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Pressure effects on the opto-electronic and mechanical properties of the double perovskite $\text{Cs}_2\text{AgInCl}_6$ A A Sholagberu¹, W A Yahya¹  and A A Adewale^{1,2}¹ Department of Physics and Materials Science, Kwara State University, Nigeria² Department of Pure and Applied Physics, Ladoke Akintola University of Technology, Ogbomoso, NigeriaE-mail: wasiu.yahya@gmail.com**Keywords:** double perovskite, opto-electronic properties, mechanical propertySupplementary material for this article is available [online](#)RECEIVED
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29 July 2022**Abstract**

The double perovskite $\text{Cs}_2\text{AgInCl}_6$ is a potential material for the absorbing layer of a thin film solar cell due to its direct band gap. The only current limitation the material has is its wide band gap. A careful engineering of its structural, mechanical and opto-electronic properties with the aid of hydrostatic pressure ranging from 0 GPa to 16 GPa has been studied using density functional theory. The calculations were carried out using GGA-PBEsol (Perdew–Burke–Ernzerhof revised for solids) exchange correlation functional. It is found that the lattice constant reduces as the pressure increases, while the bulk modulus increases as the exerted pressure increases. The bulk moduli calculated from the elastic constants are found to be in agreement with those obtained via Birch–Murnaghan equation of state. This indicates the accuracy of the calculations, and it is achieved at all pressure values. The mechanical properties of the material are investigated, and the material is found to be anisotropic and ductile at all pressure considered. Due to the underestimation of the energy band gap by GGA-PBEsol exchange correlation functional, Tran–Blaha modified Burke Johnson (TB-mBJ), a metaGGA functional, was used to calculate the electronic and optical properties. The energy band gap is found to reduce from 2.746 eV at ambient pressure to 2.482 eV at 6 GPa and momentarily increases until it reached 2.501 eV at 16 GPa. The optical properties of $\text{Cs}_2\text{AgInCl}_6$ revealed its absorption threshold is in the visible range, although a shift in the absorption threshold is observed as pressure is applied on it. An 8.7 % increase in the refractive index is observed as pressure increases. The calculated absorption coefficient corresponds reasonably with the calculated band gap. The electron energy loss function and reflectivity of the material have also been investigated.

1. Introduction

Power Conversion Efficiency (PCE) and band gap are not the only factors that are considered in the choice of PV cell materials; other factors that are considered are stability of the material under various mechanical and environmental conditions, environmental degradability, availability of the material (cheap to find) and fabrication cost [1]. Advent of thin film technology led to the emergence of the generation of easily fabricated solar cells, such as the Dye-Synthesized Solar cell (DSSC) [2], Quantum Dot Solar Cells (QDSC) [3] and Organic-inorganic lead halide perovskite solar cells [4]. Particularly, perovskite solar cells have received considerable numerous attention in the past few years after the Power Conversion Efficiency (PCE) of MAPbI_3 (Methylammonium lead iodide), an organic-inorganic halide perovskite was reported to be 3.8% in 2009 [4]. Recently, this efficiency has improved to 25.2%, achieved by minimizing the deformation for the microstructure layers in the solar cell [5]. However, with the prospect of these perovskite solar cells, it turned out that, there are some challenges with their stability, toxicity (due to the presence of lead), strong I-V hysteresis and susceptibility to high thermal degradation [6]. Perovskite is a type of material with a unique tunable structure and has enormous diversities either by substituting the types of atoms in the compound or addition of impurity. This led

to a different class of perovskite solar cells called Double Perovskite Solar Cells (DPSC) whose B-site tetravalent cation is replaced with either a monovalent and trivalent cations or two divalent cations. The double perovskites have the general formula $A_2BB'X_6$.

Double perovskite solar cells have been dubbed as viable candidates to address the shortcomings of PSC. Thus, numerous explorations of different types of perovskites are being carried out [7]. Some of the perovskites that have been studied which entail the substitution of toxic lead (with less toxic metals) and with improved stability are yet to overcome all the challenges, as most of them possess indirect band gaps [8]. This prevents their maximum utilization as photovoltaic materials. Recently, Volonakis *et al* [9] studied a lead-free halide perovskite with a direct band gap, $\text{Cs}_2\text{AgInCl}_6$. The experimental result shows that it has a band gap energy of 3.3 eV and the results of the *ab-initio* investigation of $\text{Cs}_2\text{AgInCl}_6$ using density functional theory (DFT) at different exchange-correlation functional are 2.6 eV (HSE) and 3.3 eV (PBE0). This makes the material a potential candidate for PV application, although the value of its energy band gap is a hindrance to its efficiency. In the quest for the band gap engineering of $\text{Cs}_2\text{AgInCl}_6$ for an efficient solar cell application, the most explored method is by compositional ionic substitution (doping), as reported by [10–13]. Although compositional substitution reveals intricate opto-electronic properties of $\text{Cs}_2\text{AgInCl}_6$, both experimental and theoretical methods of compositional substitution are always exorbitant and strenuous. Therefore, strain or hydrostatic pressure which is an inexpensive alternative method of band gap engineering can be employed. Strain or hydrostatic pressure is known to distinctly impacts the structural properties of materials which is crucial in the tuning of their energy band gap.

Bhamu *et al* [14] reported variations in the magnitude of $\text{Cs}_2\text{AgInCl}_6$ band gap energy when strained. Pressure can induce semiconductor to metal transition [15], phase transition [16, 17], amorphization [17], mechanical stability and improvement in the absorption coefficient [18]. The effect of pressure on the structural and opto-electronic properties of $\text{Cs}_2\text{AgInCl}_6$ has not been reported. This research involves the study of this hypothetical perovskite material with fascinating properties under hydrostatic pressure.

The paper is organised as follows: the computational details are described in section 2. This is followed by the presentation of results and discussions of the results in section 3. Section 4 contains the conclusion.

2. Computational methods

The structural and mechanical properties of $\text{Cs}_2\text{AgInCl}_6$ were carried out using plane wave method as implemented in Quantum ESPRESSO [19, 20] to treat the electron-ion interaction and GGA-PBESol (Purdew-Burke-Enzerhof) was used to evaluate the electron-electron interaction. The kinetic energy cut-off used was 100 eV. The energy and force convergence thresholds used were 10^{-5} eV per atom and 10^{-5} eV Å⁻¹, respectively, with a k-point of $6 \times 6 \times 6$ Monkhorst-pack scheme at different pressure values ranging from ambient pressure (natural pressure of the material) to 16 GPa. These pressure values were set in the input parameter of Quantum ESPRESSO code and with the aid of THERMO_PW package [21]. The opto-electronic properties of $\text{Cs}_2\text{AgInCl}_6$ were carried out using Elk-LAPW [22], which is a Full Linearized Augmented Plane Wave (FL-APW) code. PBESol exchange correlation functional was initially employed, the maximum length of the reciprocal lattice vector (convergence parameter) $R_{MT}K_{\max}$ used was 8. Due to the fervent underestimation of the energy band gap by GGA, TB-mBJ (Trans-Blaha modified Burke Johnson) a meta-GGA functional was further adopted to calculate the opto-electronic properties of $\text{Cs}_2\text{AgInCl}_6$ setting the grid of the Brillouin zone to $12 \times 12 \times 12$ MonkhorstPack k-points at all the calculated pressure values. GGA-PBESol includes only the density and its first derivative in the exchange-correlation potential, whereas Meta-GGA (such as TB-mBJ) contains also the second derivative of the electron density.

3. Results and discussions

3.1. Structural properties and optimization

The primitive structure of $\text{Cs}_2\text{AgInCl}_6$ is a face-centered cubic structure which belongs to the $\text{Fm}\bar{3}\text{m}$ space group. It contains Cs^{2+} in 12-fold cubo-octahedral coordination surrounded by Ag^+ and In^{3+} cation each in 6-fold coordination alternating along the [001], [010] and [100] planes. Each of Ag and In cation are surrounded by an octahedron of Cl^- . Figure 1 shows that this material is composed of Cs_2AgCl_3 and InCl_3 alternating structural units in three dimensions.

