Research article

Semiconductor to metallic transition in double halide perovskites Cs₂AgBiCl₆ through induced pressure: A DFT simulation for optoelectronic and photovoltaic applications

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ABSTRACT

Double halide perovskites (A₂M⁺M₃⁺X₆) have been considered as high-performance material for optoelectronic and photovoltaic devices. Here, we investigate the structural, thermodynamic, optical, mechanical and electronic properties of pressure-induced Cs₂AgBiCl₆ samples. The phase stability is confirmed by the tolerance and octahedral factor calculations. The thermodynamic potentials such as enthalpy, free energy, entropy, and heat capacity are observed in the phonon modes. The indirect to direct band gap is observed due to disorders of Ag⁺/Bi₃⁺ cations in their sub-lattice. In this study, the induced pressure was varied between 0 and 80 GPa and the transition of the band gap energy from semiconductor to metal was observed at a hydrostatic pressure of 80 GPa. The bond length in between Ag and Bi atoms is reduced due to crystal defect, occurred under induced pressure. The narrow band gap energy and the partial density of states of the disordered Cs₂AgBiCl₆ samples refer to the relocation of charge carriers to facilitate the photocatalytic reaction. As the pressure changes, the absorbing edge also moves into the lower energy region. The pressure-induced Cs₂AgBiCl₆ sample has a strong absorption in the range of visible wavelength of light and shifted in the ultraviolet region. Simultaneously, the pressure-driven material extend the symmetry breaking of [AgBi] / C₀₆ and [AgCl] / C₀₆ octahedra and hence the total energy decreased due to narrow band gap energy. Phase-change dihalide materials have excellent properties, opening up new avenues for device applications. The mechanical properties suggest that the pure and pressure-induced Cs₂AgBiCl₆ samples have potential characteristics for an optoelectronic and photovoltaic applications.

1. Introduction

Recently, double halide perovskites are recognized as promising candidates for photovoltaic and optoelectronic devices owing to their excellent phase, thermal, structural, electrical, optical, and dynamic stability [1, 2, 3, 4, 5]. Many researchers report that Cs₂AgBiCl₆ halide perovskites have been used in solar cells, lasers, light-emitting diodes (LEDs) and radiation detection. Lead-based hybrid halide perovskites have excellent photovoltaic properties, despite the long-term negative impact on the environment [6]. Over the past few decades, researchers have attempted to find bimetallic halides for cost effective optoelectronic devices to transcend the limitations of instability and toxicity.

The standard chemical formula for metal halides is A₂M⁺M₃⁺X₆, where, A = earth metal, M⁺ = monovalent, M₃⁺ = trivalent, X = halide [7]. Recently, double halide perovskites have found potential applications in optoelectronic devices [8, 9]. Due to easy ion’s transition in monovalent and trivalent cations, Bi-based organic and inorganic double metal halides are used in a solar cell device. Non-toxic double halide Cs₂AgBiCl₆ has indirect band gap energy of 1.83 eV and the sub-lattice disorder of Ag and Bi has a great influence on the energy band gap [10]. Disordered (Ag, Bi) anti-site defects occur within the Cs₂AgBiCl₆ lattice network due to the transferred direct band gap of 0.62 eV. Here, we used driving pressure on the Cs₂AgBiCl₆ lattice network. Among the disordered Ag and Bi atoms in the Cs₂AgBiCl₆, the Ag-3d and Bi-6p orbital electrons are hybridized due to the reduced band gap.

Recently, theoretically based DFT simulations of Cs₂AgBiCl₆ [11] reported that an indirect transfer of the band gap to direct can occur via Sn⁴⁺ (Ge⁴⁺) doping. Due to Sn and Ge doping, the light absorption changes significantly and the exciton binding energy is significantly reduced. The valence band maximum (VBM) and conduction band minimum (CBM) of the pure Cs₂AgBiCl₆ sample are located at multiple k-points in the Brillouin zone, demonstrating indirect band gap
properties. This fact is especially important for comprehending the pressure depends on the distribution of space charge at various k-points energies.

