

Research Article

An Ab Initio Insight into the Structural, Mechanical, Electronic and Optical Properties of Cesium Based Double Perovskites $\text{Cs}_2\text{Ge}_2\text{X}_6$ (X=Cl, Br, I)

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Abstract

The Cubic $\text{Cs}_2\text{Ge}_2\text{X}_6$ (X=Cl, Br, I) double perovskite's structural, electronic, elastic, mechanical stability, phonons and optical properties are examined within the framework of Density Functional Theory (DFT). The calculated formation energy ΔH^F and Goldschmidt tolerance factor (t) confirm the stability of the cubic phase in $\text{Cs}_2\text{Ge}_2\text{X}_6$ (X = Cl, Br, I) compounds. Direct band gap (E_g) values for $\text{Cs}_2\text{Ge}_2\text{Cl}_6$, $\text{Cs}_2\text{Ge}_2\text{Br}_6$, and $\text{Cs}_2\text{Ge}_2\text{I}_6$ are 1.02 eV, 0.98 eV, and 0.89 eV, correspondingly. Excellent optical absorption qualities were revealed by the computed absorption spectra of $\text{Cs}_2\text{Ge}_2\text{Cl}_6$, $\text{Cs}_2\text{Ge}_2\text{Br}_6$, and $\text{Cs}_2\text{Ge}_2\text{I}_6$ indicating their applicability for photovoltaic applications. Based on the calculated optical spectra of the investigated compounds, the noted maximum absorption coefficients were $1.8 \times 10^5 \text{ cm}^{-1}$ for $\text{Cs}_2\text{Ge}_2\text{Cl}_6$, $3.3 \times 10^5 \text{ cm}^{-1}$ for $\text{Cs}_2\text{Ge}_2\text{Br}_6$ and $8.8 \times 10^4 \text{ cm}^{-1}$ for $\text{Cs}_2\text{Ge}_2\text{I}_6$. Among the investigated compounds, $\text{Cs}_2\text{Ge}_2\text{Br}_6$ exhibited the highest absorption coefficient, indicating high light harvesting capability and making it the most suitable candidate for thin film solar cells. Although $\text{Cs}_2\text{Ge}_2\text{Cl}_6$ displays a slightly lower absorption coefficient, it possesses excellent optical absorption in the visible and ultraviolet regions. The high absorption coefficient demonstrate that these materials are perfect for solar cells.

Keywords

DFT, Double Perovskites, All-inorganic, Photovoltaics, $\text{Cs}_2\text{Ge}_2\text{X}_6$ (X=Cl, Br, I)

1. Introduction

Perovskite-structured materials have attracted attention due to their wide applicability as dielectrics, superconductors and optoelectronic materials [1]. Among the optoelectronic applications, Perovskite Solar Cells (PSCs) are now regarded as a promising photovoltaic technology combining high efficiency with low manufacturing cost [2]. In a PSC, the light harvesting layer is a perovskite structured compound, typically a hybrid

organic inorganic or all inorganic lead halide such as methylammonium lead iodide or cesium lead halides [2]. The Power Conversion Efficiency (PCE) of PSCs has increased from 3.8% [3] to 25.8% in a decade, approaching that of single crystal silicon cells [3, 4]. This rapid progress reflects the favourable intrinsic properties of these absorbers, including a high electron mobility ($800 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), a long carrier diffusion length ($> 1 \text{ }\mu\text{m}$) and a high absorption coefficient (10^5

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cm⁻¹) [4].

Despite this progress, silicon based photovoltaics still dominates the market [3]. The main barriers to commercializing PSCs are the difficulty of upscaling, limited long term device stability and the toxicity of lead based absorbers [3]. Toxicity tests on *Arabidopsis thaliana* showed that MAPbI₃ (MA = CH₃NH₃) and its precursors inhibit plant growth, with MAPbI₃ doing so at concentrations above 5 micrometers (μm) and the lead-free-iodide precursors only above 500 micrometers (μm) [5]. Lead based perovskites also suffer from material instability and phase transitions [3]. These problems motivate the search for stable, lead-free alternatives. Halide double perovskites, with general formula A₂B'B''X₆, are among the most promising lead free candidates [6, 7]. In these compounds, A is a monovalent cation, B and B' are two distinct metal cations, and X is a halide anion (Cl⁻, Br⁻ or I⁻). The B' and B'' oxidation states must satisfy charge neutrality, so that their sum equals +4 when A is monovalent. Reported B'/B'' combinations include Ag⁺/Bi³⁺, Ag⁺/Sb³⁺ and Cu⁺/Bi³⁺ [6]. The presence of two distinct B-site cations allows extensive compositional engineering of the band gap, dielectric response and carrier mobility [7]. The formability of a perovskite lattice is commonly assessed with the Goldschmidt tolerance factor [8],

$$t = \frac{(r_A + r_X)}{\sqrt{2}(r_B + r_X)},$$
 Where r_A , r_B , and r_X are the radii of A, B and X atoms.

For photovoltaic use, the size and nature of the band gap are decisive because they control optical absorption and carrier transport [9]. In these halide compounds the valence band maximum is generally dominated by halide p orbitals, while the conduction band minimum arises mainly from metal cation s or p states, depending on the B-site. This orbital character produces strong metal halide bonding and largely determines the band dispersion near the gap. In double perovskites, the ordering of the B' and B'' cations offers an additional route to band-gap engineering through structural distortion and substitution [10].

Density Functional Theory (DFT) is one of the widely used methods for predicting the electronic structure of periodic solids [11]. It reformulates the many body Schrödinger equation in terms of the electron density and is available in several codes, including Quantum ESPRESSO, VASP and SIESTA [7]. Standard DFT with generalized gradient approximation (GGA) functionals underestimates band gaps because of self-interaction error and the missing derivative discontinuity of the exchange correlation potential [12]. However, it remains reliable for identifying qualitative trends and for comparing different compositions within a family of materials [13]. This current study used DFT within the Quantum ESPRESSO package to investigate the structural, electronic, mechanical and optical properties of the double perovskites Cs₂Ge₂X₆ (X = Cl, Br, I) in order to assess their suitability for photovoltaic applications.

2. Computational Details

The structural, electronic, mechanical and optical properties of the cesium based halide double perovskites Cs₂Ge₂X₆ (X = Cl, Br, I) were investigated using Density Functional Theory (DFT) to assess their potential for photovoltaic applications. The three compounds crystallize in an ordered face centered cubic double perovskite structure with space group Fm-3m (No. 225) [14]. All calculations were carried out with the plane wave pseudopotential code Quantum ESPRESSO. The exchange correlation energy was described by the Generalized Gradient Approximation (GGA) in the Perdew Burke Ernzerhof (PBE) parametrization. Pseudopotentials. Electron ion interactions were treated with scalar-relativistic Projector Augmented Wave (PAW) pseudopotentials. The valence configurations were [Xe]6s¹ for Cs, [Ar]3d¹⁰4s²4p² for Ge, [Ne]3s²3p⁵ for Cl, [Ar]3d¹⁰4s²4p⁵ for Br and [Kr]4d¹⁰5s²5p⁵ for I [15].

Convergence of the total energy with respect to the kinetic energy cutoff and the Brillouin zone sampling was tested for each compound. The wavefunction cutoff (ecutwfc) was varied from 40 to 90 Ry in steps of 10 Ry, and the charge density cutoff (ecutrho) was set to 2 × ecutwfc. Monkhorst Pack k-point meshes for the primitive cell were varied from 1×1×1 to 10×10×10. Self-consistent field (SCF) cycles were iterated until the total-energy change was below 10⁻⁸ Ry. Structures were relaxed until forces were below 10⁻³ Ry/bohr using smearing. The band structure was computed in a non-self-consistent (nscf) run, which reads the ground-state charge density from the preceding SCF calculation [16], along the high-symmetry path Γ -U-X-W-K- Γ . Band energies were extracted with bands.x. The band gap was taken from the valence-band maximum and conduction-band minimum [16]. The Projected Density of States (PDOS) was computed with projwfc.x on a denser k-mesh, using Gaussian smearing.

The mechanical properties were evaluated with thermo_pw.x using the converged parameters. The three independent elastic constants of the cubic lattice (C₁₁, C₁₂, C₄₄) were obtained. Mechanical stability was assessed with the Born criteria for cubic crystals: C₁₁ > 0, C₄₄ > 0, C₁₁ > |C₁₂| and C₁₁ + 2C₁₂ > 0. The bulk modulus B = (C₁₁ + 2C₁₂)/3, the shear modulus G (Voigt Reuss Hill average), Young's modulus E, Poisson's ratio ν, the Pugh ratio B/G and the Zener anisotropy factor A = 2C₄₄/(C₁₁ - C₁₂) were derived from these constants [17]. The optical properties were calculated with epsilon.x within the independent particle approximation. The real and imaginary parts of the frequency dependent dielectric function, ε₁(ω) and ε₂(ω), were computed. The refractive index, absorption coefficient and extinction coefficient were then derived from ε(ω) using the standard relations [17].