The quantum mechanical description of the properties of any material requires the atoms of the compound to be in their ground state. This is achieved in a solid by minimizing the energy present in the crystal. The ground state lattice parameters of the compound were optimized using the Birch-Murnaghan equation of state [23, 24]. The calculated volume is fitted against the enthalpy of the system at different pressure values as shown in figure 2 for $P = 2$ GPa and 16 GPa. The plots for the other pressure values are included in the supplementary file (figure S1-1 (available online at stacks.iop.org/PS/97/085824/mmedia)).

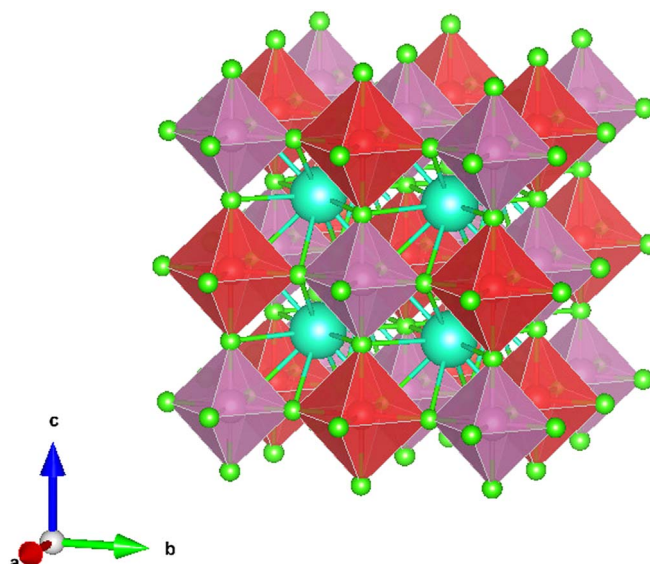


Figure 1. Polyhedral model of $\text{Cs}_2\text{AgInCl}_6$ atoms with the purple and red octahedra denoting In and Ag atoms, cyan and green balls represent Cs and Cl atoms, respectively.

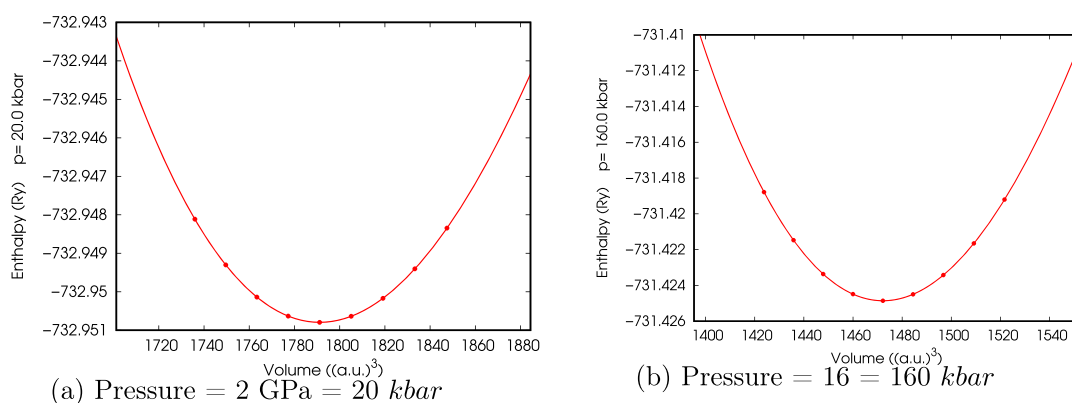


Figure 2. The E-V curve estimated using Birch-Murnaghan equation of state of $\text{Cs}_2\text{AgInCl}_6$ at pressure values of (a) 2 GPa and (b) 16 GPa. (a) Pressure = 2 GPa = 20 kbar (b) Pressure = 16 = 160 kbar.

GGA-PBESol was adopted because it is proven to give the best estimate of lattice parameters for solids, compared to other exchange-correlation functional like LDA and GGA-PBE [25]. The ground state energy E , the equilibrium lattice constant a , Bulk modulus B , the pressure derivative of bulk modulus B' and the unit cell volume V , were all calculated from the Birch-Murnaghan equation of state. The volume at minimum energy is used to determine the value of the optimized lattice parameters at different pressure values from ambient pressure to 16 GPa. The optimized lattice parameters, bulk modulus, pressure derivative of bulk modulus, volume and enthalpy are shown in table 1.

The negative value of the enthalpy denotes an exothermic reaction and thermodynamical stability of $\text{Cs}_2\text{AgInCl}_6$. The results from Birch-Murnaghan equation of state are summarized in table 1. Figure 3 shows the explicit relationship between the applied pressure values and the structural parameters of $\text{Cs}_2\text{AgInCl}_6$. Increase in the enthalpy implies an increase in the internal energy due to electrostatic repulsion between the atoms while trying to resist the induced pressure. As expected, the effect of hydrostatic pressure led to compression, which has resulted into decrease in lattice constant a (Å) of $\text{Cs}_2\text{AgInCl}_6$ as the pressure increases. Figure 4 further elucidates this claim, as the bond length in Ag-Cl, In-Cl and Cs-Cl is found to decrease when pressure is increased. This can also be proved by the increment in the bulk modulus with increasing pressure, indicating decrease in the compressibility of the material. The reduction in the compressibility of the material is due to lesser inter-atomic spacing after it has been subjected to hydrostatic pressure.

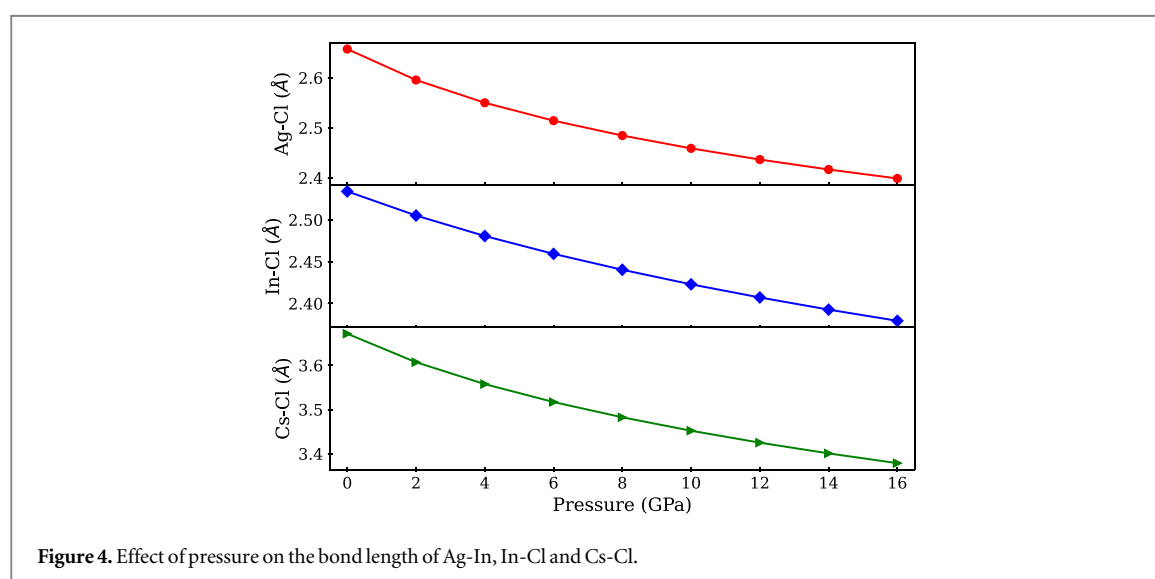
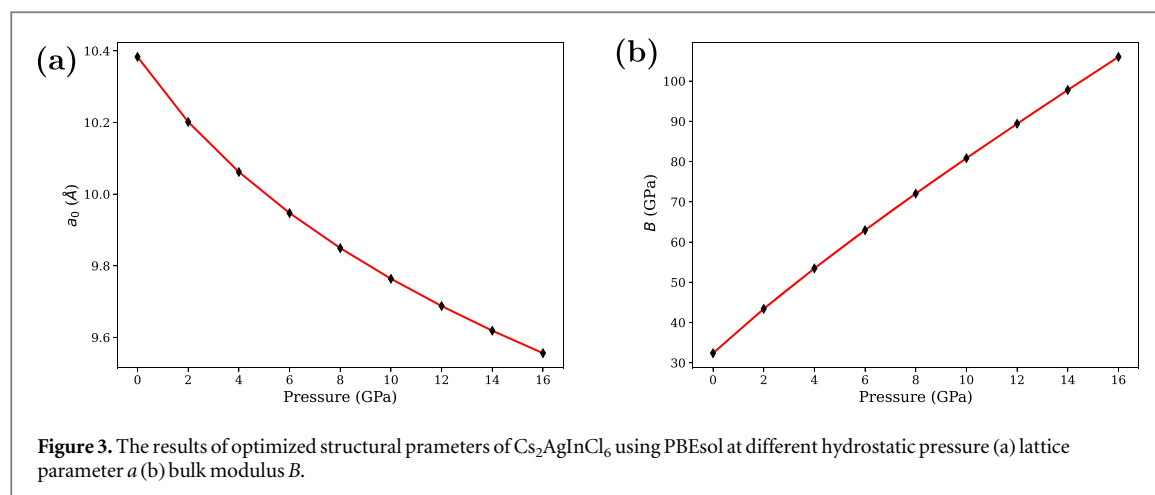


