Dimension-Dependent Bandgap Narrowing and Metallization in Lead-Free Halide Perovskite Cs$_3$Bi$_2$X$_9$ (X = I, Br, and Cl) under High Pressure

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1. Introduction

Organic–inorganic hybrid perovskites have attracted much attention from the researcher community because of their remarkable photoelectric properties, including high absorption coefficients in the visible light region, tunable bandgaps, high quantum yields, high carrier mobilities, and low effective carrier quality $[1–6]$. In addition, their processing is economical and utilizes simple solution treatments $[7,8]$. The power conversion efficiency (PCE) of perovskite solar cells (PSCs) has increased dramatically from 3.8% in 2009 to 25.5% $[9,10]$. Lead hybrid perovskites have the outstanding photovoltaic properties of perovskite solar cells (PSCs) has increased dramatically from 3.8% in 2009 to 25.5% $[9,10]$. Lead hybrid perovskites have the outstanding photovoltaic properties.
to overcome for the use of Cs$_3$Bi$_2$X$_9$ (X = I, Br, and Cl) perovskites in photovoltaic devices. The large bandgap (>2 eV) is the most important factor causing a low PCE, which limits their absorption efficiency and carrier transport performance. According to the Shockley–Queisser theory, a semiconductor with a bandgap in the range of 1.3–1.5 eV is an ideal material for solar cells. Although the PCE of Bi-based PSCs has improved slightly with the improvement of the thin-film technology, it still lags far behind that of lead-based perovskites. The traditional chemical modification cannot overcome this inherent limit. Therefore, tuning the bandgap with the aim of improving the photovoltaic performance of the Cs$_3$Bi$_2$X$_9$ perovskites has become a key challenge.

High pressure (HP), which is a non-polluting tuning method, is widely used to modulate the physical and chemical properties of materials without changing their chemical composition [27,28]. In recent years, the properties of halide perovskites have been widely studied under HP; the properties studied include piezochromism, bandgap engineering, structural phase transitions and optical properties, [29–32]. In addition, various novel physical phenomena have been observed under HP conditions. For example, the organic–inorganic hybrid perovskite nanocrystals present the comminution and recrystallization under HP and exhibit higher photoluminescence quantum yield and a shorter carrier lifetime [29]. A reversible amorphization has been observed for the CH$_3$NH$_3$PbBr$_3$ perovskite under a pressure of approximately 2 GPa; during this transition, the resistance increased by five orders of magnitude, and the material still retained its response to the visible light and semiconductor characteristics up to a pressure of 25 GPa [33]. Notably, pressure-induced structural changes and optical properties are reversible upon decompression, and a semiconductor–metal transition can be observed at 28 GPa [34]. It is notable that there are few studies on Cs$_3$Bi$_2$X$_9$ perovskite systems of different dimensions at HP [34,35], and no reports exist on the one-dimensional halide perovskite Cs$_3$Bi$_2$Cl$_9$.

In this work, we calculated the lattice constants, band structures, density of states (DOS), and optical properties of the one-dimensional perovskite Cs$_3$Bi$_2$Cl$_9$ via the density functional theory (DFT) under HP for the first time and compared with the zero-dimensional perovskite Cs$_3$Bi$_2$I$_9$ and the two-dimensional perovskite Cs$_3$Bi$_2$Br$_9$. We discussed the relationship between the bandgap of the Cs$_3$Bi$_2$X$_9$ perovskites and the HP and focused on the optimal bandgap of the Shockley–Queisser theory of the Cs$_3$Bi$_2$X$_9$ perovskites. The Cs$_3$Bi$_2$I$_9$ perovskite completed the transition from semiconductor to metal at 17.3 GPa, this finding indicated that HP is an effective means to induce the semiconductor–metal transition. Moreover, it was found that the lattice constants and bandgaps of the Cs$_3$Bi$_2$X$_9$ perovskites are dependent upon dimension, that is, the changes in the lattice constants and bandgap gradually decrease as the dimension increases from zero to two under the same pressure. Our calculated results obtained in this work strengthen the basic understanding of different structures of the Cs$_3$Bi$_2$X$_9$ (X = I, Br and Cl), providing theoretical guidance for the structure and bandgap regulation of Bi-based perovskites under HP.