3. Results and Discussions

3.1. Structural Properties

After structural optimization calculations were done, the value obtained for lattice parameter $a = b = c$ for cubic structure of $\text{Cs}_2\text{Ge}_2\text{Br}_6$ was optimal at 11.113 Å as in Figure 1. Goldschmidt tolerance factor (t), $\text{Cs}_2\text{Ge}_2\text{Br}_6$ was obtained as;

$t = \frac{(r_A + r_X)}{\sqrt{2}(r_B + r_X)}$, Where r_A , r_B , and r_X are the radii of A, B and X atoms

$$t = \frac{1.88 + 1.96}{\sqrt{2}(0.53 + 1.96)}$$

$$t = 1.091$$

The calculated Goldschmidt tolerance factor of $t = 1.091$ is greater than unity, indicating that the compound cannot lose structural properties.

Using DFT, [15] examined the structural properties of $\text{Cs}_2\text{NaScBr}_6$ double perovskites and obtained an optimal lattice parameter of 12.01 Å. The finding from [15] is in agreement to the current value for $\text{Cs}_2\text{Ge}_2\text{Br}_6$. Figure 1 shows a plot of energy (eV) as a function of lattice parameter (Bohr) for $\text{Cs}_2\text{Ge}_2\text{Br}_6$ with a value of 11.113 Å.

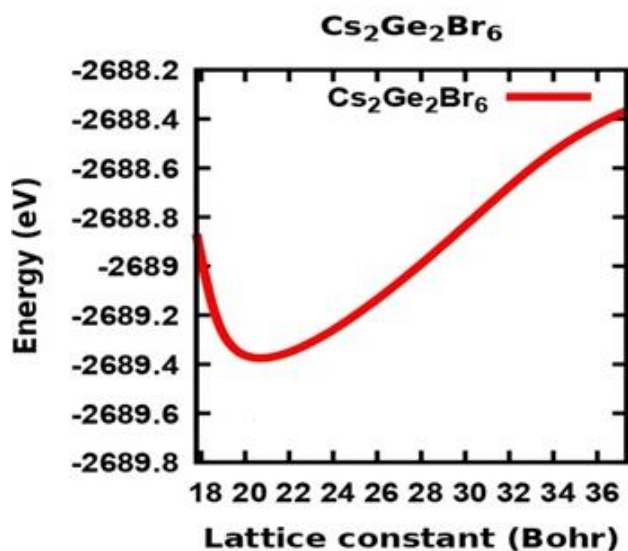


Figure 1. A plot of energy (eV) as a function of lattice parameter (Bohr) for $\text{Cs}_2\text{Ge}_2\text{Br}_6$.

Figure 2 shows a conventional Face Centered Cubic unit cell for $\text{Cs}_2\text{Ge}_2\text{Br}_6$ as obtained using xcrsden software. This software runs on quantum espresso package installed in linux operating system.

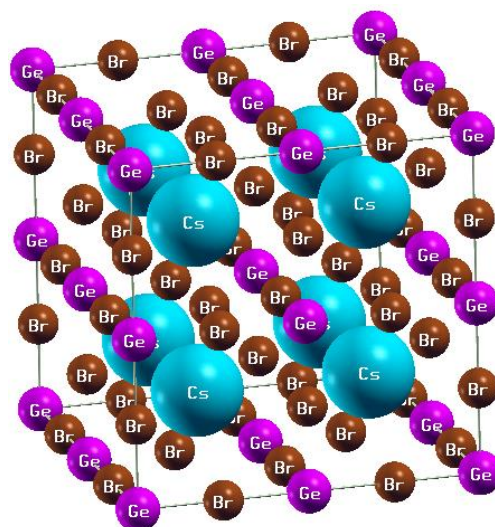


Figure 2. Conventional Face Centered Cubic unit cell for $\text{Cs}_2\text{Ge}_2\text{Br}_6$.

Lattice parameter for $\text{Cs}_2\text{Ge}_2\text{Cl}_6$ in this current study was calculated and the value obtained was 10.478 Å as in Figure 3. Similar findings were obtained on $\text{Cs}_2\text{AgCrX}_6$ by [15] who obtained a value of 10.72 Å. This value is close to the finding of this current study with minimal difference. The plot of energy (eV) as a function of lattice parameter (Bohr) for $\text{Cs}_2\text{Ge}_2\text{Cl}_6$ is given in Figure 3 with a lattice parameter of 10.478 Å.

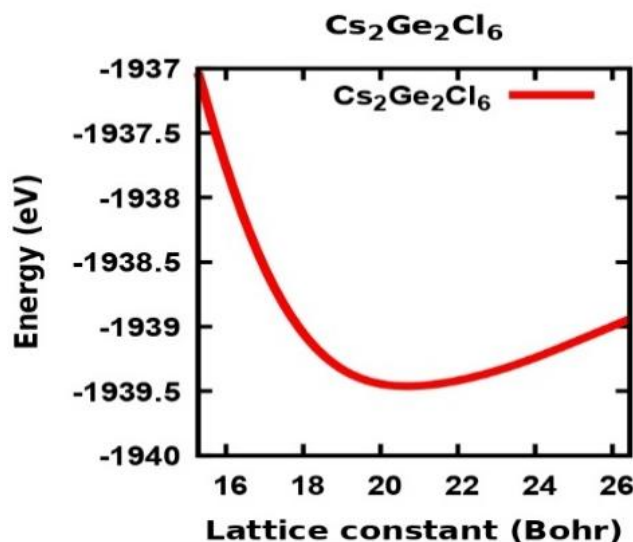


Figure 3. A plot of energy (eV) as a function of lattice parameter (Bohr) for $\text{Cs}_2\text{Ge}_2\text{Cl}_6$.

The Goldschmidt tolerance factor (t) for $\text{Cs}_2\text{Ge}_2\text{Cl}_6$ was obtained as

$t = \frac{(r_A + r_X)}{\sqrt{2}(r_B + r_X)}$, Where r_A , r_B , and r_X are the radii of A, B and X atoms

$$t = \frac{1.88+1.81}{\sqrt{2}(0.53+1.81)}$$

$$t = 1.115$$

This value is close to 1 (one), indicating that the compound is resistant to structural degradation.

Figure 4 shows a conventional Face Centered Cubic unit cell for $\text{Cs}_2\text{Ge}_2\text{Cl}_6$.

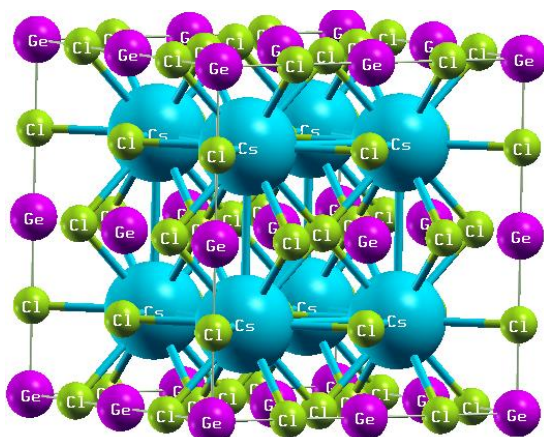


Figure 4. Conventional Face Centered Cubic unit cell for $\text{Cs}_2\text{Ge}_2\text{Cl}_6$.

Optimal lattice parameter for $\text{Cs}_2\text{Ge}_2\text{I}_6$ was obtained as $11.906 \text{ \AA}$ as in Figure 5. This value is close to $11.2711 \text{ \AA}$ as obtained by [8] under their study on $\text{Cs}_2\text{AgBiX}_6$ ($\text{X}=\text{Br}$ and Cl). Another study by [16] on $\text{Cs}_2\text{NaScX}_6$ ($\text{X}=\text{Cl}$, Br) obtained a value $11.55 \text{ \AA}$ which shows that the lattice parameter for this current work is within the range of literature. Figure 5 shows a graph of energy as a function of lattice parameter with a value of $11.906 \text{ \AA}$.

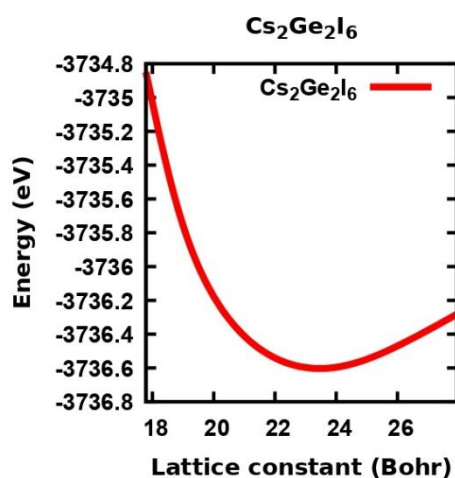


Figure 5. A plot of energy (eV) as a function of lattice parameter (Bohr) for $\text{Cs}_2\text{Ge}_2\text{I}_6$.