Table 1. The calculated lattice parameter (a), bulk modulus (B), bulk modulus derivative (B'), Volume (V) and Enthalpy of $\text{Cs}_2\text{AgInCl}_6$ using GGA-PBEsol.

Pressure (GPa)	a (Å)	B (GPa)	B'	V (Å ³)	Enthalpy (Ry)
0	10.3830	32.3900	5.8460	1119.3569	-733.2006
2	10.2015	43.3941	5.2200	1061.6760	-732.9508
4	10.0618	53.4582	4.8690	1018.6550	-732.7124
6	9.9471	62.9467	4.6310	984.2140	-732.4828
8	9.8493	72.0395	4.4620	955.4680	-732.2605
10	9.7637	80.8362	4.3320	930.7720	-732.0442
12	9.6875	89.4035	4.2320	909.1490	-731.8333
14	9.6187	97.7834	4.1450	889.9160	-731.6270
16	9.5560	106.0001	4.0690	872.6270	-731.4249

3.2. Pressure dependence of elastic and mechanical properties of $\text{Cs}_2\text{AgInCl}_6$

Probing of mechanical and elastic properties of $\text{Cs}_2\text{AgInCl}_6$ become important in order to have an in-depth knowledge of their behaviour during the manufacturing process. Materials may be subjected to some forces during their fabrication or processing. Therefore it is imperative to understand the nature of the forces in the solid and the dynamical behaviour of its constituents atoms.

It is proved that the strength and stability of a material are directly mapped to its elastic constants c_{ij} . The generic explanation of mechanical stability of materials was given by Max Born and Kun Huang in 1994 which was reviewed by M. Lax [26]. This theorem is known as Born-Huang elastic criteria. The criteria for a stable cubic crystal is reduced to a simple form as [27]:

$$C_{11} - C_{12} > 0, \quad (1)$$

$$C_{11} - 2C_{12} > 0, \quad (2)$$

$$C_{44} > 0, \quad (3)$$

and

$$C_{11} < B < C_{44}, \quad (4)$$

where B is the bulk modulus. When C_{12} has the smallest value, that indicates that the material is easily compressed in the C_{12} direction compared to other directions [28].

There is a relationship between the elastic constants and some isotropic properties like bulk modulus, shear modulus and young's modulus. This relationship was developed by Voigt, Reuss and Hill, which was harmonised by Chung and Buessem into Voigt-Reuss-Hill Approximation (VHR) [29]. Voigt, Reuss and Hill approximation is a scheme that converts anisotropic elastic constants into isotropic poly-crystalline elastic moduli.

Voigt's [30] elastic moduli equations are given below:

$$B_V = \frac{C_{11} + 2C_{12}}{3}, \quad (5)$$

$$G_V = \frac{C_{11} - C_{12} + 3C_{44}}{5}, \quad (6)$$

where B_V and G_V are the isotropic bulk modulus and shear modulus, Reuss' bulk modulus B_R and Voigt's B_V are equal for a cubic structure, but Reuss' shear modulus G_R equation is given by [31]:

$$G_R = \frac{5(C_{11} - C_{12})C_{44}}{4C_{44} + 3(C_{11} - C_{12})}. \quad (7)$$

Hill's Approximation of elastic moduli is the average of Voigt's and Reuss' elastic moduli [32] values, that is:

$$B_H = \frac{1}{2}(B_V + B_R), \quad (8)$$

$$G_H = \frac{1}{2}(G_V + G_R), \quad (9)$$

G_H and B_H are the Hill's shear and bulk moduli, respectively.

Some parameters also depict the mechanical properties of materials. These parameters have important applications in engineering and manufacturing. Parameters such as Young's elastic modulus E , anisotropy factor A , Poisson's ratio n and Pugh's ratio R_p . These parameters can be estimated using the following equations [33]:

$$E = \frac{9G_H B_H}{3B_H + G_H}. \quad (10)$$

$$n = \frac{1}{2} \left(\frac{3B_H - 2G_H}{3B_H + G_H} \right), \quad (11)$$

$$A = \frac{2C_{44}}{C_{11} - C_{12}}, \quad (12)$$

$$R_p = \frac{B_V}{G_H}, \quad (13)$$

The mechanical property is important in studying the strain, stress, hardness, ductility, brittleness, and deformation of materials either during fabrication or application.

The results of the Born stability criteria, given in equation (4), indicate that $\text{Cs}_2\text{AgInCl}_6$, having a cubic symmetry, is mechanically stable. The calculated Bulk modulus from the elastic constants, B is in good agreement with the bulk modulus calculated from the Birch-Murnaghan equation of state, B_0 at different pressure. $\text{Cs}_2\text{AgInCl}_6$ shows an increase in its resistance to fracture as the pressure increases, as shown in the calculated result of B (in table 2). The summary of the calculated elastic constants, bulk modulus B , Pugh's ratio R_p and Cauchy's pressure P_c at different pressure is shown in table 2. C_{44} has the smallest value compared to other elastic constants considered. This is an indication that the material is easily compressible in the C_{44} direction.

Pugh's ratio is the parameter used when describing the ductility and brittleness of a material. The critical value for brittleness is $R_p < 1.75$, for ductility $R_p > 1.75$ [34]. Thus, it is evident (from table 2) that $\text{Cs}_2\text{AgInCl}_6$ is ductile at all the pressure values considered here. Zener Anisotropy factor of a material A is an indication of the material's level of isotropy. Material with $A = 1$ is an isotropic material but, it is an elastic anisotropy if less than 1. It is apparent from table 2 that $\text{Cs}_2\text{AgInCl}_6$ is an elastically anisotropic material.

Table 2. Calculated result of elastic constants (C_{11} , C_{12} , C_{44}), bulk modulus B , Pugh's ratio R_p and Cauchy's pressure P_c at different pressure using GGG-PBEsol.

