; Sebastian, M.; Im, J.; Chasapis, T.C.; Wibowo, A.C.; Chung, D.Y.; Freeman, A.J.; et al. Crystal growth of the perovskite semiconductor CsPbBr₃: A new material for high-energy radiation detection. *Cryst. Growth Des.* **2013**, *13*, 2722–2727. [CrossRef]
- 41. Yaffe, O.; Guo, Y.; Tan, L.Z.; Egger, D.A.; Hull, T.; Stoumpos, C.C.; Zheng, F.; Heinz, T.F.; Kronik, L.; Kanatzidis, M.G.; et al. The nature of dynamic disorder in lead halide perovskite crystals. In *Physical Chemistry of Interfaces and Nanomaterials XV, SPIE Nanoscience + Engineering, 28 August–1 September 2016;* Bakulin, A.A., Lovrincic, R., Banerji, N., Eds.; SPIE: San Diego, CA, USA, 2016; Volume 9923, p. 99231B.
- 42. Akkerman, Q.A.; Motti, S.G.; Srimath Kandada, A.R.; Mosconi, E.; D'Innocenzo, V.; Bertoni, G.; Marras, S.; Kamino, B.A.; Miranda, L.; De Angelis, F.; et al. Solution Synthesis Approach to Colloidal Cesium Lead Halide Perovskite Nanoplatelets with Monolayer-Level Thickness Control. *J. Am. Chem. Soc.* **2016**, *138*, 1010–1016. [CrossRef] [PubMed]
- 43. Paul, T.; Chatterjee, B.K.; Maiti, S.; Sarkar, S.; Besra, N.; Das, B.K.; Panigrahi, K.J.; Thakur, S.; Ghorai, U.K.; Chattopadhyay, K.K. Tunable cathodoluminescence over the entire visible window from all-inorganic perovskite CsPbX₃ 1D architecture. *J. Mater. Chem. C* **2018**, *6*, 3322–3333. [CrossRef]
- Liu, Z.; Peters, J.A.; Stoumpos, C.C.; Sebastian, M.; Wessels, B.W.; Im, J.; Freeman, A.J.; Kanatzidis, M.G. Heavy metal ternary halides for room-temperature X-ray and gamma-ray detection. In *Hard X-ray Gamma-ray Neutron Detect. Phys. XV, Proceedings of SPIE—The International Society for Optical Engineering*, 25–29 *August* 2013; Fiederle, M., Burger, A., Franks, L., James, R.B., Eds.; SPIE: San Diego, CA, USA, 2013; Volume 8852, p. 88520A.
- 45. Koller, D.; Tran, F.; Blaha, P. Merits and limits of the modified Becke-Johnson exchange potential. *Phys. Rev. B* **2011**, *83*, 195134. [CrossRef]
- Rubel, O.; Bokhanchuk, A.; Ahmed, S.J.; Assmann, E. Unfolding the band structure of disordered solids: From bound states to high-mobility Kane fermions. *Phys. Rev. B Condens. Matter Mater. Phys.* 2014, 90, 115202. [CrossRef]
- 47. Maspero, R.; Sweeney, S.J.; Florescu, M. Unfolding the band structure of GaAsBi. *J. Phys. Condens. Matter* 2017, 29, 075001. [CrossRef]
- 48. Medeiros, P.V.C.; Stafström, S.; Björk, J. Effects of extrinsic and intrinsic perturbations on the electronic structure of graphene: Retaining an effective primitive cell band structure by band unfolding. *Phys. Rev. B Condens. Matter Mater. Phys.* **2014**, *89*, 041407. [CrossRef]
- 49. Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas. Phys. Rev. 1964, 134, B864. [CrossRef]
- 50. Nordström, L.; Madsen, G.K.H.; Blaha, P.; Schwarz, K.; Sjöstedt, E. Efficient linearization of the augmented plane-wave method. *Phys. Rev. B Condens. Matter Mater. Phys.* **2001**, *64*, 195134.
- Blaha, P.; Schwarz, K.; Luitz, G.K.H.M.D.K.J.; Tran, R.L.F.; Marks, L.D. An Augmented Plane Wave Plus Local Orbitals Program for Calculating Crystal Properties, 3rd-9501031st-ed.; Schwarz, K., Ed.; Vienna University of Technology: Vienna, Austria, 2019; Volume 2, ISBN 3-9501031-1-2.