The properties of semiconductor material can easily tune by applying a hydrostatic pressure [12, 13, 14]. L. Wang et al. noted the structural phase change of lead halide perovskite CH(NH3)2PbBr3 at a pressure of 2.2 GPa [15]. The pressure-driven Cs2AgBiCl6 sample decreases the energy of the band gap and oriented the electron orbits towards the electric field. As the outcome, the bond energy of the octahedral state changes, affecting the boundary conditions of the electron wave function, thereby reducing the band gap energy. We find that under driving pressure, the absorption peaks shift to the red-shifted-region owing to distortion inside the [AgBr6]3- and [BiBr6]3- octahedral states.

In this study, we investigated the indirect to the direct band gap transition in Cs2AgBiCl6 through the disordered Ag⁺/Bi³⁺ cations in their sub-lattices and also search semiconductors to metals by hydrostatic pressure. Hence, this study will provide a better understanding of double halide perovskites on tunability of the electronic band gap and metallization. Furthermore, we investigate uncompressed and compressed structural, mechanical, optical, electronic and photocatalytic properties of Cs2AgBiCl6 double halide perovskites applying the Density Functional Theory (DFT). We anticipate that Cs2AgBiCl6 would be a favorable candidate for the applications in optoelectronic and photovoltaic devices.

2. Theoretical methodology

DFT was carried out applying plane-wave-based CASTEP Code material studio, 2017 package [16, 17]. The exchange correlation potential energy and the projected enhancement wave (PAW) pseudopotential are described using the non-spin polarized Perdew-Burke-Ernzerhof (PBE) function in the general gradient approximation (GGA) method [18, 19, 20]. We applied 4 × 4 × 4 gamma centered (Γ) k-points to pure and pressure-induced Cs2AgBiCl6. 5s² 5p⁶ 6s¹ for Cs, 4d¹⁰ 5s¹ for Ag, 6s² 6p³ for Bi, and 3s² 3p³ for Cl, the electron configuration is done in the valence band based on the partial density of states (PDOS) calculations. In this work, the unit cell of Cs2AgBiCl6 is used for all calculations in a 1 × 1 × 1 super-cell model. The results of plane wave cutoff energy convergence for structural optimization are shown in Figure 1. An energy cutoff of 420 eV was found to be sufficient to achieve converged ground state energy for Cs2AgBiCl6. Hence, the cutoff energy 420 eV was applied for uncompressed and compressed Cs2AgBiCl6.

To see the absorption and dielectric spectra, a value of 0.25 eV was applied instead of the theoretical and experimental band gap energy of the double halide Cs2AgBiCl6 1.91 eV and 2.16 eV, respectively [21, 22]. Both pure and pressure-driven Cs2AgBiCl6 are maximized by decreasing the total energy, internal force, and external stress using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm with change of constant lattice parameters and internal coordinates. The unit cell structure and atomic relaxation of Cs2AgBiCl6 have been accomplished under the residual forces 0.03 eV/Å. To calculate the elastic modulus Cij, the finite strain theory was applied [16, 25, 24]. The stress tensor has six independent stress parameters σij, and each strain σ̄j corresponds to a unit cell. Finite displacement super-cell technology is used to calculate lattice dynamics such as phonon dispersion.

3. Results and discussion

3.1. Structural parameters and phase stability

The metal halide Cs2AgBiCl6 perovskite is a cubic-structure having space group Fm3 m (No. 225). Hence, Cs atoms are occupied at face centered position with 8c Wyckoff site and fractional coordinates (0.25 0.25 0.25), Bi atoms are positioned at the body-centered with 4b Wyckoff site and fractional coordinates (0.5 0.5 0.5), Ag atoms are situated at corner position with 4a Wyckoff site and fractional coordinate (0 0 0), and Cl atoms are situated at a face-centered position in the unit cell with 24e Wyckoff sites and fractional coordinates (0.2513 0 0). The visualization of the 1 × 1 × 1 super-cell ordered and disordered structures of the Cs2AgBiCl6 are displayed in Figure 2. The simulated structural parameters, a match well with previously published manuscripts, as shown in Table 1. Two Cs⁺, one Bi³⁺, one Ag⁺ and six Cl ions coupled to adjacent Bi³⁺ and Ag⁺ ions form the unit cell of Cs2AgBiCl6. Ag/Bi disordered samples have a slightly different lattice parameter, a (10.86 Å) and cell volume V (1325 Å³) from the Cs2AgBiCl6 order due to the mismatch of Ag⁺ (0.89 Å) and Bi³⁺ (3.36 Å) ions. The DFT-based simulated structural parameters were found to be closer to the experimental manuscript [25].