2. Computational Model and Method

The DFT was performed in the Vienna Ab-initio Simulation Package (VASP) using the projected augmented wave (PAW) framework [36,37]. DFT is derived from the Schrodinger equation under the Born–Oppenheimer approximation, described by the Hohenberg–Kohn theorem and the Kohn–Sham equation. The pseudopotential is a hypothetical potential energy function used in place of the inner electron wave function to reduce the computation. The electron exchange–correction function was obtained via the generalized gradient approximation (GGA) parameterized using the Perdew–Burke–Ernzerhof (PBE) formalism [38]. The cut-off energy of the plane wave was set to 500 eV [34]. The convergence criteria for the energy and force were set to $10^{-5}$ eV and 0.01 eV/Å, respectively. The Brillouin zone integration were sampled with $4 \times 4 \times 4$, $4 \times 4 \times 4$, and $4 \times 4 \times 2$ Gamma-pack k-point meshes during the structure optimization of Cs$_3$Bi$_2$I$_9$, Cs$_3$Bi$_2$Br$_9$, and Cs$_3$Bi$_2$Cl$_9$, respectively. The entire optimization of the structures was completely relaxed [39]. The
valence electronic configurations of the Cs, Bi, I, Br, and Cl atoms are \(5s^25p^66s^1\), \(5d^{10}6s^26p^3\), \(5s^25p^5\), \(4s^24p^5\), and \(3s^23p^5\), respectively. The \(\Gamma\) Brillouin zone center has a highly symmetric path, with coordinates \(\Gamma (0, 0, 0)\) to the \(M (0.5, 0, 0), K (0.333, 0.333, 0), \Gamma (0, 0, 0), A (0, 0, 0.5), L (0.5, 0, 0.5),\) and \(H (0.333, 0.333, 0.5)\). The spin–orbit coupling is not considered due to the high computational cost. Previous studies have shown that higher levels of calculation (including the spin–orbit coupling, the GW method, or hybrid functionals) obtain more accurate bandgaps; However, they induce little change in the band structure of the heavy-metal halide perovskites [40].

3. Results and Discussion

The structures of the three halogenated perovskite crystals \(\text{Cs}_3\text{Bi}_2\text{X}_9\) (\(X = \text{I}, \text{Br}, \text{and Cl}\)) are shown in Figure 1. The one-dimensional \(\text{Cs}_3\text{Bi}_2\text{Br}_9\) perovskite has an orthogonal-crystal structure; the two-dimensional \(\text{Cs}_3\text{Bi}_2\text{Br}_9\) perovskite and the zero-dimensional \(\text{Cs}_3\text{Bi}_2\text{I}_9\) perovskite have hexagonal cells [41,42]. The numbers of atoms in the \(\text{Cs}_3\text{Bi}_2\text{I}_9\), \(\text{Cs}_3\text{Bi}_2\text{Br}_9\), and \(\text{Cs}_3\text{Bi}_2\text{Cl}_9\) perovskites in the primitive cell are 28, 14, and 56, respectively. The Bi atom is located at the center of the octahedron in the \(\text{Cs}_3\text{Bi}_2\text{X}_9\) perovskites and is surrounded by six halogen atoms. Unlike in lead-based perovskites, in the \(\text{Cs}_3\text{Bi}_2\text{Br}_9\) and \(\text{Cs}_3\text{Bi}_2\text{Cl}_9\) perovskites, two octahedrons share one X atom (\(X = \text{Br}\) or Cl), whereas two octahedrons share three X atoms in the \(\text{Cs}_3\text{Bi}_2\text{I}_9\) perovskite. X atoms with different sizes and the Bi atoms form a novel double-perovskite structure. Figure 2 shows the changes in the lattice parameters and volume of the \(\text{Cs}_3\text{Bi}_2\text{X}_9\) perovskites under HP. In the primary cell of the \(\text{Cs}_3\text{Bi}_2\text{I}_9\) and \(\text{Cs}_3\text{Bi}_2\text{Br}_9\) perovskites, the lattice constants \(a\) and \(b\) are equal. The lattice constant and volume of \(\text{Cs}_3\text{Bi}_2\text{X}_9\) clearly decrease with an increase in pressure, and the slope also decreases gradually. As is well established, pressure induces a reduction in the lattice constant. From a microscopic point of view, the pressure shrinks the distance between two atoms. The strong Coulomb force makes it increasingly difficult to further compress the material as the pressure increases.

