Density Functional Study of Cubic, Tetragonal, and Orthorhombic CsPbBr₃ Perovskite

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ABSTRACT: Cesium lead bromide (CsPbBr₃) perovskite has recently gained significance owing to its rapidly increasing performance when used for light-emitting devices. In this study, we used density functional theory to determine the structural, electronic, and optical properties of the cubic, tetragonal, and orthorhombic temperature-dependent phases of CsPbBr₃ perovskite using the full-potential linear augmented plane wave method. The electronic properties of CsPbBr₃ perovskite have been investigated by evaluating their changes upon exerting spin-orbit coupling (SOC). The following exchange potentials were used: the local density approximation (LDA), Perdew–Burke–Ernzerhof generalized gradient approximation (PBE-GGA), Engel–Vosko GGA (EV-GGA), Perdew–Burke–Ernzerhof GGA revised for solids (PBEsol-GGA), modified Becke–Johnson GGA (mBJ-GGA), new modified Becke–Johnson GGA (nmBJ-GGA), and unmodified Becke–Johnson GGA (umBJ-GGA). Our band structure results indicated that the cubic, tetragonal, and orthorhombic phases have direct energy bandgaps. By including the SOC effect in the calculations, the bandgaps computed with mBJ-GGA and nmBJ-GGA were found to be in good agreement with the experimental results. Additionally, despite the large variations in their lattice constants, the three CsPbBr₃ phases possessed similar optical properties. These results demonstrate a wide temperature range of operation for CsPbBr₃.

1. INTRODUCTION

Organic—inorganic halide perovskites have emerged as promising materials for efficient, low cost, thin film optoelectronic devices such as solar cells and light-emitting diodes (LEDs). These materials have properties that are important from both theoretical and experimental perspectives. Several interesting features of these materials have been observed, including the interplay between their structural and optical properties, ferroelectricity, spin-dependent transport, and superior magnetoresistance. Solar cell devices based on lead halide perovskites have exhibited efficiencies between 15 and 22%, rivaling other solar cell materials, including copper indium gallium selenide, cadmium telluride, and single crystalline Si. In addition, perovskites have great potential for use in light-emitting devices owing to their high photoluminescence quantum efficiency (PLQE), high color rendering ability, and abundant colors obtained by mixing different halide compounds with various stoichiometric ratios. The stability of organic—inorganic hybrid perovskite light-emitting diodes (PeLEDs) can be enhanced by replacing the unstable organic MA cation with an inorganic Cs cation, boosting the development of high-performance PeLEDs with excellent stability. CsPbBr₃ perovskite is the most studied perovskite emitter among all reported inorganic PeLEDs.

The structural, electronic, and optical properties of CsPbX₃ (X = Cl, Br, I, and F) have been extensively examined experimentally. Several researchers have theoretically conducted bandgap calculations and showed the trends for all possible perovskites comprising Cs, methylammonium (CH₃NH₃), or formamidinium (CH(NH₂)₂) as the A-cations, Sn or Pb as the B-cations, and Cl, Br, I, or their combination as the anions in their most common crystalline structures (cubic, tetragonal, and orthorhombic). The trends in their stability and bandgaps were analyzed, and as expected, the bandgap increased when the electronegativity of the B-cations and anions increased and the lattice expanded. As CsPbX₃ perovskites are sensitive to temperature, they exist in different phases at different temperatures. For CsPbBr₃ perovskite, experimental values of the lattice constants have been previously reported along with the ionic charges and averaged ionic radii. The structural and electronic properties of CsPbBr₃ have been theoretically examined using the empirical tight binding method and density
functional theory (DFT) with the local density approximation (LDA),\textsuperscript{40,44} Perdew–Burke–Ernzerhof generalized gradient approximation (PBE-GGA),\textsuperscript{3,40,45}–\textsuperscript{47} and modified Becke–Johnson GGA (mBJ-GGA).\textsuperscript{40,46} At temperatures below 88 °C, CsPbBr\textsubscript{3} possesses orthorhombic symmetry. As the temperature is increased, structural distortion occurs, and the structure of CsPbBr\textsubscript{3} converts to tetragonal (88 °C < T < 130 °C) and then to cubic at higher temperatures (T > 130 °C).\textsuperscript{8,14,40,41,48–61}

The accuracy of DFT calculations (with respect to experimentally measured values) for perovskites is a concern because of their recently discovered potential for application in solar cells and LEDs.\textsuperscript{62,63} The accuracy of DFT calculations was found to be highly dependent on the exchange potential used in the calculations.\textsuperscript{64,65} For example, the CsPbBr\textsubscript{3} bandgap varies significantly among recent DFT-based calculations, with considerable deviations from experimental values (reported calculated bandgaps of 1.7–4.53 eV,\textsuperscript{3,35,40,46,52,53,66} compared to the experimental values of ∼2.3 eV\textsuperscript{14,56,57,67–70} for all phases). In addition to these deviations, the existing studies compared only one or two exchange potentials and, in most cases, did not consider all three temperature-dependent phases of CsPbBr\textsubscript{3}.\textsuperscript{3,40,45,47} Therefore, the literature lacks a comprehensive study in which different exchange potentials are compared for all crystalline phases of this potential perovskite material.