As expected, the unit cell parameters decrease under compression. As a result, the repulsion becomes more powerful in between the atoms, changing the hardness of the sample compression under applied pressure. The material should have phase stability to be used for precise device applications. First, the material must have a fully filled elastic modulus condition to achieve mechanical stability. The stability of the phase tolerance is measured using Eq. (1) [26].

\[
t = (R_X + R_S)/\sqrt{2} \times (\sigma_{R_X}^2 + \sigma_{R_S}^2)/2 + R_X.
\]

(1)

The octahedral factor is given by Eq. (2).

\[
\mu = (R_{R_X} + R_{R_S})/2R_X
\]

(2)

In order to calculate the stability, the tolerance and octahedral factor are to be in the range 0.81 < t < 1.0 and 0.81 < μ < 1.0. In order to find the phase stability, Shannon ion radius was used. For Cs2AgBiCl6 the calculated, μ = 0.41 and t = 0.92 depicts that the sample belongs to standard halide perovskites.

3.1.1. Dynamic and thermodynamic stability

In order to obtain stable natural gain, the sample must meet some special requirements. To observe the dynamic properties, we employ the finite displacement method by analyzing the phonon dispersion curve. The crystal lattice must be constant for dynamic stability. Second, there would not be the shifting of phonon modes in the graph of the phonon dispersion. Soft phonon mode refers to the movement of a group of atoms from a structure of high crystal symmetry to a structure of low crystal symmetry indicates that the sample is unstable. Soft mode, phonon dispersion contains imaginary mode frequency (negative). The phonon dispersion graphs are shown in Figure 3 (a). The phonon frequency must have positive values in a dynamic stable crystal. Notably, imaginary frequencies are not maintained at points W, L, K, Γ and X, indicating a stable mode.

To observe the thermodynamic stability, we calculated the phonon properties. We calculated the thermodynamic potentials viz. enthalpy (H), the free energy (F), and the entropy (S) at the constant temperature
with the help of phonon properties. The involvement of vibrations to enthalpy, free energy and entropy are represented by eqn. no. (3), (4) and (5), respectively [27].

\[
H(T) = E_{\text{tot}} + \frac{1}{2} \int g(\omega)\hbar\omega d\omega + \int \frac{\hbar\omega}{e^{\frac{\hbar\omega}{k_B T}} - 1} g(\omega) d\omega
\]  
(3)

\[
F(T) = E_{\text{tot}} + \frac{1}{2} \int g(\omega)\hbar\omega d\omega + k_B T \int g(\omega) \ln \left(1 - e^{-\frac{\hbar\omega}{k_B T}}\right) d\omega
\]  
(4)

\[
S(T) = k_B \left[ \int \frac{\hbar\omega}{e^{\frac{\hbar\omega}{k_B T}} - 1} g(\omega) d\omega - \int g(\omega) \ln \left(1 - e^{-\frac{\hbar\omega}{k_B T}}\right) d\omega \right]
\]  
(5)

Table 1. The simulated lattice parameter \(a\) compared with the previously published manuscript.

| Pressure (GPa) | Present study | Simulation | Experimental |
|---------------|--------------|------------|--------------|
| 0             | 11.11        | 10.92 [25] | 10.77 [25], 10.78 [11] |
| 20            | 9.81         | -          | -            |
| 40            | 9.35         | -          | -            |
| 50            | 9.19         | -          | -            |
| 60            | 9.06         | -          | -            |
| 70            | 8.93         | -          | -            |
| 80            | 8.84         | -          | -            |

Figure 2. 1×1×1 super cell (a) ordered and (b) disordered structure of CsAgBiCl₆.

Figure 3. (a) Phonon dispersion curves high symmetry direction, (b) thermodynamic properties, (c) Debye temperature and (d) heat capacity of 80 GPa for CsAgBiCl₆.
Cs$_2$AgBiCl$_6$ are thermodynamically stable in nature.

Dynamically, we predict that pure and pressure-induced systems express the Dulong-Petit limit at high temperature. Based on the third law of thermodynamics, Remarkably, the thermal capacity ad-dress the Dulong-Petit limit at high temperature. Based on the thermodynamic properties, we predict that pure and pressure-induced Cs$_2$AgBiCl$_6$ are thermodynamically stable in nature.