![Figure 1](image_url)

**Figure 1.** Crystal structures of the zero-dimensional perovskite \(\text{Cs}_3\text{Bi}_2\text{I}_9\) (a), two-dimensional perovskite \(\text{Cs}_3\text{Bi}_2\text{Br}_9\) (b), and one-dimensional perovskite \(\text{Cs}_3\text{Bi}_2\text{Cl}_9\) (c).
Based on the semiconductor theory, analyzing the band structure and the DOS very closely, the Fermi level is important for establishing the possible applications of a material in the photoelectric and photovoltaic fields. We therefore calculated the band structure near the Fermi level (from $-5 \, \text{eV}$ to $+5 \, \text{eV}$) under different pressures. The calculated bandgaps at a pressure of $0 \, \text{GPa}$ of the $\text{Cs}_3\text{Bi}_2\text{I}_9$, $\text{Cs}_3\text{Bi}_2\text{Br}_9$, and $\text{Cs}_3\text{Bi}_2\text{Cl}_9$ are $2.38$, $2.60$, and $3.08 \, \text{eV}$, respectively. The scissor value approach was used to establish the band structure of the $\text{Cs}_3\text{Bi}_2\text{X}_9$ perovskites in order to obtain the accurate value for the $\text{Cs}_3\text{Bi}_2\text{X}_9$ perovskites when they reached the optimal bandgap of the Shockley–Queisser theory and the transition from semiconductor to metal; this methodology overcame the limitations of the GGA–PBE calculation method and has already been applied in the study of the photoelectric properties of the $\text{CsSnCl}_3$ perovskite at HPs [40]. Many experimental studies have been conducted regarding the bandgaps of the $\text{Cs}_3\text{Bi}_2\text{I}_9$, $\text{Cs}_3\text{Bi}_2\text{Br}_9$, and $\text{Cs}_3\text{Bi}_2\text{Cl}_9$ perovskites. Among these, Daniel R. Gamelin et al. synthesized $\text{Cs}_3\text{Bi}_2\text{X}_9$ perovskites nanocrystals via the thermal injection method, and the bandgaps of the $\text{Cs}_3\text{Bi}_2\text{I}_9$, $\text{Cs}_3\text{Bi}_2\text{Br}_9$, and $\text{Cs}_3\text{Bi}_2\text{Cl}_9$ perovskites were measured as $2.07$, $2.76$, and $3.26 \, \text{eV}$, respectively [43]. Therefore, the scissors values of $-0.31 \, \text{eV}$, $0.16 \, \text{eV}$, and $0.18 \, \text{eV}$ were used for the $\text{Cs}_3\text{Bi}_2\text{I}_9$, $\text{Cs}_3\text{Bi}_2\text{Br}_9$, and $\text{Cs}_3\text{Bi}_2\text{Cl}_9$ perovskites, respectively.