The most commonly used approximate functionals for the exchange–correlation (xc) energy (E\textsubscript{xc}) include LDA,\textsuperscript{71} GGA,\textsuperscript{72} and the hybrid\textsuperscript{73} approximation. When LDA and GGA were used for solids, the bandgap was strongly underestimated, sometimes obtaining a metallic state instead of an insulating state.\textsuperscript{74} The reasons for these deviations are that the LDA and GGA functionals contain the self-interaction error\textsuperscript{4,7} and do not show a derivative discontinuity for comparing the Kohn–Sham (KS) bandgap with the experimental bandgap.\textsuperscript{7} Hence, other (screened) hybrid functionals, which showed higher accuracy, were used to calculate the bandgap.\textsuperscript{76,77} However, these functionals were more computationally expensive than LDA or GGA.\textsuperscript{74} LDA + U,\textsuperscript{78} LDA + dynamical mean-field theory (DMFT),\textsuperscript{79} and GW\textsuperscript{80,81} are other theoretical methods that provide more accurate excited states.\textsuperscript{74} However, LDA + DMFT and GW are more computationally expensive, while LDA + U, which is as computationally inexpensive as LDA, can only be applied to localized states.\textsuperscript{74}

In this study, the structural, electronic, and optical properties of cubic, tetragonal, and orthorhombic CsPbBr\textsubscript{3} perovskite were estimated to determine the band structure, density of states (DOS), complex dielectric functions (ε(ω)), refractive indices, (n(ω)), reflectivities (R(ω)), optical conductivities (σ(ω)), and absorption coefficients (α(ω)) using the full-potential linearized augmented plane wave (FP-LAPW) method with LDA,\textsuperscript{75} the Engel–Vosko GGA (EV-GGA),\textsuperscript{82} PBE-GGA,\textsuperscript{72} mBJ-GGA,\textsuperscript{45,64} the new modified Becke–Johnson GGA (nmBJ-GGA), the unmodified Becke–Johnson GGA (umBJ-GGA), and the Perdew–Burke–Ernzerhof GGA modified for solids (PBEsol-GGA), as implemented in the WIEN2k code. The aim of this theoretical study was to analyze and compare the ground state structural parameters, electronic behavior, and optical properties of CsPbBr\textsubscript{3} perovskite using the most accurate DFT methods available. Additionally, a comprehensive review and comparison with experimentally generated values is also presented for all three CsPbBr\textsubscript{3} temperature-dependent crystalline phases.

2. COMPUTATIONAL METHODS

The ground state properties of cubic, tetragonal, and orthorhombic CsPbBr\textsubscript{3} were calculated using the FP-LAPW method within the framework of DFT, as implemented in the WIEN2k code.\textsuperscript{10,11,43,44,83} For the structural properties, the
Previously Obtained Experimental and Theoretical Results

Brillouin zones were sampled using 14 cutspheres. The convergence of the basis set was controlled using charge leakage from the core and total energy convergence. The charge density Fourier expansion was used in the plane wave expansion within the interstitial region, used to be \(-6.0\) Ry, which defined the separation of the valence and core states. The charge convergence was selected to be 0.0001 \(e\) during self-consistency cycles.

Table 1. Comparison of the Lattice Constants (\(a, b,\) and \(c\)), Volume (\(V\)), Bulk Modulus (\(B\)) and Its Pressure Derivative (\(B'\)), and Relative Error % of Cubic, Tetragonal, and Orthorhombic \(\text{CsPbBr}_3\) Calculated Using LDA, PBE-GGA, and PBEsol-GGA with Previously Obtained Experimental and Theoretical Results

| parameters | cubic \(\text{Pm\text{3m}}\) | tetragonal \(\text{P4mm}\) | orthorhombic \(\text{Pnma}\) |
|------------|------------------|------------------|------------------|
|            | this study       | others (exp.)    | this study       | others (exp.)    | this study       | others (exp.)    |
| \(a (\text{Å})\) | 5.7724           | 5.77\(^e\)       | 5.7722           | 5.979\(^f\)       | (5.864)\(^d\)      | 8.5614           | 8.3764\(^g\)     |
| \(b (\text{Å})\) | 5.740\(^b\)      | (5.8445)\(^e\)   | (5.874)\(^d\)      | 5.797\(^f\)       | (5.864)\(^d\)      | 12.1869          | 11.4974\(^f\)    |
| \(c (\text{Å})\) | 5.8276           | 5.982\(^f\)      | 5.8138            | 7.6171\(^f\)      | 5.1138            | 8.2032\(^h\)    |
| \(V (\text{Å}^3)\) | 192.3398         | (202.676)\(^d\) | 194.1657          | (202.227)\(^d\)   | 888.3058          | 795.6\(^e\)     |
| relative error % | -5.1             | 5\(^e\), -2.3\(^b\) | -4               | 12.08             | 5.96\(^a\)        |
| \(B (\text{GPa})\) | 25.3956          | 25.4128          | 26.8417           | 21.4556           | 21.4546           | 19.2032          |
| \(B'\) | 4.7240           | 4.7131           | 4.7763            | 5.8513            | 8.5138            | 8.2638\(^g\)    |
| PBE-GGA | \(a (\text{Å})\) | 6.0074           | 6.009\(^e\)       | 6.0076            | 8.5613            | 8.5309\(^e\)    |
| \(b (\text{Å})\) | 6.005\(^e\)      | 6.0076            | 8.2854            | 19.2032           | 21.4536           | 11.9664\(^e\)  |
| \(c (\text{Å})\) | 6.0133           | 6.0133            | 4.9178            | 8.5138            | 8.2638\(^g\)    |
| \(V (\text{Å}^3)\) | 216.800          | 216.9734\(^e\)   | 217.0276          | 217.0276          | 217.0276          | 888.2861         |
| relative error % | 7.0               | 7\(^e\)          | 7.3               | 12.09             | 5.1\(^a\)         |
| \(B (\text{GPa})\) | 18.1465          | 18.2854          | 19.2032           | 18.2854           | 19.2032           | 19.2032          |
| \(B'\) | 5.0511           | 4.9070           | 4.9178            | 4.9070            | 4.9178            | 4.9178           |
| PBEsol-GGA | \(a (\text{Å})\) | 5.875            | 5.87\(^e\)        | 5.8758            | 8.1607            | 8.1607           |
| \(b (\text{Å})\) | 5.8821           | 5.8821            | 8.1154            | 11.6166           | 11.6166           |
| \(c (\text{Å})\) | 202.779          | 202.0796         | 769.3366           | 769.3366          | 769.3366          |
| \(V (\text{Å}^3)\) | 21.4556          | 21.4546          | 22.7598           | 2.9               | 0.76\(^d\)        |
| relative error % | 5.1               | 0\(^e\)          | 0.4               | 2.9               | 0.76\(^d\)        |
| \(B (\text{GPa})\) | 4.8168           | 4.7920           | 5.3740            | 4.8168           | 4.7920           |