Pressure (GPa)	B (GPa)	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)	A	P_c	R_p	Y (GPa)	G (GPa)	n (GPa)
0	32.301	42.679	27.112	11.324	1.455	15.788	3.315	26.561	9.744	0.363
2	43.315	66.264	31.839	12.506	0.727	19.334	3.047	38.438	14.215	0.352
4	53.345	85.974	37.031	13.455	0.550	23.577	3.113	46.427	17.135	0.355
6	62.951	104.191	42.331	14.402	0.466	27.929	3.201	53.411	19.665	0.358
8	71.960	121.153	47.364	15.270	0.414	32.095	3.281	59.689	21.933	0.361
10	80.805	137.558	52.429	16.037	0.377	36.391	3.366	65.462	24.005	0.364
12	89.346	153.358	57.340	16.722	0.348	40.617	3.446	70.830	25.928	0.366
14	97.795	168.800	62.293	17.410	0.327	44.883	3.520	76.024	27.786	0.368
16	106.047	183.828	67.157	18.076	0.310	49.081	3.586	81.024	29.576	0.370

Another mechanical property reported for $\text{Cs}_2\text{AgInCl}_6$ is Cauchy's pressure. Cauchy's pressure, P_c indicates the dominant bonding in a material. It could also indicate the brittleness and ductility of a material. $P_c > 0$ implies ductility and presence of ionic nature while $P_c < 0$ denotes brittleness and covalent-like material. The result of P_c for $\text{Cs}_2\text{AgInCl}_6$ as shown in table 2 is a further indication of the ductility of this material at this pressure range (2–16 GPa), since $P_c > 0$ at all pressure values.

Poisson's ratio is another prominent parameter that describes the ductility of a material and the nature of its bond [35]. Its critical value is 0.26. A material is ductile if its Poisson ratio (n) is greater than 0.26 and brittle otherwise. From the calculated values presented in table 2, it is glaring that $\text{Cs}_2\text{AgInCl}_6$ is ductile with its value of $n = 0.3521$ at 2 GPa and $n = 0.3698$ at 16 GPa. Shear modulus represents the resistance of a material to plastic deformation. The higher the value, the higher the ductility of a material. It is apparent from the summary given in table 2 that this material has a relatively low shear modulus but increases with increase in pressure. Young's modulus (Y), which denotes the overall strength of a material in the face of applied pressure. It is also evident from the calculated values of Y at different pressure that the material gains more strength with increment in the applied hydrostatic pressure. This strength is developed essentially to resist the applied hydrostatic pressure. However, its maximum value of 81.024 GPa (at 16 GPa) is still small, $\text{Cs}_2\text{AgInCl}_6$ is therefore a soft material [36].

3.3. Screening of pressurized electronic state and energy band gap, (E_g) of $\text{Cs}_2\text{AgInCl}_6$ with PBEsol and TB-mBJ Density functional

After investigating the effect of pressure on the structural and elastic properties of $\text{Cs}_2\text{AgInCl}_6$, the most notable effect was observed on its lattice constant, enthalpy and elastic moduli. Now, we analyse the impact of pressure on the electronic state of the constituents atoms and the influence of these changes on the band structure and the band gap energy. The band structure of $\text{Cs}_2\text{AgInCl}_6$ is investigated along a high symmetry $\mathbf{k}$ -path in the Brillouin zone. For a cubic structure this is given as [37]:

$$\Gamma \rightarrow X \rightarrow W \rightarrow K \rightarrow \Gamma \rightarrow L \rightarrow U \rightarrow W \rightarrow L \rightarrow K \rightarrow U \rightarrow X. \quad (14)$$

The band structure of $\text{Cs}_2\text{AgInCl}_6$ showed a semiconductor property with a direct type band gap; the conduction band minimum (CBM) and valance band maximum (VBM) are at the Γ - point of the Brillouin zone. The calculated band structure of $\text{Cs}_2\text{AgInCl}_6$ in this research is very identical to those in the literature [9, 38, 39], at ambient pressure (0 GPa), but changes were observed as the pressure increases. High dispersion is observed in the CBM but low dispersive bands are seen in the VBM, thus high carrier mobility will occur in the CBM and VBM. However, no midgap state is present in the band.

It is observed from the summary of the energy band gap given in table 3 that the effect of pressure is significant on the energy band gap. The band gap initially decreases till it reaches a pressure of 8 GPa when it momentarily started increasing. This increment is a result of the decrease in the lattice constants which increases the electron transition integral. This makes the band gap increase [18]. To further obtain an accurate value of the energy band gap, a more robust exchange-correlation function, TB-mBJ is used to investigate the electronic band structure of $\text{Cs}_2\text{AgInCl}_6$. PBEsol calculated band structure did not show band gap Fermi energy level variation as pressure is applied as shown in figure 5, but TB-mBJ showed a shift in the Fermi level towards the conduction band as $\text{Cs}_2\text{AgInCl}_6$ is pressurized as shown in figure 6. The band structure plots are shown for only ambient pressure and pressure of 16 GPa. The band structure plots for other pressure values are in the supplementary file figure SI-2 to SI-5.

The calculated band gaps are given in table 3, and the plot of the variation of the energy band gap against pressure is shown in figure 7(a) for PBE-sol and figure 7(b) for TB-mBJ. Based on the Shockley–Queisser theory, the optimum band gap energy (E_g) for high-efficiency solar cells is in the range of 1.3 eV to 1.4 eV [40]. From the

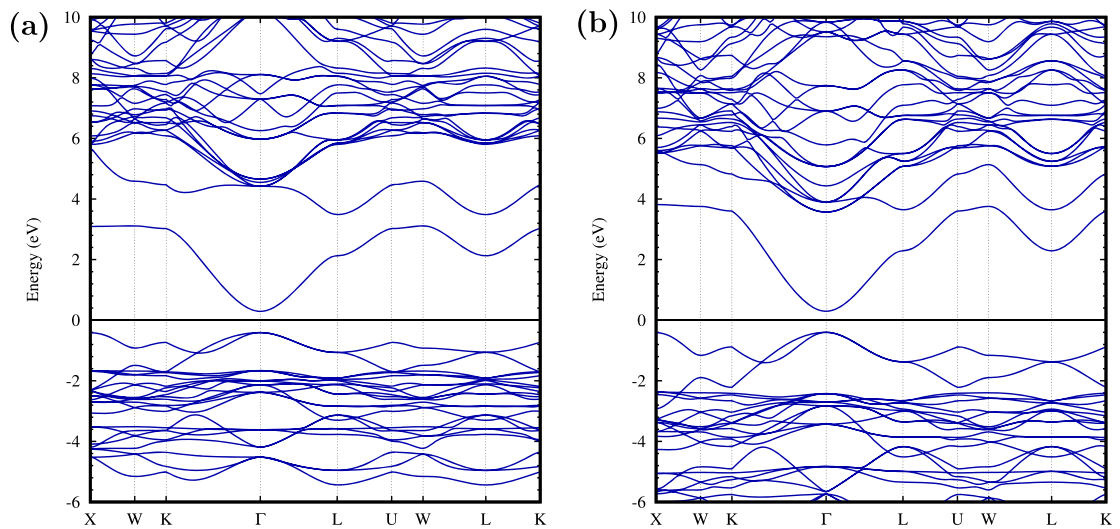


Figure 5. Band structure of $\text{Cs}_2\text{AgInCl}_6$ using PBEsol Exchange correlation functional at (a) ambient pressure and (b) $P = 16$ GPa.