Figure 3 shows the change in the band structure of the $\text{Cs}_3\text{Bi}_2\text{I}_9$ perovskite under the pressures of $0$ (a), $4$ (b), $10$ (c), and $40 \, \text{GPa}$ (d). Without external pressure, the conduction band minimum (CBM) and the valence band maximum (VBM) of $\text{Cs}_3\text{Bi}_2\text{I}_9$ perovskite are located at the $\Gamma$- and M-points, respectively. We found the $\text{Cs}_3\text{Bi}_2\text{I}_9$ perovskite to be an indirect bandgap material, which is consistent with the existing literature [44]. The semiconductor with the optimized band gap energy of $1.34 \, \text{eV}$ is critical to achieve the efficiency limit of $33.7\%$ based on the Shockley–Queisser theory [34]. In Figure 3, it can be seen that the bandgap of the $\text{Cs}_3\text{Bi}_2\text{I}_9$ perovskite decreases sharply with the increase in pressure and reaches its optimal bandgap value given by the Shockley–Queisser theory at $2–3 \, \text{GPa}$. In addition, with the high pressure further increasing, the CBM continues to decrease and
the VBM moves from the M-point to near the K-point. The Cs$_3$Bi$_2$I$_9$ perovskite completed the transition from semiconductor to metal at 17.3 GPa, and this finding indicated that HP is an effective means to induce the semiconductor–metal transition. The band structure of the Cs$_3$Bi$_2$Br$_9$ perovskite under the pressures of 0 (a), 4 (b), 10 (c), and 40 GPa (d) is presented in Figure 4. As can be seen from Figure 4, when the pressure is 0 GPa (a), the calculated band structure of the Cs$_3$Bi$_2$Br$_9$ perovskite is consistent with the results reported by Brent C. Melot et al. [45] They found a low-lying 2.52 eV indirect transition as well as a slightly larger direct gap of 2.64 eV, which are essentially in agreement with our calculated results. This structural characteristic becomes increasingly evident with the increase in pressure. The Cs$_3$Bi$_2$Br$_9$ perovskite reaches the optimal bandgap given by the Shockley–Queisser theory at 21–26 GPa, which means that the electron transitions from the valence band to conduction band become easier. Figure 5a–d shows the change of the band structure of Cs$_3$Bi$_2$Cl$_9$ perovskite with HP. The Cs$_3$Bi$_2$Cl$_9$ perovskite reaches the optimal bandgap in the range of 25–29 GPa; it is an indirect bandgap material. The CBM is at the Γ-point, and the VBM moves from the Γ-point to the Y-point, which is consistent with the results reported previously [41]. However, it was found that the Cs$_3$Bi$_2$Br$_9$ and Cs$_3$Bi$_2$Cl$_9$ perovskites did not metallize under HP despite the pressure reaching 40 GPa in both cases, which may be related to their unique structure. The bandgap changes in the Cs$_3$Bi$_2$X$_9$ perovskites under a range of HP (0, 2, 4, 6, 8, 10, 20, 30, and 40 GPa) are shown in Supplementary Figures S1–S3.

![Figure 3. Calculated band structure of the Cs$_3$Bi$_2$I$_9$ perovskite under the pressures of 0 (a), 4 (b), 10 (c), and 40 GPa (d).](image-url)
Figure 4. Calculated band structure of the Cs$_3$Bi$_2$Br$_9$ perovskite under the pressures of 0 (a), 4 (b), 10 (c), and 40 GPa (d).

Figure 5. Calculated band structure of the Cs$_3$Bi$_2$Cl$_9$ perovskite under the pressures of 0 (a), 4 (b), 10 (c), and 40 GPa (d).

Figure 6 shows the changes in the bandgaps of the Cs$_3$Bi$_2$I$_9$, Cs$_3$Bi$_2$Br$_9$, and Cs$_3$Bi$_2$Cl$_9$ perovskites under HP. It can be seen that the bandgap of the Cs$_3$Bi$_2$X$_9$ perovskites decreases with the increase in pressure (Figure 6a); the bandgap of the Cs$_3$Bi$_2$I$_9$ perovskite takes a negative value, which is a typical indicator of metallic behavior. Figure 6b shows the change in the bandgap of the Cs$_3$Bi$_2$X$_9$ perovskites after using the scissor values under...
HP. When the pressure is varied from 0 to 40 GPa, the bandgap differences of the Cs$_3$Bi$_2$I$_9$, Cs$_3$Bi$_2$Br$_9$, and Cs$_3$Bi$_2$Cl$_9$ perovskites are 3.05, 1.95, and 2.39 eV, respectively. It was found that with the increase in dimension, the bandgap differences of the Cs$_3$Bi$_2$I$_9$, Cs$_3$Bi$_2$Br$_9$, and Cs$_3$Bi$_2$Cl$_9$ perovskites decrease in turn, which indicates that the bandgap of the Cs$_3$Bi$_2$X$_9$ perovskites depends on dimension.