\(^a\)Ref 40. \(^b\)Ref 89. \(^c\)Ref 51. \(^d\)Ref 54. \(^e\)Ref 86. \(^f\)Ref 90. \(^g\)Ref 91. \(^h\)Ref 92.

The exchange–correlation potential was calculated using the PBE-GGA, \(^b\) LDA, \(^71\) and PBEsol-GGA methods. The mBJ-GGA, PBE-GGA, LDA, nmBJ-GGA, EV-GGA, PBEsol-GGA, and umBJ-GGA schemes were used to calculate the electronic properties of \(\text{CsPbBr}_3\) perovskite. Owing to the heavy lead element, the SOC effect was included in the DFT calculation to accurately describe the band structures.

The muffin-tin radius \(R_{\text{MT}}\) was selected to ensure zero charge leakage from the core and total energy convergence. The maximum value of the angular momentum of \(l_{\text{max}} = 10\) was considered for the wave function expansion inside the atomic spheres. The convergence of the basis set was controlled using the cutoff parameter \(R_{\text{MT}}\). The largest reciprocal lattice vector used in the plane wave expansion within the interstitial region, \(K_{\text{max}}\) was 9 for the cubic and tetragonal phases and 8 for the orthorhombic phase. 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 using 14 \(\times 9 \times 14\), 10 \(\times 10 \times 9\), and 12 \(\times 12 \times 12\) k-point meshes for orthorhombic, tetragonal, and cubic \(\text{CsPbBr}_3\), respectively. The cutoff energy was selected to be \(-6.0\) Ry, which defined the separation of the valence and core states. The charge convergence was selected to be 0.0001 \(e\) during self-consistency cycles.

### 3. RESULTS AND DISCUSSION

#### 3.1. Structural Properties

To calculate the electronic structures and optical properties of cubic \(\text{Pm\text{3m}}\), tetragonal \(\text{P4mm}\), and orthorhombic \(\text{Pnma}\) \(\text{CsPbBr}_3\) perovskite, the structural properties, such as the lattice constant \(a\) (Å), bulk modulus \(B\) (GPa), and its pressure derivative \(B'\), bond length, bond angle, and relative error, were obtained using LDA, PBE-GGA, and PBEsol-GGA.\(^86\) During optimization, the Birch–Murnaghan equation of state, shown as eq 1, was used to plot the calculated total energy (Ry) of each phase against the corresponding calculated volumes,\(^88\) as presented in Figure 1a–c, d–f, and g–i for the cubic, tetragonal, and orthorhombic phases, respectively.
where \( E_0 \) is the ground state energy, \( V_0 \) is the reference volume, \( V \) is the deformed volume, \( B_0 \) is the bulk modulus, and \( B_0' \) is the derivative of the bulk modulus.

The lattice parameters for the cubic phase and for the tetragonal and orthorhombic phases were calculated using two-dimensional and three-dimensional optimizations, respectively. Table 1 summarizes the calculated lattice parameters and other parameters for the three CsPbBr\(_3\) structures. A comparison with previously published theoretical and experimental data is also presented in Table 1. All theoretical lattice parameters of the CsPbBr\(_3\) phases calculated by PBE-GGA were larger than the experimental lattice constants, whereas LDA usually underestimated the lattice constants. The lattice constants calculated by the PBEsol-GGA method were the most similar to the experimental values compared to the other methods. The relative errors between the volume optimized by LDA, PBE-GGA, and PBEsol-GGA and the experimental parameters for cubic, tetragonal, and orthorhombic CsPbBr\(_3\) are shown in Table 1. This comparison demonstrates that PBEsol-GGA reproduced the experimental values more accurately, supported by minimum values of the relative error of 5.2, 4, and 2.9% for cubic, tetragonal, and orthorhombic CsPbBr\(_3\), respectively, which were comparable to the relative errors of the other methods. The calculated bond lengths and bond angles are given in Table S1, highlighting the idea of structural orientation and information about the bandgap of the CsPbBr\(_3\) phases. The available structural information is presented in Supporting Information, Figure S1 and Tables S1–S4.