### 3.2. Electronic properties

In viewing the electronic properties of ordered and disordered cubic hybrid perovskites Cs$_2$AgBiCl$_6$, we study the electron band energies along the high symmetry points. We applied hydrostatic pressure to the metatallization in the estimated Cs$_2$AgBiCl$_6$ compound. **Figure 4(a-d)** shows the simulated electronic band structure. The HSC (Heyd-Scuseria-Ernzerhof) method is suitable for accurate band gap measurements [28]. However, our main goal is to see metallization, since the band gap error of the general gradient approximation (GGA) method is ignored. **Figure 4(a)** shows that the k-points in the valence and conduction bands are different and the ordered samples show indirect band gap. The pure Cs$_2$AgBiCl$_6$ has strong absorption, long charge carrier lifetime and the indirect band gap nature. The indirect band gap samples are applications for optoelectronic devices [29].

The simulated energy band gap is found in good fitting with the published theoretical and experimental results [28, 30, 31]. Due to the orbital motion towards the electric field, the electronic band gap decreases with pressure and eventually experiences the metallic band gap. The total density of states (TDOS) and the partial density of states (PDOS) of ordered and disordered Cs$_2$AgBiCl$_6$ double halide perovskites are shown in Figures 5 (a-d). As shown in the images of TDOS and PDOS, the VB is mostly Ag-4d and Bi-5d orbits with small contributions of Cs-6s and Cl-3p states. The high energy band has little contributions from Cs-6s and Cl-3p orbitals. The TDOS of disordered Cs$_2$AgBiCl$_6$ becomes wider than that of ordered Cs$_2$AgBiCl$_6$, specifies that the higher order electron delocalization due to the loss of crystal symmetry.

#### 3.2.1. Analysis of Mulliken population and charge density distribution

Mulliken population analysis gives information on the charge, bond length and bond population in a solid crystalline sample, which helps to determine the distribution of charge in forming the bonds [31, 32]. Mulliken effective charge is determined by the eqn. no. (6) [32]

$$Q(\alpha) = \sum_k W_k \sum_{\mu} \sum_{\nu} P_{\mu\nu}(k) S_{\mu\nu}(k)$$

**Figure 4.** The electronic band structure of (a) pure, (b) disordered, (c) pressure induced at 70 GPa and (d) pressure induced at 80 GPa of Cs$_2$AgBiCl$_6$. 
Here, $P_{\mu \nu}$ refers the density matrix of an element and $S_{\mu \nu}(k)$ represents the overlap matrix.

The overlapped population is occurred within two atoms, $a \beta$ can be expressed by the following Eq. (7) [32]

\[
(p(a\beta)) = \sum_k W_1 \sum_{i=1}^{n_a} \sum_{j=1}^{n_\beta} 2P_{\mu \nu}(k)S_{\mu \nu}(k)
\]

Figure 5. The total and partial density of states (a) pure, (b) disordered, (c) pressure induced at 70 GPa and (d) pressure induced at 80 GPa of Cs$_2$AgBiCl$_6$.

Notably, the Mulliken effective charge of the spacer Cs, Ag, Bi, and Cl atoms were found to be smaller than their ionic charges, viz. $^+1$, $^+2$, $^+3$, and $^-1$, respectively. To separate the Mulliken effective charge and the ionic radius, Shannon ionic radius was used. Mulliken effective charge and formal ionic radius values estimate the blend of ionic and covalent bonds.

Mulliken effective charges (e) are varying at different driven hydrostatic pressure. It is seen that the Mulliken effective charge (e) does not
follow any trend due to the variant form ionic radius of Ag atoms. A positive number of bonds indicate a high degree of covalentit
cs; conversely, a small group of bonds refers to a high degree of similarity in
covalent bonds [33, 34]. From Table 2, we observe that the pressure-driven Cl–Ag and Cl–Bi bond lengths decrease at different
induced pressures due to the binding of ionic radii to each other. The shift in
inter-octahedral Cl–Ag and Cl–Bi bond lengths is caused for the crystal
defect that occurred in Ag and Bi atoms. The intra-octahedral bonds
(Cl–Ag and Cl–Bi) are relatively stronger in compared to pressure
induced samples due to van der Waals force of the former Cl–Ag and
Cl–Bi bonds. Under the induced pressure at 80 GPa, Ag and Bi atoms
formed a weak bond. Simultaneously, symmetry breaking occurs within
the [AgBr6]3– and [BiBr6]3– octahedral sites when the induced pressure
experiences 0 GPa–80 GPa.