Figure 6. Calculated bandgap of the Cs$_3$Bi$_2$X$_9$ perovskites as a function of pressure (from 0 GPa to 40 GPa) (a). Changes in the bandgap of the Cs$_3$Bi$_2$I$_9$ perovskite after using the scissor values under HP (b). The black, red, and blue lines represent the Cs$_3$Bi$_2$I$_9$, Cs$_3$Bi$_2$Br$_9$, and Cs$_3$Bi$_2$Cl$_9$ perovskites, respectively.

To explain the dimension-dependent bandgap of the Cs$_3$Bi$_2$I$_9$, we investigate the construction of these perovskites. Based upon the primitive cell of Cs$_3$Bi$_2$I$_9$, Cs$_3$Bi$_2$Br$_9$, and the Cs$_3$Bi$_2$Cl$_9$ perovskites, the $2 \times 2 \times 1$, $2 \times 2 \times 2$, and $3 \times 1 \times 1$ supercells are shown in Figure 7a–c, respectively. In Figure 7d, $\Delta L$ represents the difference in the lattice constants of the Cs$_3$Bi$_2$X$_9$ perovskites between 0 and 40 GPa along the a, b, and c coordinate axes. In general, for centrosymmetric perovskites, the $\Delta L$ values along the a- ($\Delta L_a$), b- ($\Delta L_b$), and c- ($\Delta L_c$) axes are equal under HP. However, we found that $\Delta L_a$, $\Delta L_b$, and $\Delta L_c$ for the double perovskites were not equal; in other words, $\Delta L$ is anisotropic along the a-, b-, and c-axes. The $\Delta L_a$, $\Delta L_b$, and $\Delta L_c$ values for the Cs$_3$Bi$_2$I$_9$ perovskite (zero-dimensional) are 1.57, 1.57, and 5.2. It can be seen that $\Delta L_c$ is much larger than both $\Delta L_a$ and $\Delta L_b$. The reason for this difference is that the Bi$_2$I$_9^{3-}$ frame of the double-perovskite is continuous along the a- and b-axes but not along the c-axis. Along the c-axis, only the Cs$^+$ atoms are above or below the Bi$_2$I$_9^{3-}$ frame, which indicates that the change in the lattice constant along the c-axis is bigger than that observed along the a- and b-axes when the zero-dimensional Cs$_3$Bi$_2$I$_9$ perovskite is placed under HP.

The previous analysis shows that if the double-perovskite frame expands regularly in one direction, the $\Delta L$ in this direction will be smaller than in the other directions under HP. This indicates that the lattice constants of the Cs$_3$Bi$_2$X$_9$ perovskites are dependent on dimension. In general, the lattice constant and the bandgap decrease as the pressure increases [34]. It has also been found that the changes in the bandgap of the zero-dimensional Cs$_3$Bi$_2$I$_9$, one-dimensional Cs$_3$Bi$_2$Cl$_9$, and two-dimensional Cs$_3$Bi$_2$Br$_9$ perovskites between 40 and 0 GPa are 3.05, 2.39, and 1.95 eV, respectively. These results illustrate that the bandgaps of the Cs$_3$Bi$_2$X$_9$ perovskites are also dependent upon dimension; that is, the changes in the bandgap decrease gradually as the dimension increased from zero to two under the same pressure.
Figure 7. Crystal structure of the zero-dimensional Cs$_3$Bi$_2$I$_9$ (a), one-dimensional Cs$_3$Bi$_2$Cl$_9$ (b), and two-dimensional Cs$_3$Bi$_2$Br$_9$ (c). Difference in the lattice constants of the Cs$_3$Bi$_2$X$_9$ perovskites for the pressures between 0 and 40 GPa along the a, b, and c axes (d). The black, red, and blue lines represent Cs$_3$Bi$_2$I$_9$, Cs$_3$Bi$_2$Br$_9$, and Cs$_3$Bi$_2$Cl$_9$, respectively.