### 3.2. Electronic Properties

To obtain detailed information about the electronic structures of cubic, tetragonal, and orthorhombic CsPbBr\(_3\), the band structures were estimated using several functionals (LDA, PBEsol-GGA, PBE-GGA, umBJ-GGA, EV-GGA, mBJ-GGA, and nmBJ-GGA). We described the band structures of cubic, tetragonal, and orthorhombic CsPbBr\(_3\) (\( Pm3m \), \( P4/mnm \), and \( Pnma \) space groups, respectively) along the \( \Gamma, M, X, R, \Gamma \) (Figure 2), \( \Gamma, A, R, Z, X, M, \Gamma \) (Figure 3), and \( R, \Gamma, X, M, \Gamma \) (Figure 4) paths, respectively, where the top of the valence band (VB) was set as 0 eV for all methods.

For the high-temperature cubic CsPbBr\(_3\) phase, the band structure calculations (Figure 2) indicated that the valence band maximum (VBM) and the conduction band minimum (CBM) were located at point R, which resulted in a direct bandgap. The calculations showed that the bandgaps, as shown in Table 2, were 1.59, 1.76, 2.10, 1.65, 2.26, 2.66, and 2.00 eV within the LDA, PBE-GGA, EV-GGA, PBEsol-GGA, mBJ-GGA, nmBJ-GGA, and umBJ-GGA schemes, respectively. Owing to the heavy lead element, the SOC effect was included to accurately describe the band structures. A drastic change occurred in the electronic bandgap due to the SOC effect, which led to a decrease in the bandgaps to 0.64, 0.61, 0.99, 0.67, 1.53, 1.81, and 1.04 eV, respectively. The band structure calculations carried
Figure 3. Band structure of tetragonal CsPbBr$_3$ estimated using different potentials with and without SOC: (a) LDA, (b) PBE-GGA, (c) mBJ-GGA, (d) nmBJ-GGA, (e) umBJ-GGA, (f) EV-GGA, and (g) PBEsol-GGA. Band structures with SOC were slightly shifted down to match the VBM with $E_F$ to ensure that no change occurred in the VBM.

Figure 4. Band structure of orthorhombic CsPbBr$_3$ calculated using different potentials with and without SOC: (a) LDA, (b) PBE-GGA, (c) mBJ-GGA, (d) nmBJ-GGA, (e) umBJ-GGA, (f) EV-GGA, and (g) PBEsol-GGA. Band structures with SOC were slightly shifted down to match the VBM with $E_F$ to ensure that no change occurred in the VBM.
out using LDA, PBE-GGA, EV-GGA, PBEsol-GGA, and umBJ-GGA including the SOC effect led to severely underestimated values. The bandgap ($E_g$) values were similar to the previously calculated values (Table 2). The mBJ-GGA, mmBJ-GGA, and EV-GGA values of 2.26, 2.66, and 2.10 eV, respectively, better matched the experimental values. The energy gap calculated using the mBJ-GGA method without SOC (2.26 eV) was the closest to the experimentally measured values (2.36 and 2.32 eV, see Table 2). The mBJ-GGA exchange potential has been demonstrated to yield accurate $E_g$ values for a wide range of materials, such as wide-bandgap insulators, semiconductors, and 3d transition-metal oxides, and this accuracy also extended to CsPbBr$_3$ perovskite. The $E_g$ values obtained through mBJ-GGA+SOC and mmBJ-GGA+SOC were 1.53 and 1.81 eV, respectively, in good agreement with the experimental values.

The VBM and CBM of tetragonal CsPbBr$_3$ were located at point A (Figure 3), with direct energy gaps of approximately 1.38, 1.49, 1.92, 1.40, 2.22, 2.35, and 1.74 eV without SOC for LDA, PBE-GGA, EV-GGA, PBEsol-GGA, mBJ-GGA, mmBJ-GGA, and umBJ-GGA, respectively. By applying the SOC effect, the bandgaps decreased to 0.37, 0.56, 1.01, 0.39, 1.50, 1.69, and 0.97 eV, respectively. Previously reported DFT-calculated values for the tetragonal phase are shown in Table 2. No experimental value could be found in the literature for the CsPbBr$_3$ tetragonal phase.

As shown in Figure 4 and Table 2, the VBM and CBM of the room-temperature orthorhombic CsPbBr$_3$ phase were located at point $\Gamma$, resulting in direct $E_g$ of approximately 1.65, 1.78, 2.16, 1.68, 2.44, 2.58, and 2.03 eV without SOC for LDA, PBE-GGA, EV-GGA, PBEsol-GGA, mBJ-GGA, mmBJ-GGA, and umBJ-GGA, respectively. The $E_g$ values after applying SOC were 0.71, 0.84, 1.24, 0.67, 1.62, 1.82, and 1.04 eV for LDA, PBE-GGA, EV-GGA, PBEsol-GGA, mBJ-GGA, mmBJ-GGA, and umBJ-GGA, respectively. The $E_g$ values obtained through mmBJ-GGA+SOC and mmBJ-GGA+SOC were 1.53 and 1.81 eV, respectively, in good agreement with the experimental values.