The conventional Face Centered Cubic unit cell for $\text{Cs}_2\text{Ge}_2\text{I}_6$ is given in Figure 6.

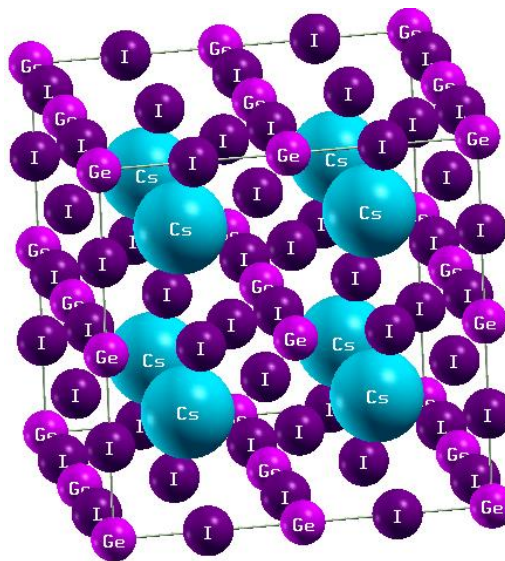


Figure 6. Conventional Face Centered Cubic unit cell for $\text{Cs}_2\text{Ge}_2\text{I}_6$.

The value of Goldschmidt tolerance factor (t') for $\text{Cs}_2\text{Ge}_2\text{I}_6$ was obtained as;

$t = \frac{(r_A+r_X)}{\sqrt{2}(r_B+r_X)}$, Where r_A , r_B , and r_X are the radii of A, B and X atoms

$$t = \frac{1.88+2.20}{\sqrt{2}(0.53+2.20)}$$

$$t = 1.057$$

This value is close to 1 (one), indicating that the compound is resistant to structural degradation and is therefore expected to maintain its structural integrity.

3.2. Mechanical Properties

For cubic crystals, there are three specified elastic constants; C_{11} , C_{12} , and C_{44} . This study employed DFT to study mechanical properties for $\text{Cs}_2\text{Ge}_2\text{Br}_6$, $\text{Cs}_2\text{Ge}_2\text{Cl}_6$ and $\text{Cs}_2\text{Ge}_2\text{I}_6$. In order to study mechanical properties of the cubic structures, the following conditions have to be met for the compounds: $C_{11} > 0$, $C_{44} > 0$, $C_{11} - C_{12} > 0$, $C_{11} + 2C_{12} > 0$, and $C_{11} > B > C_{12}$ [17]. All of the compounds in Table 1 met the stability requirements. The shear and bulk modules, respectively, were determined using the Voigt-Reuss-Hill (VRH) isotropic elastic modulus technique. The additional polycrystalline elastic characteristics were computed using the isotropic bulk and shear modules as employed in VRH technique. This calculation employed DFT and the values of bulk modulus (B), Young's modulus (E), shear modulus (G), and elastic constants were obtained. The highest values of B, G and E were

calculated for all the compounds as given in Table 1.

The Pugh's (B/G) criteria were applied to determine if the compound is brittle or ductile. The materials under study are regarded as ductile if the B/G ratio is more than 1.75; otherwise, it is brittle [18]. Every compound in this current study was found to be ductile. This implies that they are mechanically flexible and crack-resistance. This makes the study's compounds to be applicable where mechanical endurance is crucial, including flexible electronic devices and coatings. Ductile materials are typically more mechanically stable under stress [18]. Some of compounds from this study like Cs₂Ge₂I₆ was found to have greater ductility, translating into improved resilience to impact mechanical shocks, which can increase the dependability of perovskite-based devices, particularly in optoelectronic and photovoltaic applications [19].

Due to the ability of B/G ratio being greater than 1.75 as in Table 1, all compound under this study shows that the perovskite-based material obtained are good for structural or electronic applications and can sustain mechanical stress without breaking, which qualifies them for flexible and wear able electronics. These compounds may also withstand lattice flaws without experiencing a major drop in performance, which is a symptom of their superior defect tolerance and also in perovskites used in solar cells, where structural flaws may reduce efficiency [19].

Brittle behavior is indicated by a lower Poisson's ratio (ν) is less than 0.26, whereas ductile behavior is suggested by a larger than 0.26 [20]. In this current study, all the compounds were found to be ductile in nature by considering the Poisson's ratio (ν) and Pugh's ratio (B/G) obtained in Table 1.

Table 1. Elastic constants (C_{11} , C_{12} , C_{44}), Cauchy pressure ($C_{12}-C_{44}$), Young Modulus (E), bulk modulus (B), shear modulus (G), Pugh's ratio (B/G), and Poisson's ratio (ν) for Cs₂Ge₂X₆ ($X=Cl$, Br, I).

material	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)	$C_{12}-C_{44}$ (GPa)	E (GPa)	B (GPa)	G (GPa)	B/G	ν
Cs ₂ Ge ₂ Br ₆	44.03	7.59	6.74	37.33	26.00	19.74	10.17	1.94	0.28
Cs ₂ Ge ₂ Cl ₆	62.61	16.26	11.80	50.81	40.00	31.71	15.51	2.04	0.29
Cs ₂ Ge ₂ I ₆	48.23	17.10	8.19	40.04	28.23	27.47	10.63	2.58	0.33

The study used Cauchy pressure ($C_{12}-C_{44}$) to affirm the ductility and brittleness of the compounds under the study. All the values obtained for Cauchy pressure were found to have a positive Cauchy pressure. A positive Cauchy pressure signifies a metallic bonding materials while those with negative Cauchy pressure signifies materials with a strong resistance to bond bending, such as covalently bound solids [21]. Comparing the values in Table 1 for the present work and what researchers have obtained, for example, [22], it shows that this current study's findings are within the range of literature. Another area of interest in this analysis is the hardness of the material that give it ability to tolerate formation. This is due to its intrinsic mechanical complexity.

The knowledge on a material's machinability is always valuable since it indicates the most cost-effective degree of machine utilization, cutting forces, temperature, and plastic strain [23]. Machinability is the term used to describe how easily a material can be formed or cut using tools. One can also assess material's plasticity and lubricating qualities using the machinability index value, which is written as follows: $\mu M = \frac{B}{C_{44}}$. Materials with a high machinability value are said to have More plastic strain, lower feed forces, superior lubrication properties, and a lower friction value [24]. Table 2 displays the computed values of the compounds' machinability indices in this work.

Young's modulus and Poisson's ratio were used to express

Vickers hardness through Equation (1);

$$H_v = \frac{(1-\nu)E}{6(1+\nu)} \quad (1)$$

where ν is Poisson's ratio and E is Young's modulus [25].

Table 2. Machinability index (μM), Vicker's hardness (H_v) in GPa, and Kleinman parameter (ξ) for Cs₂Ge₂X₆ ($X=Cl$, Br, I).

Compound	μM	H_v	ξ
Cs ₂ Ge ₂ Br ₆	2.9288	1.4896	0.3240
Cs ₂ Ge ₂ Cl ₆	2.6873	2.1705	0.4093
Cs ₂ Ge ₂ I ₆	3.3541	1.2028	0.4976
K ₂ Ge ₂ Br ₆	3.2844	1.5005	0.3702
K ₂ Ge ₂ Cl ₆	3.2408	1.6172	0.3782
K ₂ Ge ₂ I ₆	3.4798	1.1977	0.4220

The mechanical hardness is essential for assessing structural stability of the perovskites and their uses in a number of industries, including catalysis, optoelectronics, and photovol-

taics [26]. The Vickers Hardness (H_V), which gives information on the material's resistance to deformation under applied stress, is one of the primary mechanical characteristics used to assess the hardness of double perovskites. This is a common method for evaluating the mechanical toughness of double perovskites. Under a fixed stress, a perovskite material is pressed into the material's surface using this micro indentation technique, and the diagonal length of the indentation is measured [27]. Understanding the material's resilience to wear, durability, and mechanical stresses is made easier by the resulting hardness value.

The Kleinman parameter is a useful tool for comprehending the mechanical stability and flexibility of double perovskites. For example, [28] used the PBEsol functional to calculate the ξ value in their study of the double perovskite $\text{Rb}_2\text{LiTiF}_6$, and obtained a value of 0.665. This implies that bond stretching can be reduced more readily than bond bending in this material, which sheds light on its mechanical robustness and structural application possibilities [28]. Additionally, the response of double perovskites to external stresses can be evaluated using the Kleinman parameter [29]. The expression used in obtaining the Kleinman parameter is given in Equation (2);

$$\xi = \frac{c_{11} + 8c_{12}}{7c_{11} + 2c_{12}} \quad (2)$$

In considering Table 2, all the values for $\text{Cs}_2\text{Ge}_2\text{Br}_6$, $\text{Cs}_2\text{Ge}_2\text{Cl}_6$ and $\text{Cs}_2\text{Ge}_2\text{I}_6$ were found to fall between 0 to 1 as requirement of Kleinman parameter in double perovskites.