The partial density of states (PDOS) of the zero-dimensional Cs$_3$Bi$_2$I$_9$ (a), one-dimensional Cs$_3$Bi$_2$Cl$_9$ (b), and two-dimensional Cs$_3$Bi$_2$Br$_9$ (c) perovskites were shown in Figure 8. It can be seen that the VBM of the Cs$_3$Bi$_2$X$_9$ perovskites is dominated by p-X states, whereas the CBM is dominated by the p-Bi and p-X states (see Figure 8a–c). The changes in the DOS under HP are shown in Figure 8d–f. It is clear that many valence bands in the Cs$_3$Bi$_2$X$_9$ perovskites move to a deep level, and the conduction bands approach to the FE with an increase in pressure for Cs$_3$Bi$_2$X$_9$ perovskites; the shift of the conduction bands under the HP will induce the changes in the bandgap. In contrast to those of the Cs$_3$Bi$_2$Br$_9$ and Cs$_3$Bi$_2$Cl$_9$ perovskites, the forbidden band width of the Cs$_3$Bi$_2$I$_9$ gradually decreases and subsequently disappears, which indicates that the Cs$_3$Bi$_2$I$_9$ perovskite is no longer a semiconductor; it becomes a metal at 17.3 GPa. This conclusion is agreement with the calculated results for the band structure.
A large absorption coefficient is of great significance in photoelectric and photovoltaic applications. Such a property improves the PCE of solar cells and the luminous efficiency. The absorption coefficient is usually described by the dielectric function according to the following expression [46]:

$$\alpha = 2\omega \left[ \frac{(\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega))^{1/2} - \varepsilon_1(\omega)}{2} \right]^{1/2}$$

where the $\omega$ is the frequency of light, and $\varepsilon_1$ and $\varepsilon_2$ are the real and imaginary parts of the dielectric function, respectively. The calculated $\varepsilon_1$ and $\varepsilon_2$ values of the Cs$_3$Bi$_2$X$_9$ perovskites are presented in Supplementary Figures S4–S6 along the a-, b-, and c-axes. The static dielectric function of the Cs$_3$Bi$_2$X$_9$ perovskites increases gradually with increasing pressure from 0 to 40 GPa. The $\varepsilon_2$ value is closely related to the optical absorption and usually used to describe the absorption behavior of materials.

The calculated absorption coefficients of the Cs$_3$Bi$_2$X$_9$ perovskites are shown in Figures 9 and 10 along the a-, b-, and c-axes. It was found that the Cs$_3$Bi$_2$I$_9$ perovskite has the same absorption coefficient along the a- and b-axes with the increase in pressure, as is the case for the Cs$_3$Bi$_2$Br$_9$ perovskite. The absorption coefficients of the Cs$_3$Bi$_2$Cl$_9$ perovskite are unequable along the a-, b-, and c-axes under HP. The $\Delta L$ value of the Cs$_3$Bi$_2$X$_9$ perovskites in Figure 7d is consistent with these behaviors, which suggests that the changes in the structure of the Cs$_3$Bi$_2$X$_9$ perovskites under HP will affect the optical properties considerably. The Cs$_3$Bi$_2$X$_9$ perovskites exhibit a redshift with the increase in pressure, which indicates that the Cs$_3$Bi$_2$X$_9$ can absorb the low-energy photons. Moreover, the absorption coefficients of the Cs$_3$Bi$_2$X$_9$ perovskites increase gradually in the ultraviolet region as the pressure increases from 0 to 40 GPa. It was also found that the Cs$_3$Bi$_2$X$_9$ perovskites have a large absorption coefficient in the visible region (on the order of $10^5$ cm$^{-1}$). Therefore,
the Cs$_3$Bi$_2$X$_9$ perovskites are an attractive candidate in applications of photoelectric and photovoltaic devices.

**Figure 9.** Absorption coefficients of the Cs$_3$Bi$_2$I$_9$ along the $a$- and $b$-axes (a), Cs$_3$Bi$_2$I$_9$ along $c$-axis (b), Cs$_3$Bi$_2$Br$_9$ along the $a$- and $b$-axes (c), and Cs$_3$Bi$_2$Br$_9$ along the $c$-axis (d) as a function of the pressure (from 0 to 40 GPa).