### Table 2. Comparison between Calculated Bandgaps and Reported Theoretical and Experimental Bandgaps for Cubic, Tetragonal, and Orthorhombic CsPbBr$_3$

| method          | CsPbBr$_3$ (cubic) | CsPbBr$_3$ (tetragonal) | CsPbBr$_3$ (orthorhombic) |
|-----------------|--------------------|-------------------------|---------------------------|
|                 | without SOC       | with SOC                | without SOC               |
| LDA             | 1.59               | 0.64                    | 1.75 (0.64)               |
| PBE-GGA         | 1.76               | 0.61                    | 1.56                      |
| EV-GGA          | 2.10               | 0.99                    | 1.764                     |
| PBEsol-GGA      | 1.65               | 0.67                    | 2.633 (1.528)             |
| mBJ-GGA         | 2.26               | 1.53                    | 1.61                       |
| mmBJ-GGA        | 2.66               | 1.81                    | 2.36                       |
| umBJ-GGA        | 2.00               | 1.04                    | 2.07                       |
| exp.            |                    |                         |                           |

5 Ref 45. 6 Ref 5. 7 Ref 44. 8 Ref 40. 9 Ref 53. 10 Ref 3. 11 Ref 89. 12 Ref 35. 13 Ref 67. 14 Ref 68. 15 Ref 46. 16 Ref 66. 17 Ref 52. 18 Ref 14. 19 Ref 69. 20 Ref 57. 21 Ref 98. 22 Ref 102. 23 Ref 56. 24 Ref 103. 25 Ref 101.

![Figure 5. Band structures of (a) cubic CsPbBr$_3$ for mmBJ-GGA, (b) cubic CsPbBr$_3$ for mmBJ-GGA+SOC, (c) tetragonal CsPbBr$_3$ for mmBJ-GGA, (d) tetragonal CsPbBr$_3$ for mmBJ-GGA+SOC, (e) orthorhombic CsPbBr$_3$ for mmBJ-GGA, and (f) orthorhombic CsPbBr$_3$ for mmBJ-GGA+SOC.](https://dx.doi.org/10.1021/acsomega.0c00197)
GGA, PBEsol-GGA, mBJ-GGA, nmBJ-GGA, and umBJ-GGA, respectively. The fundamental transitions of orthorhombic CsPbBr$_3$ were reduced to 0.94, 0.94, 0.92, 1.01, 1.18, 0.76, and 0.99 eV, respectively. Previously reported DFT-based values are also presented in Table 2. The mBJ-GGA, nmBJ-GGA, and EV-GGA without SOC values of 2.44, 2.58, and 2.16 eV, respectively, were in good agreement with the experimentally determined values. When including the SOC effect, the $E_g$ values obtained through mBJ-GGA and nmBJ-GGA were 1.62 and 1.82 eV, respectively, in good agreement with experimental values.

As seen in Figure 5b,d,f, the SOC had a significant effect on the conduction band (CB) region, with a sharp reduction in the bottom of the CB at $99,100$. This reduction was caused by the splitting of the CB into a 2-fold degenerate state $\{1/2, \pm 1/2\}$ corresponding to light electrons and a 4-fold degenerate state $\{3/2, \pm 3/2\}$, $(3/2, \pm 1/2)$ corresponding to heavy electrons at this point. The triplet level in the CB of cubic (at the R-point), tetragonal (at the A-point), and orthorhombic (at the Γ-point) CsPbBr$_3$ around the Fermi level was split into a 4-fold degenerate state $(p_{3/2})$ at the higher energy level and a 2-fold degenerate state $(p_{1/2})$ at the lower energy level. The VB showed no significant change in this area, except for a weak upward shift.

Figure 6 summarizes the calculated $E_g$ values for the three CsPbBr$_3$ phases with and without SOC and compares them with experimental $E_g$ values except for the tetragonal phase. The $E_g$ for cubic CsPbBr$_3$ obtained using the mBJ-GGA potential was marginally higher than that for tetragonal CsPbBr$_3$ and marginally lower than that for orthorhombic CsPbBr$_3$, owing to the variation in the lattice constants of tetragonal and orthorhombic CsPbBr$_3$ compared to those of cubic CsPbBr$_3$, where the bandgap was determined not only by the electronegativity of the constituent elements but also by the volume. The $E_g$ (2.26 eV) for cubic CsPbBr$_3$ calculated using the mBJ-GGA potential was between those of tetragonal (2.20 eV) and orthorhombic CsPbBr$_3$, as the volume of tetragonal CsPbBr$_3$ was smaller than those of cubic and orthorhombic CsPbBr$_3$. The $E_g$ values for tetragonal CsPbBr$_3$ obtained using the other potentials were marginally lower than those for cubic and orthorhombic CsPbBr$_3$.

To obtain a detailed perspective of the band structure of orthorhombic CsPbBr$_3$, the total density of states and partial density of states (TDOS and PDOS, respectively) were plotted with respect to the band structure using the nmBJ-GGA+SOC potential that has $E_g$ values in good agreement with the experimentally values (Figure 7). Both the TDOS and PDOS are based on the variable control approach and were obtained to further determine the factors that could control the bandgap trends (Figure 7b–d). The PDOS shown in Figure 7c indicated that the effect of the Cs atom did not follow any specific rule. The PDOS shown in Figure 7d was used to analyze the effects of Pb and Br on the bandgap trends. The results revealed that the VBM was formed by the p orbitals of Br and s orbitals of Pb and their overlap indicated significant hybridization. The p orbitals of Pb and a small fraction of the p orbitals of Br constituted the CBM (similar band structures of cubic and tetragonal CsPbBr$_3$ along with the TDOS and PDOS are reported in Figure S2 of the Supporting Information).