- 52. Momma, K.; Izumi, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *J. Appl. Crystallogr.* **2011**, *44*, 1272–1276. [CrossRef]
- Ghaithan, H.M.; Alahmed, Z.A.; Qaid, S.M.H.; Aldwayyan, A.S. First principle-based calculations of the optoelectronic features of 2 × 2 × 2 CsPb(I_{1-x}Br_x)₃ perovskite. *Superlattices Microstruct.* 2020, 140, 106474. [CrossRef]
- 54. Trots, D.M.; Myagkota, S.V. High-temperature structural evolution of caesium and rubidium triiodoplumbates. *J. Phys. Chem. Solids* **2008**, *69*, 2520–2526. [CrossRef]
- 55. Eperon, G.E.; Paternò, G.M.; Sutton, R.J.; Zampetti, A.; Haghighirad, A.A.; Cacialli, F.; Snaith, H.J. Inorganic caesium lead iodide perovskite solar cells. *J. Mater. Chem. A* **2015**, *3*, 19688–19695. [CrossRef]
- Ghaithan, H.M.; Alahmed, Z.A.; Qaid, S.M.H.; Hezam, M.; Aldwayyan, A.S. Density Functional Study of Cubic, Tetragonal, and Orthorhombic CsPbBr₃ Perovskite. ACS Omega 2020, 5, 7468–7480. [CrossRef] [PubMed]
- 57. Murtaza, G.; Ahmad, I. First principle study of the structural and optoelectronic properties of cubic perovskites CsPbM₃ (M = Cl, Br, I). *Phys. B Condens. Matter* **2011**, 406, 3222–3229. [CrossRef]
- 58. Sandor, E.; Wooster, W.A. Crystal Structure and Photoconductivity of Cæsium Plumbohalides. *Nature* **1958**, *182*, 1436.
- 59. Dixit, H.; Saniz, R.; Cottenier, S.; Lamoen, D.; Partoens, B. Electronic structure of transparent oxides with the Tran-Blaha modified Becke-Johnson potential. *J. Phys. Condens. Matter* **2012**, *24*, 205503. [CrossRef]

- 60. Fan, S.W.; Ding, L.J.; Yao, K.L. Electronic structure and ferromagnetism of boron doped bulk and surface CdSe: By generalized gradient approximation and generalized gradient approximation plus modified Becke and Johnson calculations. *J. Appl. Phys.* **2013**, *114*, 113905. [CrossRef]
- 61. Traoré, B.; Bouder, G.; Lafargue-Dit-Hauret, W.; Rocquefelte, X.; Katan, C.; Tran, F.; Kepenekian, M. Efficient and accurate calculation of band gaps of halide perovskites with the Tran-Blaha modified Becke-Johnson potential. *Phys. Rev. B* **2019**, *99*, 035139. [CrossRef]
- 62. Popescu, V.; Zunger, A. Effective band structure of random alloys. Phys. Rev. Lett. 2010, 104, 236403. [CrossRef]
- 63. Popescu, V.; Zunger, A. Extracting E versus *k* Effective band structure from supercell calculations on alloys and impurities. *Phys. Rev. B Condens. Matter Mater. Phys.* **2012**, *85*, 085201. [CrossRef]
- Chen, M.X.; Weinert, M. Revealing the substrate origin of the linear dispersion of Silicene/Ag(111). *Nano Lett.* 2014, 14, 5189–5193. [CrossRef] [PubMed]
- 65. Lang, L.; Yang, J.H.; Liu, H.R.; Xiang, H.J.; Gong, X.G. First-principles study on the electronic and optical properties of cubic ABX₃ halide perovskites. *Phys. Lett. A* **2014**, *378*, 290–293. [CrossRef]
- Heidrich, K.; Schäfer, W.; Schreiber, M.; Söchtig, J.; Trendel, G.; Treusch, J.; Grandke, T.; Stolz, H.J. Electronic structure, photoemission spectra, and vacuum-ultraviolet optical spectra of CsPbCl₃ and CsPbBr₃. *Phys. Rev. B* 1981, 24, 5642–5649. [CrossRef]
- Wang, K.; Yang, Q.; Duan, J.; Zhang, C.; Zhao, F.; Yu, H.; Hu, B. Spin-Polarized Electronic Transport through Ferromagnet/Organic–Inorganic Hybrid Perovskite Spinterfaces at Room Temperature. *Adv. Mater. Interfaces* 2019, 1, 1900718. [CrossRef]
- Qaid, S.M.H.; Al-Asbahi, B.A.; Ghaithan, H.M.; AlSalhi, M.S.; Al dwayyan, A.S. Optical and structural properties of CsPbBr₃ perovskite quantum dots/PFO polymer composite thin films. *J. Colloid Interface Sci.* 2020, 563, 426–434. [CrossRef]
- 69. Ghebouli, M.A.; Ghebouli, B.; Fatmi, M. First-principles calculations on structural, elastic, electronic, optical and thermal properties of CsPbCl₃ perovskite. *Phys. B Condens. Matter* **2011**, *406*, 1837–1843. [CrossRef]
- 70. Amin, B.; Ahmad, I.; Maqbool, M.; Goumri-Said, S.; Ahmad, R. Ab initio study of the bandgap engineering of Al_{1-x}Ga_xN for optoelectronic applications. *J. Appl. Phys.* **2011**, *109*, 023109. [CrossRef]
- 71. Xu, B.; Li, X.; Sun, J.; Yi, L. Electronic structure, ferroelectricity and optical properties of CaBi₂Ta₂O₉. *Eur. Phys. J. B* **2008**, *66*, 483–487. [CrossRef]



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).