The bond length of Cl–Ag is 2.80 Å in the ordered Cs2AgBiCl6, which decreases to 2.65 Å when the structure transitions to a disordered
structure. Likewise, the bond length of Bi–Cl in Cs2AgBiCl6 decreases from 2.75 Å to 2.65 Å when the system is transformed from an ordered
system to a disordered one. Finally, the lower bond length is found when
the band gap energy undergoes indirect to direct. For the pressure-
induced samples, the Ag–Br bond length was reduced and the Cs2Ag-
BiCl6 sample was transformed from semiconductors to metals. It gives an
idea about the bonding properties through charge density (e/Å2) of pure
and pressure-induced distribution of Cs2AgBiCl6. Figure 6 shows the estimated charge density of the Cs2AgBiCl6 sample. We have seen that
the charge densities of the pure Cs2AgBiCl6 sample and the pressure-
driven Cs2AgBiCl6 sample overlap with each other. The pristine Cs2Ag-
BiCl6 sample has the covalent bond, which is ensured by charge density
distribution image. As the pressure changes, the bonding charge density
increases due to the decreasing interatomic distance. The covalent bond
is formed in between Bi and Ag atoms with the maximum charge density and exhibits strong electron localization.

### 3.3. Photo-catalytic activity

Photocatalysis is playing a key role for optoelectronic device appli-
cations. The most important parameters for efficient photocatalyst ma-
terials are considered to be narrow band gap, low recombination rate of
electron-hole pair, and appropriate redox potential. The band energy
diagrams of ordered and disordered Cs2AgBiCl6 are shown in Figure 7.
The redox potential is measured from the states of the valence band
maximum (VBM) and conduction band minimum (CBM) and the value is
compared with the oxidation/reduction potential of water. Normally, a
large CBM potential indicates a greater reduction power for electrons
compared to the hydrogen reduction potential, while a lower VBM po-
tential indicates a strong oxidative power for holes compared to the
water oxidation potential [35].

| Samples | 0 GPa | 20 GPa | 40 GPa | 60 GPa | 80 GPa |
|---------|-------|-------|-------|-------|-------|
| Atoms   |       |       |       |       |       |
| Cs      | 0.88  | 0.90  | 0.97  | 1.05  | 1.12  |
| Ag      | 0.14  | -0.22 | -0.44 | -0.55 | -0.66 |
| Bi      | 1.19  | 1.15  | 1.02  | 0.87  | 0.74  |
| Cl      | -0.52 | -0.46 | -0.43 | -0.40 | -0.39 |
| Bond    |       |       |       |       |       |
| Cl–Ag   | 0.16  | 0.17  | 0.15  | 0.13  | 0.10  |
| Cl–Bi   | 0.19  | 0.13  | 0.07  | 0.02  | -0.04 |
| Bond length (Å) |       |       |       |       |       |
| Cl–Ag   | 2.80  | 2.39  | 2.26  | 2.19  | 2.14  |
| Cl–Bi   | 2.75  | 2.51  | 2.40  | 2.33  | 2.27  |

The theoretical position of VBM and CBM are calculated by the following Eqs. (8) and (9):

\[
E_{\text{CB}} = X - E_g \frac{1}{2} F_g
\]

(8)

\[
E_{\text{VB}} = E_{\text{CB}} + E_g
\]

(9)

Here, \(E_{\text{CB}}\) and \(E_{\text{VB}}\) represent the band edge positions of CB and VB, respectively; \(X\) is the absolute electronegativity of Cs2AgBiCl6. The mean
value of the electronegativity of the constituent elements is equal to the
Mulliken electronegativity of the material. The initial ionization energy
of an atom and the electron affinity are calculated by the Mulliken
electronegativity of an atom [36]. \(E_g\) is the energy of the free electrons
of hydrogen (4.5 eV) and \(E_g\) is the band gap energy.