The TDOS and PDOS for cubic, tetragonal, and orthorhombic CsPbBr$_3$ calculated using the nmBJ-GGA+SOC method are illustrated in Figure 8a–c. The three phases showed similar energy distributions of the eigenstates. The semicore state of the p state of Cs formed narrow bands located at deep energy values of $\pm 8$ and $\pm 8.5$ eV for the orthorhombic and tetragonal phases, respectively, indicating no contribution to the VBM or CBM. The VBM consisted of the antibonding of the s orbitals of Pb and the p hybrid state of Br for all three phases. The PDOS shown in Figure 7c indicated that the effect of the Cs atom did not follow any specific rule. The PDOS shown in Figure 7d was used to analyze the effects of Pb and Br on the bandgap trends. The results revealed that the VBM was formed by the p orbitals of Br and s orbitals of Pb and their overlap indicated significant hybridization. The p orbitals of Pb and a small fraction of the p orbitals of Br constituted the CBM (similar band structures of cubic and tetragonal CsPbBr$_3$ along with the TDOS and PDOS are reported in Figure S2 of the Supporting Information). The effective mass of the carriers (electrons and holes) is an important index of the transport properties of photovoltaic
materials. Pb cations, Br anions, and the symmetries of the perovskite structure play an important role in determining the effective mass of the electrons and holes.

These effective masses along the R to Γ, A to R, and Γ to X directions for cubic, tetragonal, and orthorhombic C\textsubscript{2}Pb\textsubscript{2}Br\textsubscript{6} respectively, are listed in Table S5. The effective masses (m\textsubscript{e}\* and m\textsubscript{h}\*) were calculated via the following equation:

\[
(m^*)_{ij} = \frac{\hbar^2}{m_e} \left( \frac{\partial^2 \epsilon(k \rightarrow \omega)}{\partial k_i^j} \right)^{-1}
\]

(2)

where m\textsuperscript{*} is the effective mass of the charge carrier, i and j denote reciprocal components, \(\epsilon_k(k \rightarrow \omega)\) is the energy dispersion function of the jth band, k \(\rightarrow \omega\) is the wave vector, and \(\hbar\) represents the reduced Planck’s constant. The reduced masses (\(\mu\)) were calculated using the formula

\[
\mu = \frac{m_e^* m_h^*}{m_e^* + m_h^*}
\]

(3)

where m\textsuperscript{*} and m\textsuperscript{h} represent the effective masses of electrons and holes, respectively.

Compared to the results without SOC, a majority of the effective masses including SOC exhibited lower values. For the cubic structure, m\textsuperscript{*} and m\textsuperscript{h} were calculated from 0.214 m\textsubscript{0} to 0.069 m\textsubscript{0} and from 0.069 to 0.095 m\textsubscript{0}, respectively, and those without SOC ranged from 0.068 to 0.082 m\textsubscript{0} and from 0.063 to 0.084 m\textsubscript{0}, respectively. For the tetragonal structure, m\textsuperscript{*} and m\textsuperscript{h} were calculated from 0.130 to 0.178 m\textsubscript{0} and from 0.077 to 0.082 m\textsubscript{0}, respectively, and those with SOC ranged from 0.056 to 0.073 m\textsubscript{0} and from 0.056 to 0.064 m\textsubscript{0}, respectively. For the orthorhombic structure, m\textsuperscript{*} and m\textsuperscript{h} were calculated from 0.165 to 0.254 m\textsubscript{0} and from 0.064 to 0.113 m\textsubscript{0}, respectively, and those with SOC ranged from 0.067 to 0.087 m\textsubscript{0} and from 0.069 to 0.081 m\textsubscript{0}, respectively. The effective masses of electrons and holes of cubic Cs\textsubscript{2}Pb\textsubscript{2}Br\textsubscript{6} without the SOC effect were similar to the values presented in previous publications.

Within effective mass theory, the effective Bohr diameter of a Wannier-Mott exciton (\(a_0\)) can be defined as

\[
a_0 = \frac{2 \hbar^2 \epsilon(\infty)}{\mu e^2}
\]

(4)

where \(\mu\) is the reduced mass, and \(\epsilon(\infty)\) is the dielectric constant in the limit of infinite wavelength. With this value of the exciton diameter, the exciton binding energy \(E_b\) is

\[
E_b = \frac{2 \hbar^2 \epsilon(\infty)}{\mu a_0^2}
\]

(5)

To calculate \(E_b\), we need to know the dielectric constant of the material \(\epsilon(\infty)\) and the reduced masses (\(\mu\)), which can be obtained through a DFT calculation. A weaker \(E_b\) indicates that the charge carriers behave more like free charge carriers.

The estimated \(a_0\) and \(E_b\) for cubic Cs\textsubscript{2}Pb\textsubscript{2}Br\textsubscript{6} were 5.7–9.9 nm and 28–67 meV, respectively, in good agreement with other theoretical and experimental values. Meanwhile, for tetragonal Cs\textsubscript{2}Pb\textsubscript{2}Br\textsubscript{6}, the estimated \(a_0\) and \(E_b\) were 6.4–10 nm and 24–57 meV, respectively. For orthorhombic Cs\textsubscript{2}Pb\textsubscript{2}Br\textsubscript{6}, the calculated \(E_b\) was 27–63 meV with an exciton diameter of 5.6–9.9 nm, which is also comparable to other theoretical and experimental values. The available information on m\textsuperscript{*}, m\textsuperscript{h}, \(\mu\), \(a_0\), and \(E_b\) is reported in Supporting Information, Table S5.