This study also computed the Zener anisotropy index (A_z), the universal anisotropy index (A^U), the equivalent Zener anisotropy measure (A^{eq}), and the anisotropy ratios E_{max}/E_{min} and G_{max}/G_{min} . These indices are defined by the Equations (3), (4) and (5) [30].

$$A_z = \frac{2c_{44}}{c_{11} - c_{12}} \quad (3)$$

$$A^{eq} = \left(1 + \frac{5}{12}A^U\right) + \sqrt{\left(1 + \frac{5}{12}A^U\right)^2 - 1} \quad (4)$$

$$A^U = 5 \left(\frac{G_V}{G_R}\right) + \frac{B_V}{B_R} - 6 \geq 0 \quad (5)$$

where $B_V = B_R$ in Equation (5) for cubic crystals, whereas B_V , B_R , G_V , and G_R are the bulk and shear moduli in the Voigt and Reuss techniques. A perfect isotropic nature is represented by the zero value for A^U ; nonetheless, Isotropic nature is defined by a value equal to unity for A^{eq} and A [25].

Using the Voigt-Reuss constraints for bulk and shear moduli, the universal elastic anisotropy index (A^U) was computed to provide a more thorough measure of elastic anisotropy. For the double perovskites under investigation, the computed A^U values range from 0.51 to 1.36, indicating moderate to significant elastic anisotropy. Table 4 shows the values of G_V and G_R that were used to calculate A^U . For $\text{Cs}_2\text{Ge}_2\text{Br}_6$, $A^U = 1.29$, which exhibits moderate elastic anisotropy for the Cs-based compounds, indicating a substantial directional dependency of elastic moduli as a result of moderate Br^- size and lattice distortion. On the other hand, Cl^- and I^- result in somewhat balanced bonding contacts inside the Ge_2X_6 with $\text{Cs}_2\text{Ge}_2\text{Cl}_6$ (0.57) and $\text{Cs}_2\text{Ge}_2\text{I}_6$ (0.51) showing lower anisotropy, indicating more uniform elastic behavior. The anisotropy ratios E_{max}/E_{min} and G_{max}/G_{min} describe the anisotropic extent of the shear and Young's moduli.

The Zener anisotropic index was used to assess the elastic anisotropy of $\text{Cs}_2\text{Ge}_2\text{Br}_6$, and the result for A_z was found at 0.67. Moderate elastic anisotropy in the crystal lattice is indicated by this value's substantial deviation from unity. Another system that was studied was $\text{Cs}_2\text{Ge}_2\text{Cl}_6$. Its Zener anisotropic index A_z was found to be 0.71, which represent a moderate elastic anisotropy. The Zener anisotropic index for $\text{Cs}_2\text{Ge}_2\text{I}_6$ was also investigated and the value obtained was $A_z=0.73$. This value falls under moderate elastic anisotropy. The value for Zener anisotropic index in $\text{K}_2\text{Ge}_2\text{Br}_6$ was found to be $A_z=0.67$, which demonstrate strong elastic anisotropy. For $\text{K}_2\text{Ge}_2\text{Cl}_6$, Zener anisotropic index A_z was found to be 0.86. This value demonstrates moderate elastic anisotropy. In the same way, Zener anisotropic index for $\text{K}_2\text{Ge}_2\text{I}_6$, was found at $A_z=0.71$. This value represents a moderate anisotropy. All the values obtained in this study were within the literature as in Table 3.

Table 3. The calculated shear modulus (Voigt and Reuss in Gpa), Zener anisotropic index (A_z), universal anisotropy index (A^U), equivalent Zener anisotropy measure (A^{eq}), minimum and maximum values of Young's modulus (E_{min} and E_{max} in Gpa), shear modulus (G_{min} and G_{max} in GPa) and their ratios for $\text{Cs}_2\text{Ge}_2\text{X}_6$ ($X=\text{Cl}, \text{Br}, \text{I}$).

Compound	G_V	G_R	A_z	A^U	A^{eq}	E_{min}	E_{max}	G_{min}	G_{max}	E_{max}/E_{min}	G_{max}/G_{min}
$\text{Cs}_2\text{Ge}_2\text{Br}_6$	113.33	90.11	0.67	1.29	2.70	181.52	418.03	67.39	182.22	2.30	2.70
$\text{Cs}_2\text{Ge}_2\text{Cl}_6$	163.47	146.75	0.71	0.57	1.97	314.72	559.16	117.9	231.80	1.78	1.97
$\text{Cs}_2\text{Ge}_2\text{I}_6$	111.45	101.1	0.73	0.51	1.90	223.6	392.9	81.94	155.71	1.76	1.38

The significant mechanical interdependence between resistance to shear and tensile deformation were confirmed by Young's modulus, which closely tracks the shear modulus trend. For $\text{Cs}_2\text{Ge}_2\text{X}_6$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) systems, reported Young's modulus values were 26.00 GPa for $\text{Cs}_2\text{Ge}_2\text{Br}_6$, 40.00 GPa for $\text{Cs}_2\text{Ge}_2\text{Cl}_6$ and 28.33 GPa for $\text{Cs}_2\text{Ge}_2\text{I}_6$. Chloride halide has the highest young modulus, followed by bromide and lastly iodide. The mechanical softness of Ge-based double perovskites is confirmed by the fact that these values are far lower

than those of traditional semiconductors like silicon (~130 GPa). Increased bond stretching and octahedral tilting under uniaxial stress cause E to decrease as halide size increases [31]. Although it restricts load-bearing applications, this mechanical softness is beneficial for thin-film optoelectronics, where strain tolerance is crucial [32].

Figure 7 shows spatial dependency of the shear, Poisson's ratio and Young's moduli (The highest and lowest values are shown in blue and green, respectively) for $\text{Cs}_2\text{Ge}_2\text{Br}_6$.

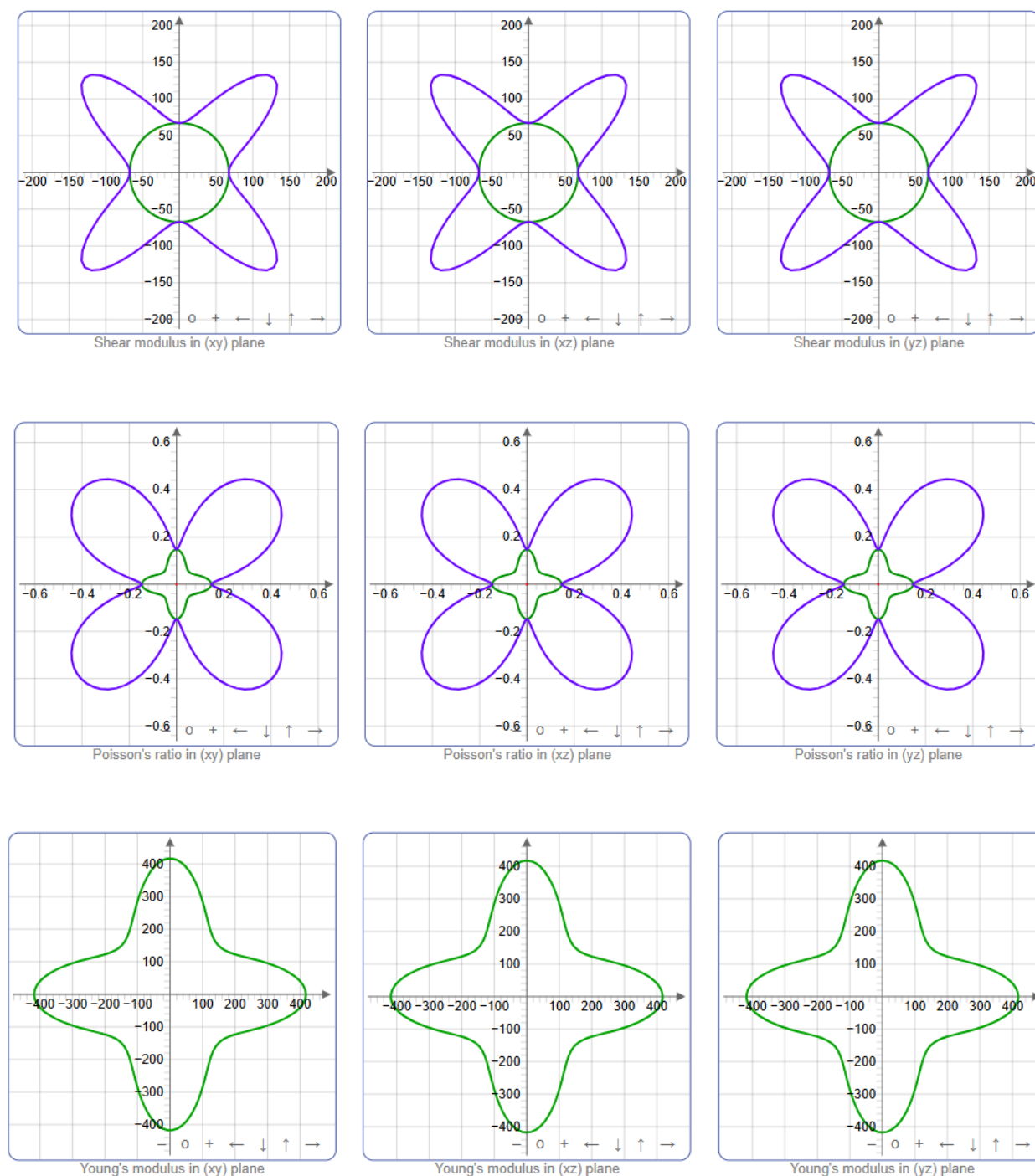


Figure 7. $\text{Cs}_2\text{Ge}_2\text{Br}_6$ spatial dependency of the shear, Poisson's ratio and Young's moduli (The highest and lowest values are shown in blue and green, respectively).