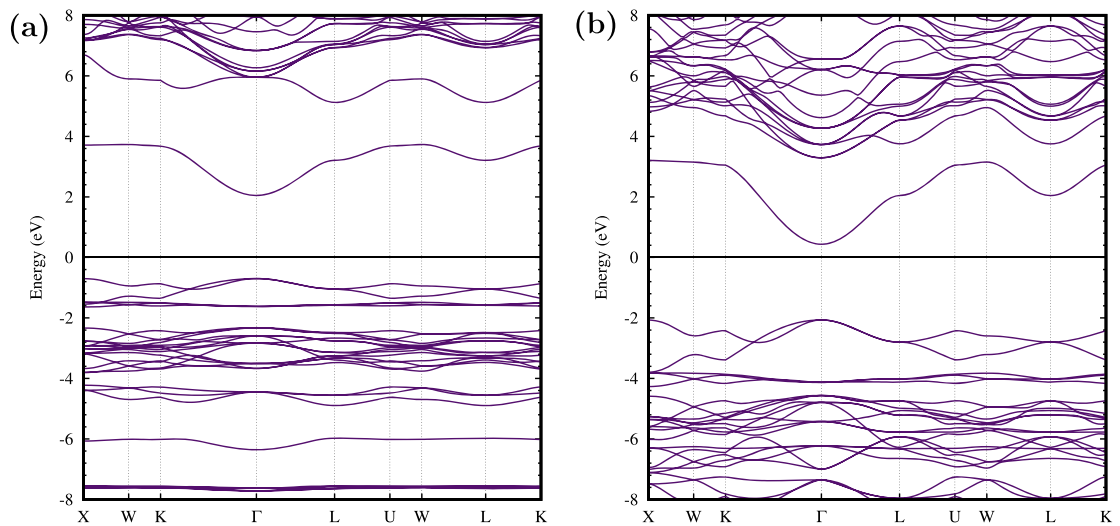


Figure 6. Band structure of $\text{Cs}_2\text{AgInCl}_6$ using TB-mBJ Exchange correlation functional at (a) ambient pressure and (b) $P = 16$ GPa.

Table 3. Result of Energy band gap E_g at different pressure using GGA-PBEsol and TB-mBJ exchange-correlation functional.

Pressure (GPa)	GGA-PBEsol E_g (eV)	TB-mBJ E_g (eV)
0	0.9215	2.7468
2	0.7018	2.5196
4	0.6818	2.5037
6	0.6753	2.4821
8	0.6748	2.4843
10	0.6790	2.4868
12	0.6844	2.4944
14	0.6907	2.4986
16	0.6972	2.5010

TB-mBJ results in the third column of table 3, the band gap energy at pressure of 6 GPa (i.e. 2.4821 eV) is the closest to the optimum band gap energy.

The electronic density of state (DOS) shows the fundamental atomic orbitals interaction and contribution of the constituent atoms towards the electronic state at the valence band and conduction band, which made up the

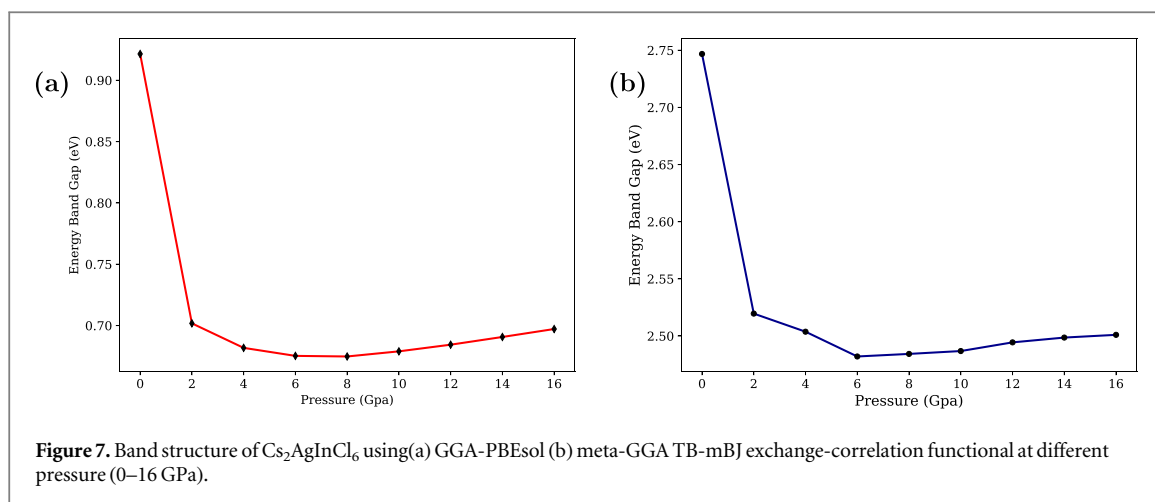


Figure 7. Band structure of $\text{Cs}_2\text{AgInCl}_6$ using (a) GGA-PBESol (b) meta-GGA TB-mBJ exchange-correlation functional at different pressure (0–16 GPa).

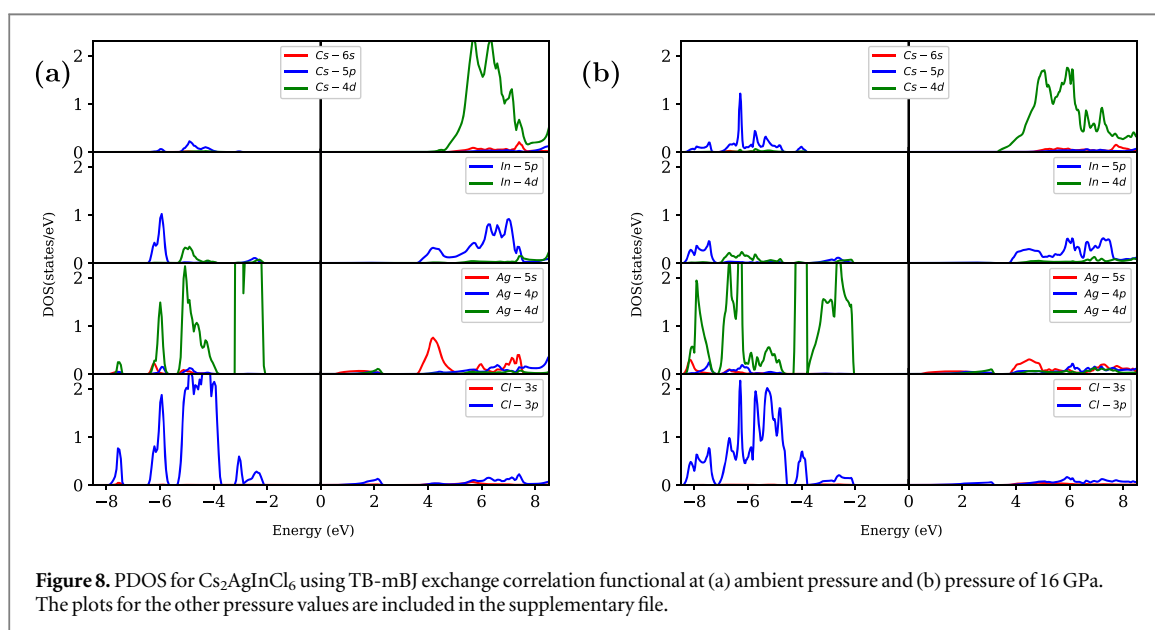


Figure 8. PDOS for $\text{Cs}_2\text{AgInCl}_6$ using TB-mBJ exchange correlation functional at (a) ambient pressure and (b) pressure of 16 GPa. The plots for the other pressure values are included in the supplementary file.

band structure. The partial density of state (PDOS) and the total density of state were calculated using metaGGA TB-mBJ, to further reveal the photoelectric properties exhibited by $\text{Cs}_2\text{AgInCl}_6$. The partial density of state (PDOS) using TB-mBJ at ambient pressure shows that the valence band mostly consists of Ag-4d and Cl-3p orbitals which is consistent with their respective electronic configuration, while the conduction band is dominated by Cs-4d, In-5p and Ag-5s orbital. The hybridization between Cs-4d and In-5p orbital in the conduction band is glaring and the antibonding hybridization of Ag-4d and Cl-3p in the valence band can be observed, shown in figure 8(a).

As pressure is applied on $\text{Cs}_2\text{AgInCl}_6$, Cs-5p and In-5p orbitals become hybridized as a result of the strain exerted on their electrostatic potential. These changes are usually observed in the energy band gap of perovskites when subjected to hydrostatic pressure, emanating from the changes in their valence band minimum [41]. The increase in the applied pressure led to the orbital coupling of the In-5p and Ag-5s orbital which diminished them from the conduction band minimum (CBM) till they have vanished into the valence band maximum (VBM), which resulted in the increment of the band gap energy as depicted in figure 8 (b) and PDOS plots in the supplementary file (figure SI-6 to SI-8). The increment in the energy band gap is evident by the energy range of the empty state between the VBM and CBM. [1] The calculated energy band gap and lattice constant of $\text{Cs}_2\text{AgInCl}_6$ at ambient pressure compared with other calculated and experimental data is summarized in the supplementary file (table SI-1).