### 3.3. Optical Properties

The study of the optical properties of cubic, tetragonal, and orthorhombic Cs\textsubscript{2}Pb\textsubscript{2}Br\textsubscript{6} perovskite is very important because of the potential for use in LEDs and solar cells. To accurately estimate the optical properties, the number of k-points in the irreducible Brillouin zone must be increased.

Therefore, we used 5000, 2000, and 1000 k-points for cubic, tetragonal, and orthorhombic Cs\textsubscript{2}Pb\textsubscript{2}Br\textsubscript{6} perovskite. The frequency-dependent optical properties of Cs\textsubscript{2}Pb\textsubscript{2}Br\textsubscript{6} were studied and calculated using the dielectric function. The optical properties could be described using the complex dielectric function \(\epsilon(\omega)\) that exhibits two parts: real \(\epsilon_1(\omega)\) and imaginary \(\epsilon_2(\omega)\).

\[
\epsilon(\omega) = \epsilon_1(\omega) + i \epsilon_2(\omega)
\]

(6)

The imaginary part, \(\epsilon_2(\omega)\), indicates the possible transitions from occupied to unoccupied states featuring fixed k-vectors beyond the Brillouin zone, which are dependent on the DOS and momentum matrix P. The following equation can be used to define \(\epsilon_2(\omega)\):

\[
\epsilon_2(\omega) = \frac{(2\pi)}{\pi} \sum_{ll'jj'} \int d^3k \epsilon_e(k,l,l') \epsilon_h(k,j,j') \times \delta(\epsilon_e - \epsilon_h - \omega)
\]

(7)

where \(P\) is the momentum matrix element between the band \(a\) and \(b\) states within crystal momentum \(k\), and \(l\) and \(j\) are the crystal wave functions corresponding to the CB and VB with crystal wave vector \(k\). The real part \(\epsilon_1(\omega)\) of the dielectric function can be expressed as follows:

\[
\epsilon_1(\omega) = 1 + \frac{4\pi}{\omega} \int_0^\infty \frac{\omega' \epsilon_2(\omega')}{(\omega')^2 - \omega^2} d\omega
\]

(8)

where \(\omega\) is the principal of the integral.

The absorption coefficient, optical conductivity, refractive index, extinction coefficient, and reflectance \((\alpha(\omega), \sigma(\omega), n(\omega), K(\omega), R(\omega))\), respectively) are directly related to the dielectric function and can be calculated using the following equations:

\[
\alpha(\omega) = \sqrt{2} \omega (\sqrt{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)} - \epsilon_1(\omega))^{1/2}
\]

(9)

\[
\sigma(\omega) = \frac{\pi \omega}{4\epsilon_0} \epsilon_2(\omega)
\]

(10)

\[
n(\omega) = \frac{1}{\sqrt{2}} (\sqrt{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)} + \epsilon_1(\omega))^{1/2}
\]

(11)

\[
K(\omega) = \frac{1}{\sqrt{2}} (\sqrt{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)} - \epsilon_1(\omega))^{1/2}
\]

(12)

\[
R(\omega) = \left| \frac{\epsilon_1(\omega) - 1}{\epsilon_1(\omega) + 1} \right|^2
\]

(13)

Deep insights into the electronic structure of the three Cs\textsubscript{2}Pb\textsubscript{2}Br\textsubscript{6} phases can be obtained from the calculated optical properties. The most important quantity in the Mott exciton ((Figure 9a) is the zero frequency limit, \(\epsilon_1(0)\), which is the electronic part of the static dielectric function (the available information on \(\epsilon_1(0)\) is reported in Supporting Information, Figure S3 and Table S6). The calculated \(\epsilon_1(0)\) values were 3.83 for cubic C\textsubscript{2}Pb\textsubscript{2}Br\textsubscript{6}, 3.79 for tetragonal Cs\textsubscript{2}Pb\textsubscript{2}Br\textsubscript{6}, and 3.85 for...
orthorhombic CsPbBr$_3$. The $\varepsilon_2(\omega)$ values started increasing from $\varepsilon_2(0)$, reached maximum values, and then decreased and became negative for certain energy ranges. In these energy ranges, the incident photon beam was completely attenuated in CsPbBr$_3$ perovskite. This indicated an inverse relationship between $E_g$ and $\varepsilon_2(0)$. A similar relation has also been reported for other types of materials. Moreover, the reflectivity, $R(\omega)$, increased with the change in the CsPbBr$_3$ phase at the point of maximum reflectivity (where $\varepsilon_2(\omega)$ goes below zero), which can be observed in Figure 9a–f. When $\varepsilon_2(\omega)$ was negative, the materials showed a metallic nature. The $R(\omega)$ values increased from the initial values of 10.4, 10.3, and 10.5% to the maximum values of 47.8, 48.1, and 46.4% for the cubic, tetragonal, and orthorhombic phases, respectively (the available information on $R(0)$ is reported in Supporting Information, Figure S5 and Table S6).