The Poisson's ratio obtained for $\text{Cs}_2\text{Ge}_2\text{Cl}_6$ was 0.29. Figure 8 shows spatial dependency of the shear, Poisson's ratio and Young's moduli (The highest and lowest values are shown in blue and green, respectively) for $\text{Cs}_2\text{Ge}_2\text{Cl}_6$.

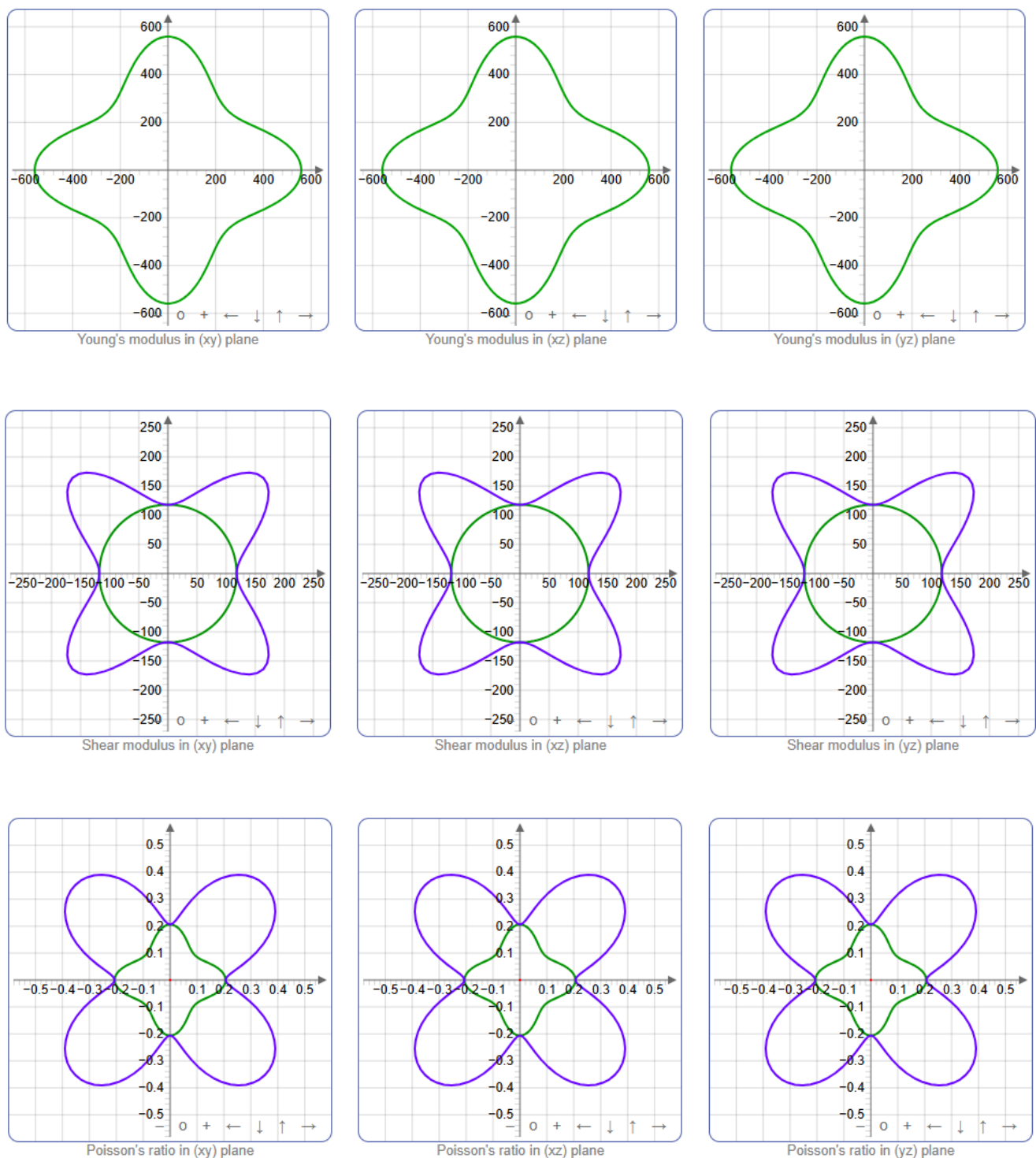


Figure 8. $\text{Cs}_2\text{Ge}_2\text{Cl}_6$ spatial dependency of the shear, Poisson's ratio and Young's moduli (The highest and lowest values are shown in blue and green, respectively).

The computed Poisson's ratio for $\text{Cs}_2\text{Ge}_2\text{I}_6$ was found to be 0.33, which puts it in the usual range for ionic and mechanically soft materials. This comparatively high number reflects the predominance of central-force ionic bonding inside the crystal lattice and shows that the material experiences significant transverse deformation under uniaxial stress.

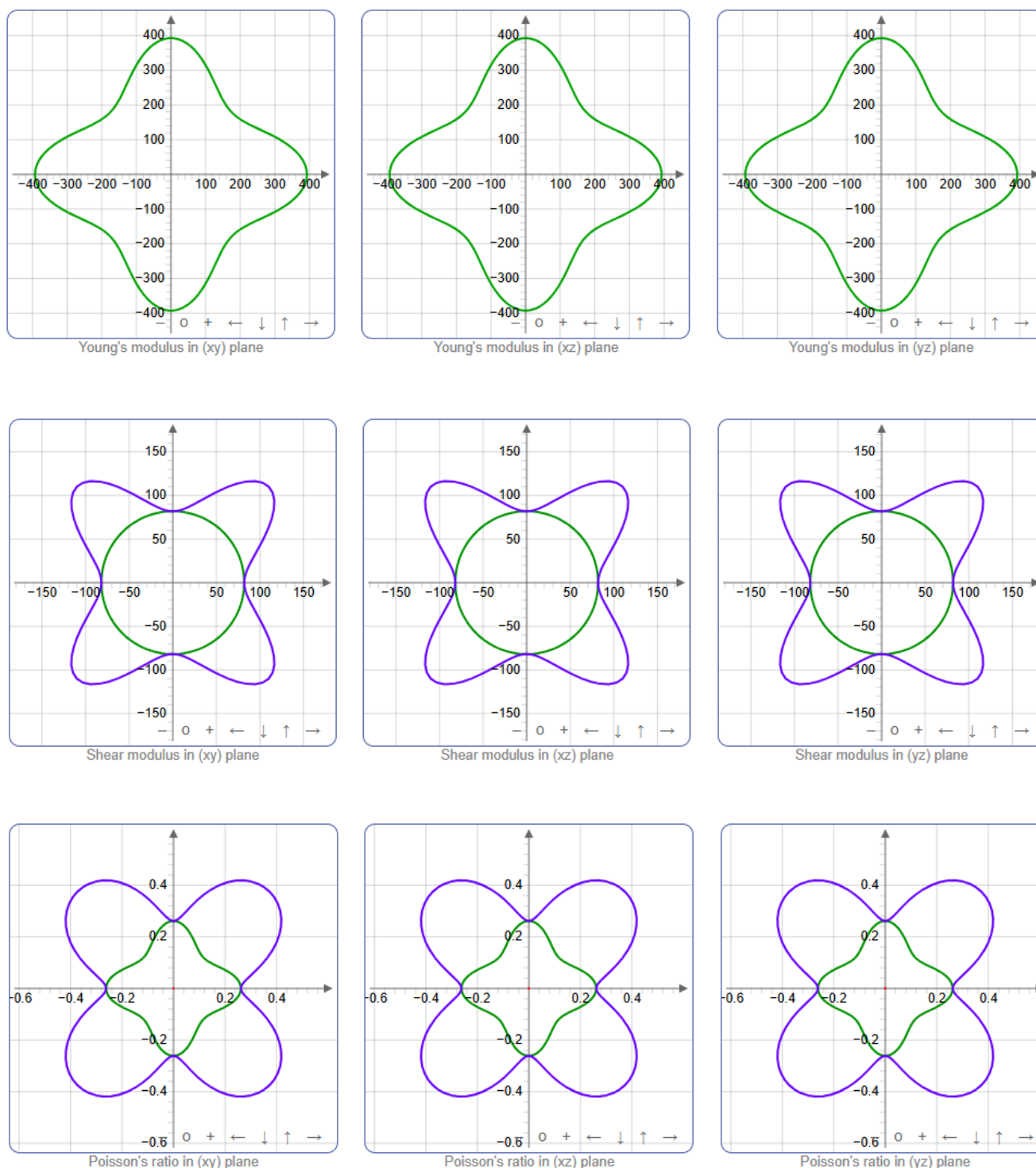


Figure 9. $\text{Cs}_2\text{Ge}_2\text{I}_6$ spatial dependency of the shear, Poisson's ratio and Young's moduli (The highest and lowest values are shown in blue and green, respectively).