3.4. Optical properties

One of the most important properties of a material is its reaction when photon energy is irradiated on it. The optical properties of $\text{Cs}_2\text{AgInCl}_6$ were thoroughly studied using TB-mBJ exchange correlation functionals at

ambient condition and under pressure ranging from 2 GPa to 16 GPa. The results of the calculated dielectric constants using momentum matrix elements showed that this material has its absorption threshold in the visible range. This makes it a promising candidate for photonic applications.

The optical behaviours of the material investigated are: the real and imaginary dielectric constants, refractive index, extinction coefficients, reflectivity, and the electron energy loss spectrum. They were calculated from the momentum matrix element. The imaginary part of the dielectric tensor can be computed from the electronic band structure of solid. The complex dielectric function is expressed as [42]:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega). \quad (15)$$

Here $\varepsilon_1(\omega)$ is the real part of the dielectric function, $\varepsilon_2(\omega)$ is the imaginary part, ω is the optical frequency. The imaginary dielectric function, $\varepsilon_2(\omega)$, is strongly correlated to the joint density of states (DOS) and transition momentum matrix elements. The real and imaginary parts of dielectric functions can be used to calculate the other optical parameters such as refractive index, optical conductivity, absorption coefficient and extinction coefficient. The following well-known relations have been used to calculate the optical properties [43]:

$$Im[\varepsilon_{\alpha\beta}(\omega)] = \frac{4\pi e^2}{m^2\omega^2} \sum_{c,v} \int_0^\infty dk \langle c_k | P^\alpha | v_k \rangle \langle v_k | P^\beta | c_k \rangle (\varepsilon_{ck} - \varepsilon_{vk} - \omega) \quad (16)$$

The real part $Re[\varepsilon_{\alpha\beta}(\omega)]$ can be derived from the imaginary part by using the Kramers-Kronig relations [44, 45]

$$Re[\varepsilon_{\alpha\beta}(\omega)] = \frac{2}{\pi} \mathcal{P} \int_0^\infty \frac{\omega' Im[\varepsilon_{\alpha\beta}(\omega')]}{\omega'^2 - \omega^2} d\omega', \quad (17)$$

where $\mathcal{P}$ implies the principal value of the integral and c_k and v_k are the electron states in the conduction and valence bands, respectively, with the wave vector k .

The knowledge of both the real and imaginary parts of the dielectric function allows the calculation of important optical functions such as the refractive index $n(\omega)$, optical conductivity $\sigma_{\alpha\beta}$, extinction coefficient $k(\omega)$, which are given, respectively, by [44, 46]

$$n(\omega) = \sqrt{\frac{|\varepsilon(\omega)| + Re[\varepsilon(\omega)]}{2}}, \quad (18)$$

$$Re[\sigma_{\alpha\beta}] = \frac{\omega}{4\pi} Im[\varepsilon_{\alpha\beta}(\omega)], \quad (19)$$

$$k(\omega) = \sqrt{\frac{|\varepsilon(\omega)| - Re[\varepsilon(\omega)]}{2}}. \quad (20)$$

The electron energy-loss spectrum $L(\omega)$ can be calculated from the following relations

$$L(\omega) = \frac{\varepsilon_2}{\varepsilon_1^2 + \varepsilon_2^2}, \quad (21)$$

the reflectivity $R(\omega)$ from [45]:

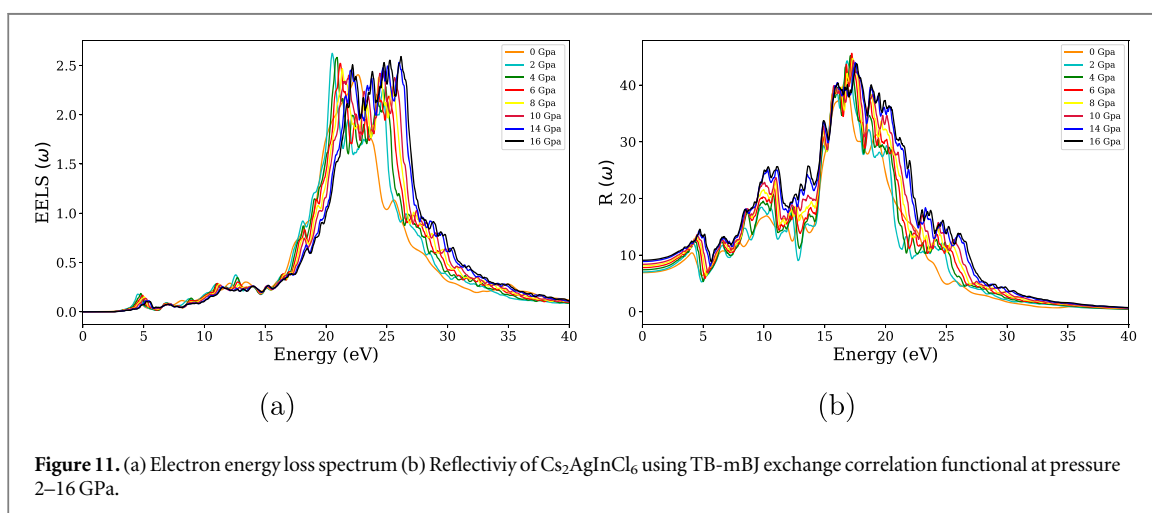
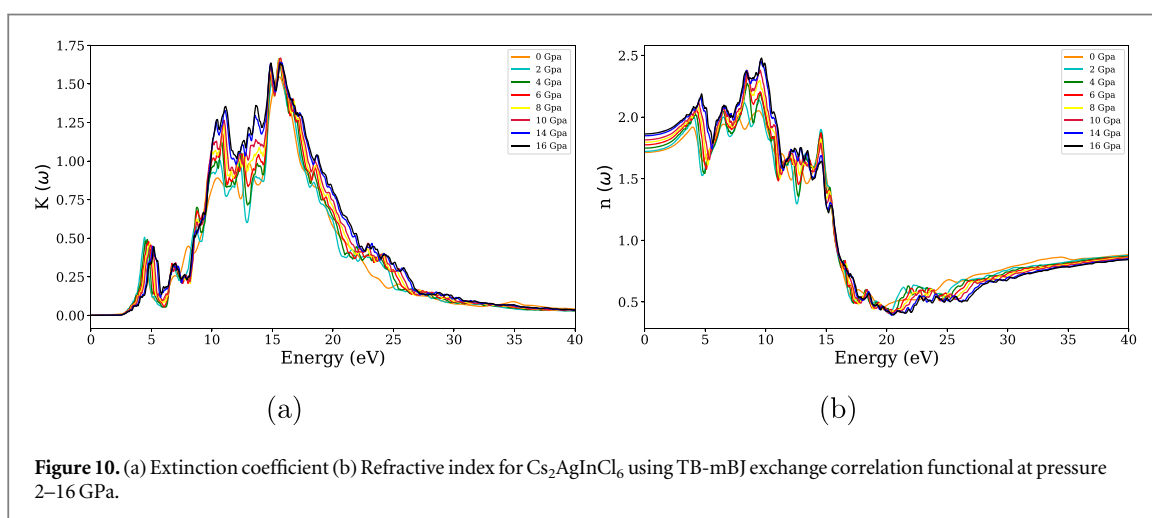
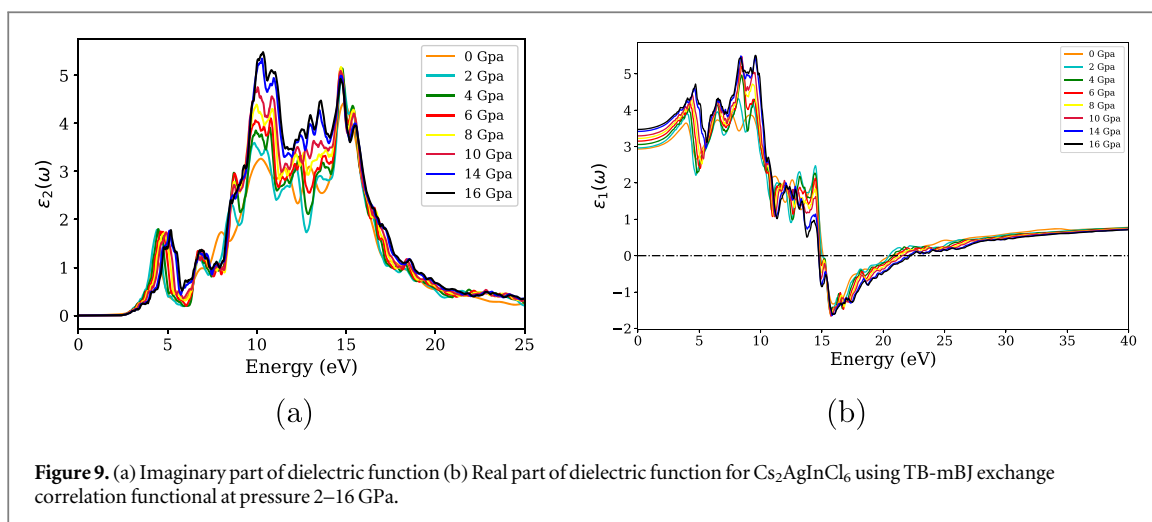
$$R(\omega) = \left| \frac{\sqrt{\varepsilon(\omega)} - 1}{\sqrt{\varepsilon(\omega)} + 1} \right|^2, \quad (22)$$