The electronegativity \((X)\) of Cs2AgBiCl6 is calculated 5.54 eV. The band-edge potentials of VB and CB of Cs2AgBiCl6 are shown in Figure 8
(a, b). Thermodynamically, the positive value of the momentum of
Cs2AgBiCl6 ensures that the reduction of \(H^+\) to \(H_2\) is impossible. The
CBM and VBM calculated potentials of Cs2AgBiCl6 are shown in Figure 8.
VBM potentials have higher (1.97 eV) for ordered samples than \(O_2/H_2O\)
(1.23 eV) and 1.37 eV for disordered samples, provide insights into the
generation of \(O_2\) from water. Furthermore, the presentation of the band-
edge potentials shows the plausible reduction of \(H_2\) and the evolution of
\(O_2\) since the redox potentials satisfy both oxidation and reduction pro-
cess. As a consequence, the water splitting by Cs2AgBiCl6 is thermody-
namically beneficial and the material under consideration is likely to be
a good candidate for photocatalysis. Consequently, Cs2AgBiCl6 can
degrade some organic pollutants and oxidize \(H_2O\) to generate \(H_2\) and \(O_2\)
through photogenerated in the visible energy range. For optimum photo-
catalytic performance, the oxidation and reduction processes must be
equally efficient.

The Cs2AgBiCl6 sample is highly responsive to photocatalytic prop-
erties, which is guaranteed by the redox potential. In the disordered Ag
and Bi atoms belonging to the Cs2AgBiCl6 sample, the photocatalytic
activity tends to increase compared with the ordered Cs2AgBiCl6 sample.
The charge carrier mobility transition is one of the fundamental criteria
for photocatalytic performance. In this study, the ordered Cs2AgBiCl6
shows indirect band gap, while the disordered Cs2AgBiCl6 sample shows
direct band gap type. The indirect band gap belongs to ordered Cs2Ag-
BiCl6 samples require a long time for the excitation of electron under
fluence of light. The disordered Cs2AgBiCl6 sample with new dopant
significantly reduced the band energy. This data will be applicable to
optoelectronic devices, especially solar cell applications.

### 3.4. Mechanical properties

To calculate the three independent elastic moduli of the cubic-
structured double perovskite Cs2AgBiCl6 sample, finite strain theory
was applied [37]. The elastic properties are simulated with the help of
CASTEP code of material studio 8.0 and presented in Tables 3 and 4. The
simulated elastic moduli of Cs2AgBiCl6 are in well matches with previ-
ous theoretical manuscript [25]. The simulated elastic constants of
Cs2AgBiCl6 justified the cubic symmetry criterion under the condition of
Eq. (10) [24]:

\[
C_{11} + 2C_{12} > 0, C_{44} > 0 \text{ and } C_{11} - C_{44} > 0
\]

(10)

The simulated elastic constants of Cs2AgBiCl6 satisfy the mechanical
stability under ambient conditions. The quantity C12–C44, is called as
Cauchy pressure [38, 39], which identifies the sample mostly brittle-
ductile nature. The simulated positive Cauchy pressure value ensures
that both uncompressed and compressed Cs2AgBiCl6 are ductile.

The mechanical stability of the material has been studied under high
pressure using the elastic stiffness coefficient, described by Eq. (11) [40].

\[
B_{ijkl} = C_{ijkl} + 1/2 [\delta_{lk} \sigma_{ij} + \delta_{kj} \sigma_{il} + \delta_{ij} \sigma_{lk} + \delta_{lj} \sigma_{ik} - 2 \delta_{ik} \sigma_{lj}]
\]

(11)
Where, $C_{ijk}$ is the elastic constant evaluated under applied stress, $\sigma_{ij}$ specifies the external stress, and $\delta_{jk}$ is the Kronecker delta. Eq. (11) implies that the stiffness coefficient tensor depends on the state of the applied stress. Therefore, it has a different symmetry than the elastic constant tensor, except that it is isotropic or zero stress. Under applying the hydrostatic pressure to a cubic crystal system, the elastic stiffness coefficients are in Voigt's notation as follows: $B_{ij}$ is $B_{11} = C_{11} - P$, $B_{12} = C_{12} + P$, $B_{44} = C_{44} - P$, where $P$ is the hydrostatic pressure.