**Figure 10.** Absorption coefficients of Cs$_3$Bi$_2$Cl$_9$ along the $a$-axis (a), along the $b$-axis (b), and along the $c$-axis (c) as a function of the pressure (from 0 to 40 GPa).
4. Conclusions

In summary, we investigated the lattice constants, band structure, DOS, and optical absorption of the cesium bismuth iodide $\text{Cs}_3\text{Bi}_2\text{X}_9$ ($X = I, \text{Br}$ and $\text{Cl}$) perovskites under HP by using the DFT. It was found that the optimal bandgap of the Shockley–Queisser theory for the $\text{Cs}_3\text{Bi}_2\text{I}_9$, $\text{Cs}_3\text{Bi}_2\text{Br}_9$, and $\text{Cs}_3\text{Bi}_2\text{Cl}_9$ perovskites can be obtained at 2–3 GPa, 21–26 GPa, and 25–29 GPa, respectively. The changes in the bandgap of $\text{Cs}_3\text{Bi}_2\text{I}_9$, $\text{Cs}_3\text{Bi}_2\text{Br}_9$, and $\text{Cs}_3\text{Bi}_2\text{Cl}_9$ perovskites are 3.05, 1.95, and 2.39 eV under a pressure of 40 GPa, respectively. The $\text{Cs}_3\text{Bi}_2\text{I}_9$ perovskite was found to transform from a semiconductor into a metal at 17.3 GPa. Furthermore, the dimension-dependent lattice constants, unit-cell volumes, and bandgaps of the $\text{Cs}_3\text{Bi}_2\text{X}_9$ perovskites were studied. Our calculations show that HP is an effective way to tune the photovoltaic and optoelectronic properties of the $\text{Cs}_3\text{Bi}_2\text{X}_9$ perovskites by modifying the crystal structure, which provides a promising method for material design and applications.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/nano1102712/s1. Table S1: Summarized bandgap values of $\text{Cs}_3\text{Bi}_2\text{X}_9$ perovskites under high pressure; Figure S1: Calculated band structures of the $\text{Cs}_3\text{Bi}_2\text{I}_9$ perovskite under the different pressures (a–i); Figure S2: Calculated band structures of the $\text{Cs}_3\text{Bi}_2\text{Br}_9$ perovskite under the different pressures (a–i); Figure S3: Calculated band structures of the $\text{Cs}_3\text{Bi}_2\text{Cl}_9$ perovskite under the different pressures (a–i); Figure S4: Real part of the dielectric function of the $\text{Cs}_3\text{Bi}_2\text{I}_9$ perovskite along the $a$- and $b$-axes (a), and the $c$-axis (b) as a function of pressure (from 0 to 40 GPa). Imaginary part of the dielectric function of the $\text{Cs}_3\text{Bi}_2\text{I}_9$ perovskite along the $a$- and $b$-axes (c), and along the $c$-axis (d) as a function of pressure (from 0 to 40 GPa); Figure S5: Real part of the dielectric function of the $\text{Cs}_3\text{Bi}_2\text{Br}_9$ perovskite along the $a$- and $b$-axes (a), and the $c$-axis (b) as a function of pressure (from 0 to 40 GPa). Imaginary part of the dielectric function of the $\text{Cs}_3\text{Bi}_2\text{Br}_9$ perovskite along the $a$- and $b$-axes (c), and along the $c$-axis (d) as a function of pressure (from 0 to 40 GPa); Figure S6: Real part of the dielectric function of the $\text{Cs}_3\text{Bi}_2\text{Cl}_9$ perovskite along the $a$-axis (a), along the $b$-axis (b), and along the $c$-axis (c) as a function of pressure (from 0 to 40 GPa). Imaginary part of the dielectric function of the $\text{Cs}_3\text{Bi}_2\text{Cl}_9$ perovskite along the $a$-axis (d), along the $b$-axis (e), and along the $c$-axis (f) as a function of pressure (from 0 to 40 GPa).

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