Figure 9 shows spatial dependency of the shear, Poisson's ratio and Young's moduli (The highest and lowest values are shown in blue and green, respectively) $\text{Cs}_2\text{Ge}_2\text{I}_6$.

3.3. Electronic Properties

A material's density of states gives basic information about

its electronic behavior, such as whether it is metallic, semi-conducting, or insulating, by describing the number of accessible electronic states per unit energy [33]. The valence band and conduction band are clearly separated in semiconductors, and the DOS shows a limited band gap devoid of electronic states [34]. The intrinsic conductivity of the material depends

on where the Fermi level is in relation to these bands. Therefore, DOS analysis is an essential tool for comprehending charge carrier excitation mechanisms, band gap magnitude, and electrical stability in crystalline solids [35]. The partial density of states offers a more in depth, orbital resolved breakdown of the electronic states, whereas the total DOS provides an overview. By identifying the elements and orbitals that predominate in the valence band maximum (VBM) and conduction band minimum (CBM), the bonding nature and electrical transitions inside the material can be clarified [36].

The examined double perovskites show semiconducting activity with a distinct energy band gap dividing the valence and conduction bands, according to the computed band structures. The VBM and CBM typically occur at distinct k-points, suggesting an indirect band gap nature, a characteristic shared by many halide double perovskites [22]. Halide p orbitals make up the majority of the valence bands close to the Fermi level, with significant hybridization from the metal cation states [37]. The bandwidth and curvature of the valence bands are largely determined by this hybridization. Higher hole effective masses are suggested by relatively flat valence bands seen close to the VBM, which restrict hole mobility [38]. On the other hand, the conduction bands typically exhibit more dispersion close to the CBM, suggesting lower electron effective masses and better electron transport properties. Double perovskite systems frequently exhibit this kind of asymmetry between electron and hole transport, which has significant ramifications for charge carrier dynamics in photovoltaic devices [39].

This section describes the properties obtained under DOS and band structures for the compounds of $\text{Cs}_2\text{Ge}_2\text{Br}_6$, $\text{Cs}_2\text{Ge}_2\text{Cl}_6$ and $\text{Cs}_2\text{Ge}_2\text{I}_6$. The wavelength of the associated energy band gaps was also calculated using Equation (6).

$$\lambda = \frac{hc}{E_g} \quad (6)$$

3.3.1. Density of States and Band Structures for $\text{Cs}_2\text{Ge}_2\text{Br}_6$

This study carried out calculations for the density of states and found that $\text{Cs}_2\text{Ge}_2\text{Br}_6$ was within the properties of semiconductors. With no electronic states at the Fermi level and a distinct energy gap dividing the valence band from the conduction band, the total density of states (DOS) of $\text{Cs}_2\text{Ge}_2\text{Br}_6$ clearly demonstrated a semiconducting character. Figure 10 shows how states were distributed.

$\text{Cs}_2\text{Ge}_2\text{Br}_6$'s DOS profile showed a robust electronic structure with a moderate band gap of 0.980 eV, indicating its promise for energy related and photovoltaic applications. A narrow band gap semiconductor behavior, typical of bromide based double perovskites with heavy halogen components, was revealed by the electronic band structure of $\text{Cs}_2\text{Ge}_2\text{Br}_6$. The PDOS study revealed that Br-s orbitals dominated the deep valence states at -10 eV, implying strongly localised bonding states linked to bromine atoms.

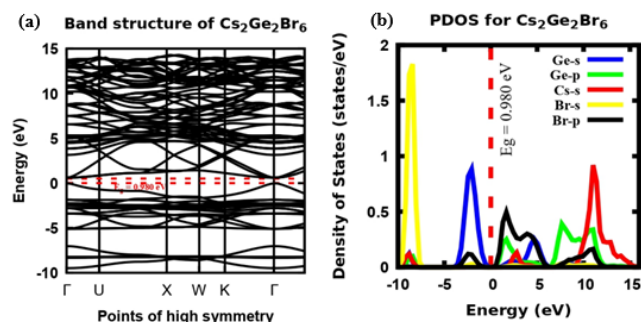


Figure 10. (a) Band structures and (b) distribution of states for $\text{Cs}_2\text{Ge}_2\text{Br}_6$.

Ge-s orbitals with minor hybridisation from Br-p states were found to make up the majority of the contribution in the upper valence band region at the Fermi level. Conversely, Cs-s states contributed at higher energies in the conduction zone, whereas Ge-p states were found make up the majority of the conduction band [40]. Thus, the findings suggested that the electronic transition across the band gap primarily took place from Ge-s states in the valence band to Ge-p states in the conduction band. Additionally, the small contribution of Cs states close to the Fermi level suggested that Cs mostly stabilized the structure rather than directly affecting the compound's electronic transport characteristics. The PDOS results showed that Ge and Br orbital interactions dominate the electrical characteristics of $\text{Cs}_2\text{Ge}_2\text{Br}_6$. This compound falls under near-infrared (NIR) spectrum semiconductor regime due to its comparatively tiny band gap of 0.980 eV, which makes it potentially useful for photovoltaic applications.

The band gap's photon wavelength was computed and found to be;

$$\lambda = \frac{1239.8}{0.980} = 1265.10 \text{ nm}$$

This wavelength is located in the near infrared, suggesting that low energy solar photons outside of the visible spectrum can be efficiently absorbed by $\text{Cs}_2\text{Ge}_2\text{Br}_6$. In terms of structure, the inclusion of Br results in intermediate Ge-Br bond lengths that balance orbital overlap and lattice deformation [41]. $\text{Cs}_2\text{Ge}_2\text{Br}_6$ has electrical characteristics that are advantageous for bottom cell photovoltaic and near infrared photovoltaic applications. Owing to the fact that Cs orbitals are distant from the Fermi level, the presence of cesium as the A-site cation mostly contributes to structural stability and electronic activity [16].

3.3.2. Density of States and Band Structures for $\text{Cs}_2\text{Ge}_2\text{Cl}_6$

The electrical structure and band generation characteristics for $\text{Cs}_2\text{Ge}_2\text{Cl}_6$ were directly revealed by the computed DOS. The lack of states at this reference point verifies that the material has a non metallic character with a distinct band gap [43]. For optoelectronic applications, a well formed semiconductor

gap without mid gap states is indicated by the smooth separation between the valence band maximum and conduction band minimum [44]. A slow but consistent increase in DOS is seen at the conduction band onset, which starts just above 0.5 eV as in Figure 11(b). The Fermi level was located at 0 eV, as shown in Figure 11(b).

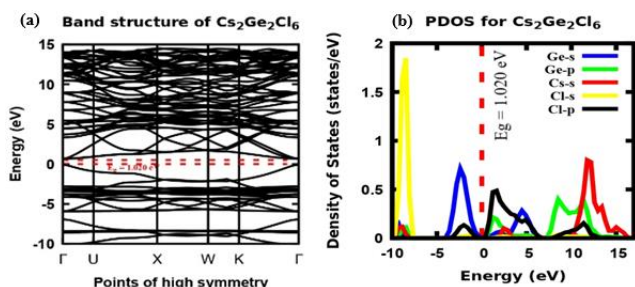


Figure 11. (a) Band structures and (b) density of states for $\text{Cs}_2\text{Ge}_2\text{Cl}_6$.

According to the PDOS analysis, Cl-s orbitals contributed mostly to the deep valence band area noted at -10 eV, suggesting strongly localized states connected to chlorine atoms. The PDOS reveals that the upper valence band near the Fermi level is primarily composed of Ge-s states, with a small contribution from Cl-p states. The overlap of these orbital contributions suggests Ge-s to Cl-p orbital hybridization. Ge-p orbitals were found to make up the majority of the contribution in the conduction band region above the Fermi level, whereas Cl-p orbitals contributed less to the appearance of Cs-s states at comparatively higher energies. As a result, the electrical transition from Ge-s states in the valence band to Ge-p levels in the conduction band primarily took place across the band gap of 1.020 eV. The PDOS results showed that the interaction between Ge and Cl orbitals primarily controlled the electrical characteristics of $\text{Cs}_2\text{Ge}_2\text{Cl}_6$.