The calculated polycrystalline properties belong to Bulk modulus; Shear modulus, Young's modulus, Pugh's ratio and Poisson's ratio of pure and pressure induced Cs$_2$AgBiCl$_6$ are presented in Table 4. Bulk modulus values of the Cs$_2$AgBiCl$_6$ sample, indicating that the sample is flexible.
In order to see the optical properties, photon energies (E) are considered in between 0 to 20 eV. Herein, a Gaussian tail of 0.5 eV was taken. The calculation of optical properties was performed on the (100) plane. The scissor value was set at 0.25 eV to calculate the light absorption and dielectric function. The calculated values of real and imaginary parts of the optical conductivity and the dielectric function are clearly shown in Fig.10 (a-f).

The first absorption peak is expected to be around 3.95 eV, the most significant value for device applications. It is observed that in the visible and ultraviolet-regions, Cs$_2$AgBiCl$_6$ sample have a strong absorption. But the pressure-driven Cs$_2$AgBiCl$_6$ perovskite has a strong optical absorption in the ultraviolet region in compared with pure sample. The absorption spectra are transferred from blue-shift into redshift with a strong absorption edge at around 130 nm.

The optical absorption of Cs$_2$AgBiCl$_6$ strongly related to the electronic structure of the material. It is well known that the stronger light-absorbing samples are suitable for photovoltaic applications. Optical conductivity (1/fs) of the sample shows the response of the electromagnetic signal [48]. When a sample is subjected to an electric field, it exhibits electrical conductivity and relates the current density at its natural frequency. The optical and electrical conduction is achieved under the response of photon absorption and the escape of electron in the higher states. It is observed that the real part disappears at around 10.5 eV, indicates an optical anisotropic nature of Cs$_2$AgBiCl$_6$. The Cs$_2$AgBiCl$_6$ sample escapes free carriers in the conduction band under absorbing energy. To calculate the level of electromagnetic radiation response in the material, the complex dielectric function [49] was used. Electron excitation is represented by the imaginary part ($\varepsilon_2$) of the dielectric function. Owing to the intra-band transitions inside the Bi 6p and Ag 3d orbital, the first peak of the imaginary part of the dielectric function ($\varepsilon_2$) is predicated more or less at $<1.5$ eV. The consideration of the frequency limit tends to zero $\varepsilon_1$ (0) is the essential part of the dielectric constant measurement. The real part of the permittivity of the pressure driven Cs$_2$AgBiCl$_6$ starts to rise from zero frequency and reaches its maximum peak. Then it starts to militate and undergoes below zero by releasing energy. Hence, the incident photon beam is totally attenuated [50]. A comprehensive data on the optical properties of pure and pressure-induced Cs$_2$AgBiCl$_6$ samples may be applicable to photocatalytic applications.

4. Conclusion

Briefly, the structure, stability of phase, mechanical, optical, electronic properties and photocatalytic activity of pure and pressure-induced Cs$_2$AgBiCl$_6$ dihalide perovskites were investigated by DFT method. The lattice constant (a) and the unit cell volume (V) decreases with increasing driving pressure. The dynamic stability was confirmed by the phonon dispersion models. The heat capacity at high temperature indicates that the pressure-driven samples are thermally stable. The disorder of Ag$^+$/Bi$^{3+}$ cations in its sub-lattice creates antisite defects, which are important for optoelectronic device applications. In disordered Cs$_2$AgBiCl$_6$, the Bi 6p and Ag 3d orbitals significantly change the conduction band due to the shift of the R and $\Gamma$’ k points. In this case, the bandgap energy is transformed indirect to direct, and the band gap energy is significantly reduced. The anti-site defect in the sub lattice of Cs$_2$AgBiCl$_6$, opens a new avenue for optoelectronic and photovoltaic material design. It is observed that the pressure-induced samples have transformed from semiconductor to metal. Pressure-driven samples in [AgBi]$^6$ and [AgCl]$^6$ octahedral sites due to conduction and valence band overlap with each other's. The bond lengths, Ag–Bi and Bi–Cl reduce the driving pressure due to crystal defects in the Ag and Bi lattice networks. Mechanical properties show that unpressured and pressured actuation Cs$_2$AgBiCl$_6$ samples are mechanically stable. The data of Pugh’s and Poisson’s ratio’s favors the pure and pressure driven Cs$_2$AgBiCl$_6$ for applications in the film coating industry. The absorption edge moves (redshift) toward the lower energy region under induced pressure. Phase-