and the absorption coefficient $I(\omega)$ from [45]

$$I(\omega) = 2\omega \left(\frac{[\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2] - \varepsilon_1(\omega)}{2} \right)^{\frac{1}{2}}. \quad (23)$$

The linear optical properties of cubic $\text{Cs}_2\text{InAgCl}_6$ have been investigated by calculating the optical parameters, dielectric function $\varepsilon(\omega)$, refractive index $n(\omega)$, optical conductivity $\sigma(\omega)$, absorption $I(\omega)$, reflectivity $R(\omega)$ extinction coefficient $k(\omega)$, and electron energy loss function $L(\omega)$.

The electron energy loss function $L(\omega)$, is a significant factor related to the energy loss of fast electron traversing in the material and usually maximum at the plasma energy. Electron energy-loss spectroscopy involves measurement of the energy distribution of electrons that have interacted with a specimen and lost energy due to inelastic scattering. The energy required for the excitation of bulk plasmons depends on the electron density in the solid. The positions of the single electron excitation peaks are related to the joint density of states between the conduction and valence bands. The interband transitions, which consist mostly of plasmon excitations, the scattering probability for volume losses is directly connected to the energy loss function. Here the electrons, which excite the atoms and thus these electrons of the outer shell is called valence interband transitions or valence Loss [46].



The plot of these properties are shown in figures 9–12. The static dielectric constants $\epsilon_1(0)$, static refractive index $n(0)$, The maximum absorption coefficients and their excitonic behaviours (precisely first peak) were extracted from the optical result obtained using equations (18)–(23).

The optical properties of $\text{Cs}_2\text{AgInCl}_6$ were studied in the energy range 0 eV to 40 eV using TB-mBJ exchange correlation functional due to its established level of accuracy and reliability. The excitonic peaks observed in the imaginary dielectric function spectra are due to electronic interband transition. The first excitonic peak is usually in the range of the energy band gap. If the excitonic energy range corresponds with the visible energy

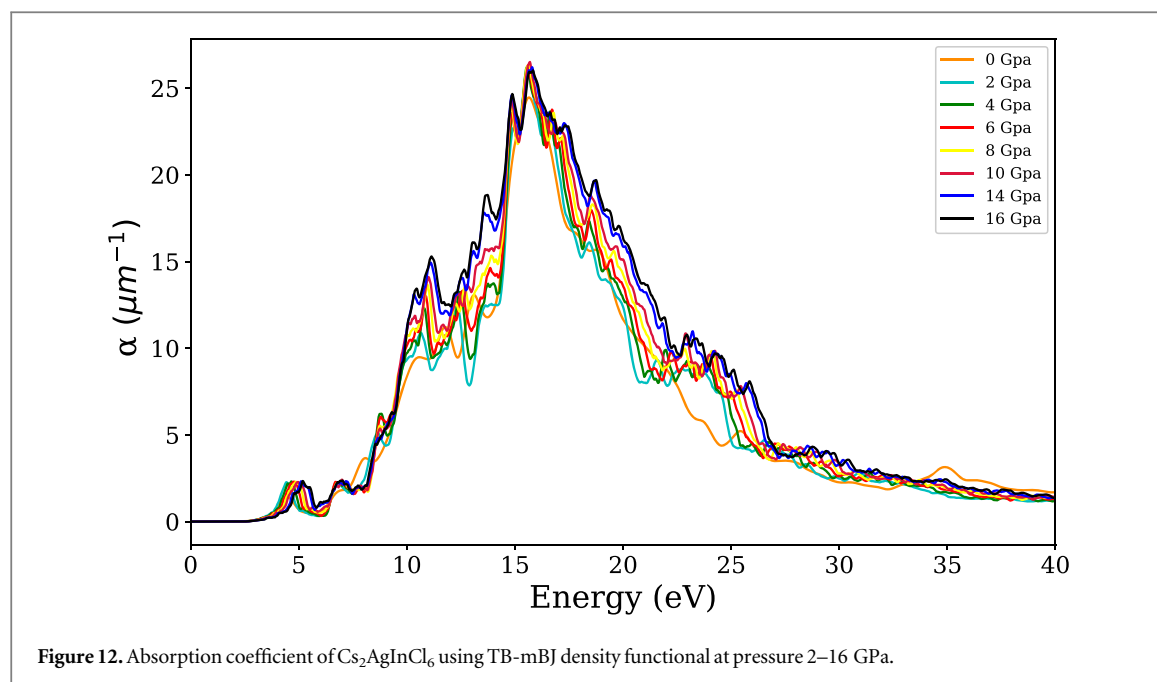


Figure 12. Absorption coefficient of $\text{Cs}_2\text{AgInCl}_6$ using TB-mBJ density functional at pressure 2–16 GPa.

Table 4. Result of the extracted optical parameters at different pressure using TB-mBJ exchange correlation functional where 1st excitonic and maximum excitonic are the first and maximum peak of the $\varepsilon_2(\omega)$, $\varepsilon_1(0)$ is the static dielectric, $n(0)$ is refractive index, $\alpha_{\max}$ (eV) and $\alpha(\omega)$ are the absorption shift and absorption strength at high energy.

Pressure (GPa)	1st excitonic peak (eV)	maximum excitonic peak (eV)	$\varepsilon_1(0)$	$n(0)$	$\alpha_{\max}$ (eV)	$\alpha(\omega)$
0	4.3810	14.9050	2.9331	1.7126	15.6670	24.4571
2	4.4219	14.7622	2.9635	1.7215	15.5445	25.6600
4	4.4694	14.7758	3.0558	1.7481	15.5513	26.2052
6	4.6123	14.6941	3.1488	1.7745	15.6329	26.2132
8	4.8368	14.7146	3.2234	1.7954	15.6329	26.3199
10	4.9185	14.6942	3.2935	1.8148	15.6942	26.5061
14	5.1072	10.2859	3.4157	1.8482	15.7962	26.2037
16	5.1838	10.3471	3.4713	1.8631	15.8370	26.0210

range then the material will have low reflectivity and high absorption coefficient [47]. The calculated reflectivity as shown in figure 11(b) shows an increment as the pressure increases, denoting that $\text{Cs}_2\text{AgInCl}_6$ is shining in the visible range. Therefore, pressure decreases its absorption and increases its reflectivity.