The absence of mid gap states and the distinct separation between valence and conduction states indicate that $\text{Cs}_2\text{Ge}_2\text{Cl}_6$ has excellent electronic purity appropriate for semiconducting applications. These features, which enhance their potential for photovoltaic are typical of halide double perovskites with balanced carrier transport properties. [45] did similar research on double perovskite $\text{Cs}_2\text{AgBiBr}_6$. Their finding exhibited a significant density of states. The organization of electronic states with these states were computed using GGA, which reflected the features of the band structures.

Because of the higher electronegativity and smaller orbital size of chlorine, the computed band structure of $\text{Cs}_2\text{Ge}_2\text{Cl}_6$ shows a larger band gap than that of its bromide counterpart. In considering that Cl-p orbitals are more localized than Br-p orbitals, they dominate the valence band and limit its dispersion. The wavelength corresponding to the band gap energy was found to be;

$$\lambda = \frac{1239.8}{1.020} = 1215.50 \text{ nm}$$

The findings from this current study on density of states for $\text{Cs}_2\text{Ge}_2\text{Cl}_6$ were found to be in agreement with literature [46].

1) Density of States and Band structures for $\text{Cs}_2\text{Ge}_2\text{I}_6$

This research carried out calculations on DOS for $\text{Cs}_2\text{Ge}_2\text{I}_6$ and no states existed at the Fermi level. This phenomenon was in line with the electrical properties of vacancy ordered halide double perovskites, which usually show distinct band gaps because the lattice structure lacks B-B connection [47, 48] carried out similar research on vacancy ordered Titanium halide double perovskite and their compounds also showed the same trend, where the electronic gap grew as halide electronegativity decreases. The electronic structure in this current data for $\text{Cs}_2\text{Ge}_2\text{I}_6$ is supported by recent research on lead free halide perovskites, which likewise shows the creation of discrete valence and conduction manifolds dominated by halogen p orbitals and Ge derived antibonding states, respectively [49].

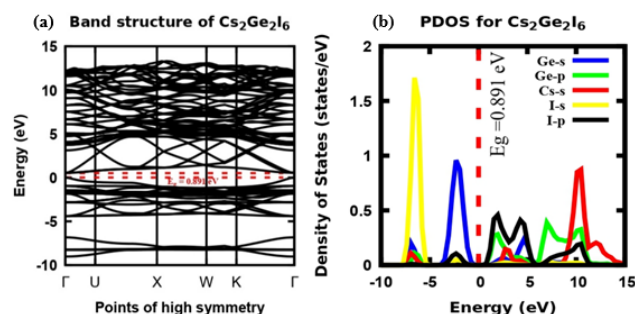


Figure 12. (a) Band structures and (b) Density of states for $\text{Cs}_2\text{Ge}_2\text{I}_6$.

The DOS plot from this current study displayed a comparatively wide range of states and a large peak intensity at -1.1 to 1.1 eV. Because of iodine's greater polarizability and bigger orbital size, iodide-based double perovskites often exhibit considerable hybridization between I-5p orbitals and Ge-4p orbitals, as indicated by this broadening [50]. In halide perovskites containing iodine, where the expanded I-p orbitals interact strongly with core metal cations to produce broad valence bands and enhanced hole mobility, such hybridization has been extensively documented [51]. A clean band gap of 0.891 eV devoid of deep defect levels was shown by the band structures and DOS profile in Figure 12, which displayed no localized states between the valence band maximum and conduction band minimum. Because it reduces non radiative recombination routes and increases charge carrier lifetimes, the lack of mid gap states is especially crucial for photovoltaic applications [44].

The conduction band pattern seen in Figure 12 is in consistent with literature for $\text{Cs}_2\text{Ge}_2\text{I}_6$, which reveals that Ge-s antibonding states dominate the conduction edge and that the band gap narrows with increasing halide atomic size [49]. For photovoltaic applications, balanced hole and electron

transport characteristics are implied by the comparatively wide valence band and continuously rising conduction band DOS [52]. Due to smaller band gaps and higher spin orbit coupling as seen in Figure 12, iodine containing perovskites usually show considerable optical absorption close to the band edge; the DOS features seen here confirm this prediction. Additionally, previous theoretical and practical studies on Ge-I halide perovskites have showed improved light harvesting efficiency and advantageous charge transport, which closely match the electrical structure and band edge clarity seen in this current DOS results [43].

According to the PDOS study, I-s orbitals mostly dominated the deep valence band area between -7 and -9 eV, showing localised bonding states connected to iodine atoms. Ge-s orbitals were found to make up the majority of the contribution in the upper valence band region at the Fermi level, with a small amount of hybridisation from I-p states, indicating covalent contact between Ge and I atoms inside the lattice. Ge-p orbitals primarily contributed to the conduction band minimum in the conduction band region above the Fermi level, whereas I-p orbitals contributed less to the appearance of Cs-s states at higher energy levels. This suggested that the primary electronic transition from Ge-s states in the valence band to Ge-p levels in the conduction band took place across the band gap. The small contribution of Cs orbitals close to the Fermi level indicated that caesium primarily served as a structural stabilising cation rather than having a major impact on the material's electronic transport characteristics. The PDOS results showed that the hybridisation between Ge and I orbitals dominates the electrical structure of Cs₂Ge₂I₆.

A narrow-gap semiconductor behavior, typical of iodine based double perovskites where heavy halogen atoms dominate the electronic environment, was revealed by the electronic band structure of Cs₂Ge₂I₆. The value of band gap obtained for Cs₂Ge₂I₆ is 0.891 eV. According to the computed band structure, Cs₂Ge₂I₆ has an indirect band gap since the valence band maximum (VBM) and conduction band minimum (CBM) are situated at various high symmetry sites in the Brillouin zone. I-5p orbitals, which are spatially extensive and energetically high because of iodine's large atomic size and poor electronegativity, dominate the valence band area. In contrast to their chloride and bromide counterparts, these orbitals hybridize with Ge-4s states to produce a valence band that is comparatively dispersive. Improved hole mobility and reduced hole effective masses are indicated by such dispersion. The conduction band, on the other hand, is primarily produced from Ge-4p states, which display moderate dispersion close to the CBM, indicating that electrons stimulated into the conduction band may have acceptable transport characteristics [53].

The wavelength corresponding to this band gap was calculated and found to be;

$$\lambda = \frac{1239.8}{0.891} = 1382.16 \text{ nm}$$

This wavelength is in the near to short wave infrared range,

suggesting that Cs₂Ge₂I₆ can effectively absorb low energy infrared photons. The material is therefore very appealing for uses like low band gap absorber layers, thermal sensing devices, and infrared photovoltaics. In comparison to its chloride and bromide counterparts, the band gap reduction seen in Cs₂Ge₂I₆ is greatly influenced by the massive iodide anion. A higher valence band edge and a smaller energy gap between the valence and conduction bands result from the weaker Ge-I bonding and enhanced orbital overlap. The band gap is further reduced by changes in band curvature brought on by iodine induced lattice expansion and octahedral distortion [54]. In halide double perovskites, these structural effects demonstrate the close relationship between electrical structure and lattice geometry.

In considering that Cs orbitals are far from the band boundaries, cesium ions occupy the A-site of the perovskite lattice and make very little contribution to the electronic states close to the Fermi level. However, Cs plays an important structural role by affecting octahedral tilting and stabilizing the crystal framework, which indirectly impacts gap magnitude and band dispersion. Effective charge transport depends on continuous Ge-I-Ge routes, which are maintained by the somewhat symmetric environment that Cs promotes [55]. From the standpoint of the device, the small band gap of Cs₂Ge₂I₆ indicates both increased susceptibility to thermal carrier excitation at ambient temperature and increased sensitivity to infrared radiation. The values obtained for energy band gap were 0.980 eV for Cs₂Ge₂Br₆, 1.020 eV for Cs₂Ge₂Cl₆ and 0.891 eV for Cs₂Ge₂I₆. It is observed that the results are in line with the literature when comparing this study's findings with those of other researchers [56].