The $\varepsilon_2(\omega)$ values show the interband transitions for semiconductor materials and describe the complete response of materials to disturbances caused by electromagnetic radiation. Furthermore, $\varepsilon_2(\omega)$ is directly related to the band structure of materials and describes their absorptive behavior. In Figure 9b, $\varepsilon_2(\omega)$ presents principal peaks of the optical critical point of 3.34, 3.33, and 3.87 (for cubic, tetragonal, and orthorhombic CsPbBr$_3$, respectively) at the corresponding energy values of 4.58, 4.59, and 5.24 eV, which increased owing to the transition between some peaks located at 5.33, 8.37, and 10.83 eV (cubic CsPbBr$_3$); 5.35, 8.38, and 10.85 eV (tetragonal CsPbBr$_3$); and 5.23, 8.69, and 10.88 eV (orthorhombic CsPbBr$_3$). The critical (onset) points in the $\varepsilon_2(\omega)$ spectra were observed at 2.13, 2.28, and 2.41 eV for cubic, tetragonal, and orthorhombic CsPbBr$_3$, respectively, which were related to the corresponding $E_g$ values of 2.26, 2.22, and 2.44 eV. Similar features were detected in the $K(\omega)$ spectra (Figure 9c). The available information on $\varepsilon_2(\omega)$ and $K(\omega)$ is reported in Supporting Information, Figures S4 and S7.

Figure 9d illustrates another useful parameter for investigating the behavior of materials when exposed to light: the electron energy loss function $L(\omega)$, which measures the propagation loss of energy inside media or materials. The peaks in the $L(\omega)$ spectra for the CsPbBr$_3$ phases indicated that energy was lost when the incident photon energy was higher than the $E_g$ of the material. The $L(\omega)$ spectra showed peaks at 18.6 and 23 eV for cubic CsPbBr$_3$, 19 and 23.2 eV for tetragonal CsPbBr$_3$, and 19 and 23 eV for orthorhombic CsPbBr$_3$. The optical properties of CsPbBr$_3$ computed in this study were in good agreement with the previously measured and reported optical properties. The peaks in the $L(\omega)$ spectra are usually known as plasma resonance, and their corresponding frequencies are called plasma frequencies.

The refractive index, $n(\omega)$, is an essential parameter when designing industrial optical materials, such as photonic crystals, waveguides, solar cells, and detectors. Furthermore, $n(\omega)$ is a crucial feature of semiconductor compounds that indicates the amount of light bent or refracted by them and is related to the microscopic atomic interactions. As the energy increased, $n(\omega)$ increased and reached the maximum value of approximately 2.4 (Figure 9e). The static refractive index, $n(0)$, values were determined to be 1.95 for the tetragonal phase and 1.96 for both the cubic and orthorhombic phases. The principal peak values of $n(\omega)$ (2.36, 2.34, and 2.4) occurred at energy values of 3.41, 3.43, and 3.48 eV for cubic, tetragonal, and orthorhombic CsPbBr$_3$, respectively. After reaching the maximum value for each phase, $n(\omega)$ started to decrease and reached values below unity for certain energy ranges. This result indicated that the group velocity of the incident radiation ($V_g = c/n$) was greater than the speed of light, $c$, for all phases. Therefore, the group velocity shifted toward the negative domain, and the medium became superluminal. The available information on $n(0)$ is reported in Supporting Information, Figure S6 and Table S6. The $\varepsilon_1(0)$, $n(0)$, and $R(0)$ values for all phases of CsPbBr$_3$ calculated using the different potentials are demonstrated in Supporting Information, Table S6.

Figure 10a provides information about $\alpha(\omega)$, which represents the attenuation percentage of the intensity of propagating light per unit of distance in a material. The critical (onset) points in the $\alpha(\omega)$ spectra were observed at approximately 2.23, 2.25, and 2.4 eV for the cubic, tetragonal, and orthorhombic phases, respectively. Starting from these values, $\alpha(\omega)$ increased, reached the maximum values at 15.74 eV for the cubic and tetragonal phases and 15.36 eV for the orthorhombic phase, and then decreased and eventually dissipated with minor variations. The prominent variations in the optical parameters in the energy range of 2.5–20 eV make CsPbBr$_3$ perovskite suitable for optical devices (LEDs and solar cells) in the major parts of the visible spectrum. Materials with $E_g$ values less than 3.1 eV work well in visible light device applications. The available information on $\alpha(\omega)$ is reported in Supporting Information, Figure S8. Similar features were also observed in the $\alpha(\omega)$ spectra (Figure 10b).
4. CONCLUSIONS

In this study, the structural, electronic, and optical properties of cubic, tetragonal, and orthorhombic CsPbBr3 perovskite were investigated using DFT calculations. The electronic band structure and optical properties of CsPbBr3 perovskite were calculated using different exchange potentials: LDA, PBE-GGA, EV-GGA, PBEsol-GGA, mBJ-GGA, nmBJ-GGA, and umBJ-GGA with and without SOC. By including the SOC effect in the calculations, the band gaps computed with the mBJ-GGA and nmBJ-GGA methods were found to be in good agreement with the experimental results. All CsPbBr3 phases presented direct bandgaps at the R, A, and Γ points. By analyzing their optical properties, the three phases of CsPbBr3 were concluded to possess similar properties, indicating a wide temperature operation range for this material.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00197.

Structural and electronic information about cubic, tetragonal, and orthorhombic CsPbBr3 and more details on optical properties (PDF)

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Notes

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