The effect of pressure on the optical properties were reported using the precisely extracted data from the results, the summary of which is given in table 4. Also their variation as the pressure is applied is given in figure 13. The effect of pressure on the static dielectric function and refractive index for both exchange-correlation functional shows corresponding increment which denotes that the refractivity of $\text{Cs}_2\text{AgInCl}_6$ increases with pressure. Pressure creates a coupling effect of the photon and the plasmon (to form polariton) due to the induced pressure on atomic orbitals in the valence band and conduction band [48].

As pressure is applied, the absorption energy peak ($\alpha_{\max}$) reduces (red-shift) by 0.8% and started increasing at 4 GPa till it reached a percentage increment (blue-shift) of 1.1% at 16 GPa. The shift in the absorption corresponds to the shift in the energy band gap and absorption threshold of $\text{Cs}_2\text{AgInCl}_6$. However, there is an increment in its absorption strength as pressure increases, although, at a higher pressure of around 12 GPa, $\text{Cs}_2\text{AgInCl}_6$ showed low absorption strength. The absorption's strength is directly proportional to the pressure exerted until 8 GPa when it is reduced drastically and a proportional increment follows until 16 GPa, this suggests that the absorption edge for $\text{Cs}_2\text{AgInCl}_6$ reduces at 10 GPa. In contrast, the absorption of $\text{Cs}_2\text{AgInCl}_6$ increases (blue-shift) as the material is pressurized.

There are several excitonic peaks in the studied energy range, but the first excitonic peak increases as the pressure increases. The maximum excitonic peak reduces with an increase in pressure, which means that the band is becoming more dispersed which is glaring in the calculated band structure using TB-mBJ at 16 GPa as shown in the figure 6.

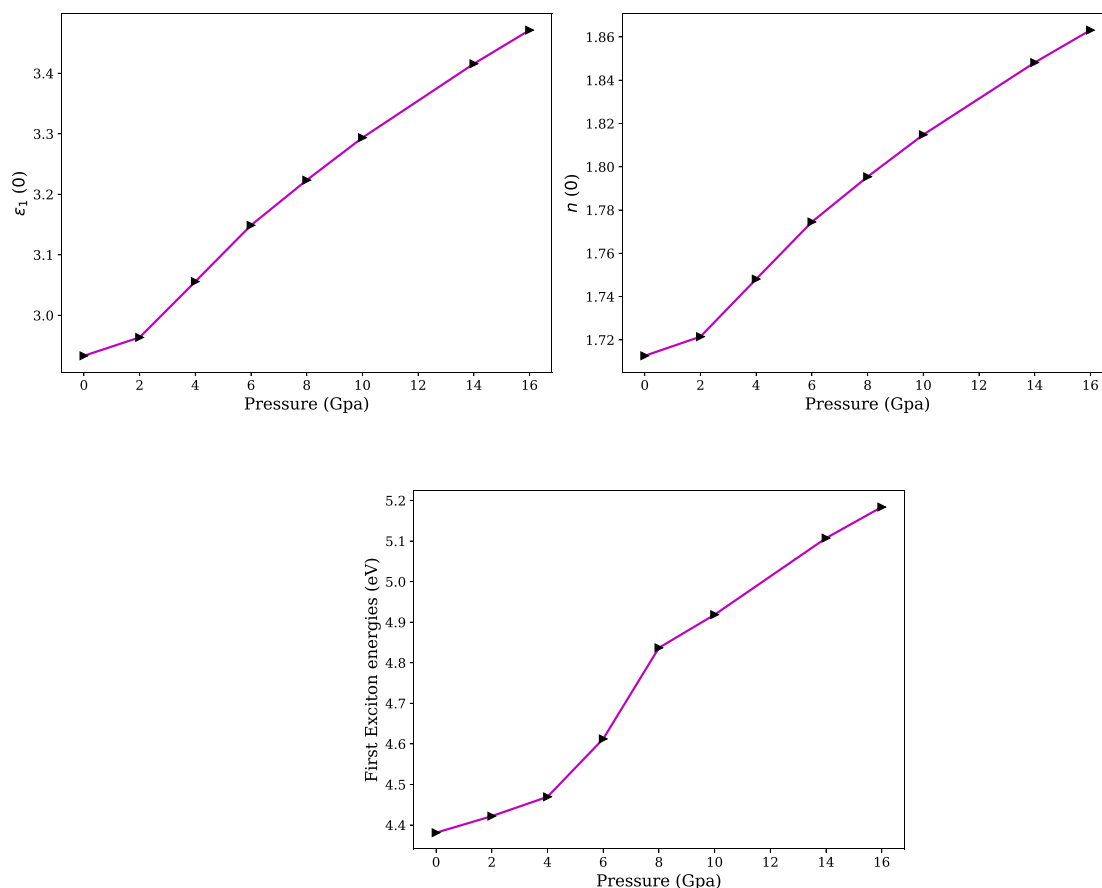


Figure 13. The effect of pressure on the optical parameters of $\text{Cs}_2\text{AgInCl}_6$ using TB-mBJ exchange correlation functional at pressure 0 GPa to 16 GPa.

4. Conclusion

The double perovskite $\text{Cs}_2\text{AgInCl}_6$ showed diverse structural mechanical and opto-electronic properties under hydrostatic pressure ranging from 2 GPa to 16 GPa. These properties were investigated using two classes of exchange-correlation functional a GGA and meta-GGA namely; PBEsol (Perdew-Burke- Ernzerhof revised for solids) and TB-mBJ (Tran-Blaha modified Burke Johnson). Two types of density functional theory codes were used to solve the Kohn–Sham equations, a plane wave as implemented in Quantum ESPRESSO and a Full-Linearized Augmented Plane Wave (FP-LAPW) as implemented in Elk-LAPW code. The calculated optimized lattice parameter $a = 10.383 \text{ \AA}$ at ambient pressure corresponds with the reported lattice parameter using PBEsol, but there are no reported calculations for optimized lattice parameters for this material under pressure. The lattice parameter decreases as the pressure increases, $a = 9.556 \text{ \AA}$ at 16 GPa. The calculated energy band gap of the material at ambient pressure using TB-mBJ was $E_g = 2.747 \text{ eV}$, and this corresponds with the ones obtained in the literature. The pressure effect on the energy band gap of the material using the two exchange-correlation functionals showed the same characteristics and pattern. Although PBEsol did underestimate the energy band gap, the results of TB-mBJ are more accurate. The energy band gap decreases from 0 GPa to 8 GPa, but increases as the pressure is increased. Mechanical properties such as the elastic moduli, elastic constants, Poisson's ration, Pugh's ratio, Cauchy's pressure and anisotropy factor were all reported at different values of pressure. The material is found to be anisotropic and mechanically stable at all pressure considered. The calculated Pugh's ratio and Poisson's ratio all indicated that the material is ductile at all pressure. The optical properties of $\text{Cs}_2\text{AgInCl}_6$ such as refractive index, extinction coefficient, real dielectric constants, imaginary dielectric constants, reflectivity and absorption coefficients were studied. $\text{Cs}_2\text{AgInCl}_6$ showed absorption properties in the visible region which makes it a good candidate in photonics. Under hydrostatic pressure using both PBEsol and TB-mBJ, the absorption coefficient of the material increases (blue-shift) as the pressure increases as well as the threshold of absorption but both reduces at 12 GPa. The refractive index, static dielectric constant and reflectivity of this material increases as the pressure increases. When $\text{Cs}_2\text{AgInCl}_6$ is pressurized its optical properties limit its application as a photovoltaic material but could be used in high energy photonic technologies. The properties calculated under hydrostatic pressure using the first principle shows the material is

a potential solar cell material. The thermodynamic and phonon transport properties of the material could also be studied under pressure to further explore its photonic properties.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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