| Table 3. The elastic constants $C_{ij}$ (in GPa) and Cauchy pressure of Cs$_2$AgBiCl$_6$ under variant pressure. |
|-------------|-------------|-------------|-------------|-------------|
| Pressure     | $C_{11}$    | $C_{12}$    | $C_{44}$    | $C_{12} - C_{44}$ |
| 0            | 42.42       | 13.65       | 9.25        | 4.44          |
| 20           | 169.12      | 46.66       | 12.74       | 33.92         |
| 40           | 314.05      | 81.98       | 10.67       | 71.31         |
| 50           | 379.77      | 104.74      | 15.93       | 88.81         |
| 60           | 434.61      | 121.58      | 13.26       | 108.32        |
| 70           | 523.45      | 149.96      | 13.91       | 136.05        |
| 80           | 560.85      | 157.75      | 14.86       | 142.89        |

| Table 4. The mechanical parameters of Cs$_2$AgBiCl$_6$ under variant pressure. |
|-------------|-------------|-------------|-------------|-------------|
| Pressure     | $B$ (GPa)   | $G$ (GPa)   | $Y$ (GPa)   | $B/G$       |
| 0            | 23.20       | 11.27       | 35.62       | 0.24        |
| 20           | 87.48       | 32.13       | 85.89       | 0.27        |
| 40           | 159.34      | 52.81       | 124.12      | 0.31        |
| 50           | 196.41      | 64.56       | 174.57      | 0.34        |
| 60           | 226.59      | 70.96       | 212.76      | 0.39        |
| 70           | 274.46      | 83.04       | 226.31      | 0.36        |
| 80           | 292.12      | 89.54       | 243.74      | 0.36        |

and soft. Pugh’s ratio (Bulk to Shear modulus) and Poisson’s ratio can identify the ductility or the brittle nature of a material [41, 42, 43, 44]. The pressure dependent elastic constant $C_{ij}$ and elastic stiffness coefficient $B_{ij}$ in Cs$_2$AgBiCl$_6$ is shown in Figure 9. The elastic constants $C_{11}$, $C_{12}$ and $C_{44}$ increase with increasing hydrostatic pressure. The same happens with $B_{11}$ and $B_{12}$ increase, but $B_{44}$ decreases with pressure reaching negative values beyond 10 GPa. This suggests that the crystal structure becomes mechanical unstable, and a phase transition could be induced by pressure [45]. The bulk modulus of 23–28 GPa makes the studied compounds as compressible as metal-organic frameworks [46]. The critical value of Pugh’s and Poisson’s determines the brittleness from ductile ones. If the Pugh’s (1.75) and Poisson’s ratio (0.26) values are higher than critical values, then the sample is said to be in ductile types, otherwise, brittle types. The Pugh’s and Poisson’s values ensured that pure and pressure induced Cs$_2$AgBiCl$_6$ samples have ductile natures. The mechanical properties indicate that the Cs$_2$AgBiCl$_6$ sample is suitable for the thin film industry.

3.5. Optical properties

To comprehend the optical properties, the optical absorption ($\alpha$), electrical conductivity ($\sigma$) and permittivity ($\varepsilon$) of pure and pressure-induced Cs$_2$AgBiCl$_6$ are measured. The dielectric function is determined by Eq. (12) [47].

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) = N^2$$

(12)

Where, $\varepsilon_1(\omega)$ and $i\varepsilon_2(\omega)$ refers to the real and imaginary part of the complex dielectric constant as a function frequency ($\omega$). $N$ represents the complex refractive index. The imaginary dielectric function is described by Eq. (13) [46].

$$\varepsilon_2 = \frac{2e_0}{\omega} \sum_{k, \epsilon} \left| \Psi_k^\epsilon \right|^2 \left( E_k - E_\epsilon - E \right)$$

(13)

Where, $e$, $\omega$, and $u$ represent the electron charge, unit cell volume, and unit volume, respectively.
change lead-free double halide materials have obtained a variety of outstanding properties, providing a broad space for industrial applications. The overall investigation suggests that pure and pressure-driven Cs$_2$AgBiCl$_6$ samples may be well suited for photovoltaic and optoelectronics, especially solar cells. It is expected that this first-principles simulation study will provide a better understanding of band structure calculations and motivate to the experimental investigations.

Declarations

Author contribution statement

Md. Nurul Islam: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.
Jiban Podder: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

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Data will be made available on request.

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The authors declare no conflict of interest.

Additional information
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