3.4. Optical Properties

The way a material reacts to electromagnetic radiation, particularly in the ultraviolet, visible, and infrared spectral bands, is described by its optical characteristics [57]. Since these characteristics dictate how light is absorbed, transmitted, reflected, and emitted by a material, knowledge of them is essential to the development of materials for electronic and optoelectronic applications. This knowledge is directly related to electronic structure and device performance [58]. Since the efficiency of devices like solar cells, photodetectors, LEDs, and optical sensors depends on their capacity to absorb sunlight, transform it into charge carriers, and facilitate charge transport, optical behavior is especially important for semiconductor and photovoltaic materials [59]. The dielectric response, arising from the electronic band structure and interband electronic transitions, governs these processes. [42]. The complex dielectric function in Equation 7, describes how a material reacts to an electromagnetic field:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \quad (7)$$

The optical properties of semiconductors are fundamental

in determining their suitability for photovoltaic applications because they govern the interaction between electromagnetic radiation and the material. The absorption coefficient, extinction coefficient and refractive index from this study collectively described the light harvesting capability, optical attenuation and photon confinement of a semiconductor. Based on the calculated optical spectra of the investigated compounds, the noted maximum absorption coefficients were $1.8 \times 10^5 \text{ cm}^{-1}$

¹ for $\text{Cs}_2\text{Ge}_2\text{Cl}_6$, $3.3 \times 10^5 \text{ cm}^{-1}$ for $\text{Cs}_2\text{Ge}_2\text{Br}_6$ and $8.8 \times 10^4 \text{ cm}^{-1}$ for $\text{Cs}_2\text{Ge}_2\text{I}_6$. Similarly, the corresponding maximum extinction coefficients were noted at 0.36, 0.47 and 0.38 for $\text{Cs}_2\text{Ge}_2\text{Cl}_6$, $\text{Cs}_2\text{Ge}_2\text{Br}_6$ and $\text{Cs}_2\text{Ge}_2\text{I}_6$ respectively while the refractive indices were found at 3.4, 3.6 and 3.8 for $\text{Cs}_2\text{Ge}_2\text{Cl}_6$, $\text{Cs}_2\text{Ge}_2\text{Br}_6$ and $\text{Cs}_2\text{Ge}_2\text{I}_6$ respectively. These values were estimated from the calculated optical spectra shown in Figures 13, 14 and 15.

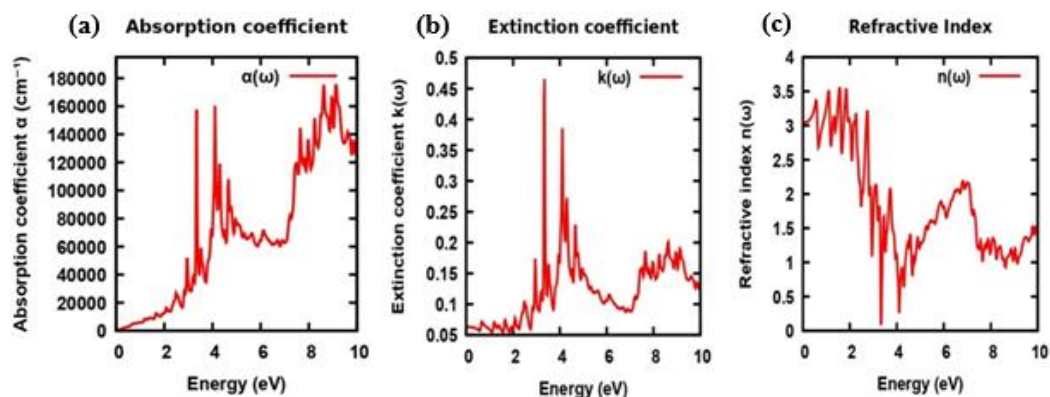


Figure 13. Plots for (a) absorption coefficient, (b) extinction coefficient and (c) refractive index for $\text{Cs}_2\text{Ge}_2\text{Br}_6$.

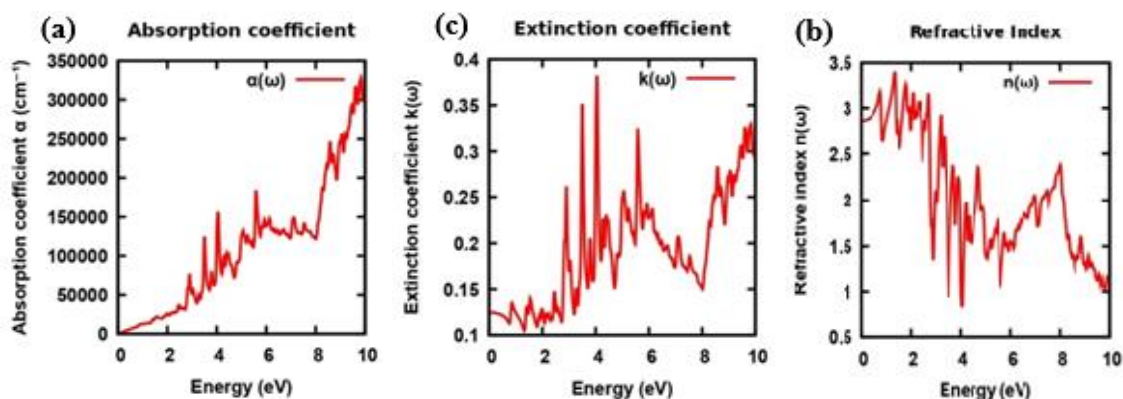


Figure 14. Plots for (a) absorption coefficient, (b) extinction coefficient and (c) refractive index for $\text{Cs}_2\text{Ge}_2\text{Cl}_6$.

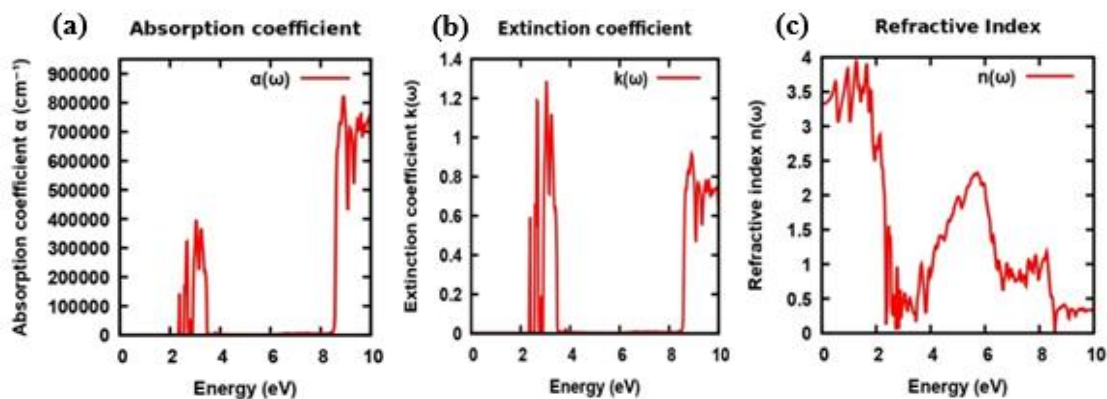


Figure 15. Plots for (a) absorption coefficient, (b) extinction coefficient and (c) refractive index for $\text{Cs}_2\text{Ge}_2\text{I}_6$.

Among the investigated compounds, $\text{Cs}_2\text{Ge}_2\text{Br}_6$ exhibited the highest absorption coefficient, indicating high light harvesting capability and making it the most suitable candidate for thin film solar cells. Although $\text{Cs}_2\text{Ge}_2\text{Cl}_6$ displays a slightly lower absorption coefficient, it still possesses excellent optical absorption in the visible and ultraviolet regions. In contrast, $\text{Cs}_2\text{Ge}_2\text{I}_6$ exhibits the highest extinction coefficient, suggesting stronger attenuation of electromagnetic waves due to enhanced interband electronic transitions associated with its narrower band gap. The relatively lower extinction coefficient of $\text{Cs}_2\text{Ge}_2\text{Br}_6$ indicates efficient photon absorption with reduced optical losses, which is beneficial for charge carrier generation and transport. The calculated refractive indices indicated strong optical polarization and enhanced photon confinement within the absorber layer, thereby increasing the optical path length and improving solar energy conversion efficiency. Similar optical behavior has been reported for other Cs-based double perovskites, including $\text{Cs}_2\text{AgBiBr}_6$ [45], Cs_2TiBr_6 [56] and Cs_2SnI_6 [46].

Abbreviations

CBM	Conduction Band Minimum
CHPC	Centre for High Performance Computing
DFT	Density Functional Theory
GGA	Generalized Gradient Approximation
NSCF	Non-Self-Consistent Field
PAW	Projector Augmented Wave
PBE	Perdew Burke Ernzerhof
PCE	Power Conversion Efficiency
PDOS	Projected Density of States
PSCs	Perovskite Solar Cells
SCF	Self Consistent Field
VBM	Valence Band Maximum

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Author Contributions

Mutava Mutinda Gabriel: Conceptualization, Data curation, Formal Analysis, Investigation, Methodology, Visualization, Writing – original draft

Fidelis Ngugi: Conceptualization, Supervision, Writing – review & editing

Winfred Mueni Mulwa: Formal Analysis, Project administration, Resources, Supervision, Writing – review & editing

Data Availability Statement

The manuscript contain all relevant data.

Conflicts of Interest

The authors declare no conflicts of interest.

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