FIRST-PRINCIPLES INVESTIGATION OF THE STRUCTURAL, MECHANICAL, AND OPTICAL PROPERTIES OF $CsPbI_3$ PEROVSKITE FOR SOLAR CELL APPLICATIONS.

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Abstract. The growing global energy crisis necessitates the search for sustainable and environmentally friendly alternatives to fossil fuels. In this study, the first-principles, density functional theory (DFT) calculations were employed to investigate the structural, electronic, optical, and mechanical properties of the all-inorganic perovskite compound $CsPbI_3$, a promising material for clean energy applications. Using the generalised gradient approximation (GGA-PBE functional) within the Materials Studio Software, the crystal structure was optimized, and the electronic band structure, density of states (DOS), and optical properties were analyzed. The results revealed that $CsPbI_3$ exhibits a suitable bandgap and strong optical absorption, making it a potential candidate for efficient solar cell applications. Mechanical property calculations, including elastic constants, bulk modulus, shear modulus, Young's modulus, and Poisson's ratio, confirmed the material's mechanical stability, satisfying the stability criteria for cubic systems. The material resisted shear deformation and ductile behaviour, as indicated by a bulk-to-shear modulus ratio (B/G) of 2.01 and supportive Pugh's and Poisson's ratios. Furthermore, low reflectance and high optical conductivity suggest excellent optoelectronic performance, while thermodynamic analysis confirmed its stability under operating conditions. Overall, the study provides valuable theoretical insights into the suitability of $CsPbI_3$ perovskite for solar energy harvesting and other energy-related applications, contributing to the advancement of clean and sustainable energy technologies.

1. Introduction

In recent years, the rising energy demand has driven experts to investigate alternatives to fossil fuels. Solar energy emerges as a crucial alternative to conventional fossil fuels, providing a clean and nearly limitless energy source [1]. As a result, considerable endeavors are underway to create affordable and environmentally sustainable technologies that harness the energy spectrum for solar cells and thermoelectric generators [1,2]. The photovoltaic process, along with the Seebeck and Peltier thermal electric conversion processes, is essential and deserves deeper investigation [3]. The primary challenge at present is identifying appropriate materials, with significant investigations carried out to evaluate their energy conversion efficiencies [3,4]. Halide perovskites, defined by the general formula ABX3, are under examination as advanced materials for the efficient capture of solar and thermal energy [3,4].

Inorganic metal halide perovskites show great potential for solar cell applications because of their extended carrier diffusion lengths, straightforward fabrication process, and tunable band gaps. Furthermore, these materials demonstrate exceptional light absorption capabilities and show enhanced chemical and thermal stability relative to other organometallic perovskites, positioning them as promising options for solar cell applications. Improving the photovoltaic and optical characteristics of inorganic solar cells by utilizing tunable perovskite compounds through modifications of A-site or X-site ions and implementing mixed-ion strategies can yield beneficial outcomes [4]. A number of studies have investigated the structural and electronic properties of double perovskites through DFT, yet thorough analyses that combine mechanical and optical evaluations are still scarce. This study utilized first-principles density functional theory (DFT) to thoroughly investigate the structural, mechanical, optical, elastic properties and thermal properties of double perovskites, highlighting their potential for energy conversion and promoting additional exploration in this area.

2. Computational Method

The density functional theory (DFT) calculations were performed using the generalised gradient approximation (GGA) classified by Perdew-Burke-Ernzerhof (PBE) to describe the exchange-correlation functional [5,6]. All calculations were conducted using the Cambridge Serial Total Energy Package (CASTEP) simulation codes on Material Studio of BIOVIA [5,6]. Geometric optimisation was performed by moving the atoms of a molecule to achieve the most stable structure with the lowest possible ground-state energy. The states of the orbitals Cs(d), I (p), and Pb (p) were studied. A cutoff energy of 500 eV was used for the plane-wave basis, and an 8×8×8 Monkhorst-Pack mesh was employed for integration over the irreducible Brillouin zone. Convergence was obtained when the highest force on all the ions was less than 0.01 eV/Å, which implied that the atomic locations and lattice parameters were relaxed.

3. Results and Discussion

3.1. Structural Properties

The structural properties, including lattice constants, bond angles, and unit cell volume, are essential in defining the stability, symmetry, and electronic behavior of perovskite materials such as $CsPbI_3$, which in turn directly affects their photovoltaic and optoelectronic performance. The optimized structural parameters of $CsPbI_3$, derived from density functional theory (DFT), are detailed in Table 1. These parameters are crucial for comprehending its phase stability and informing both theoretical and device-level design.

Table 1: Structural properties of $CsPbI_3$

Parameters	$CsPbI_3$
a (Å)	4.847
b (Å)	10.65
c (Å)	18.03
α (°)	90
β(°)	90
γ (°)	90
Volume($Å^3$)	930

The calculated structural parameters of $CsPbI_3$ are presented in Table 1. The optimized lattice constants are determined to be a = 4.847 Å, b = 10.65 Å, and c = 18.03 Å, with α = β = γ = 90°, signifying an orthorhombic crystal symmetry. The unit cell volume measured is 930.80 $Å^3$. The observed values align with the established structural properties of CsPbI3 in its orthorhombic phase. The considerable b and c parameters indicate the stratified organization of ions in the crystal lattice.

The presence of 90° angles indicates that there is no distortion or tilting present in the perovskite framework. The considerable unit cell volume suggests a roomy lattice, which may enhance ionic mobility and support optoelectronic applications.

3.2. Mechanical Properties

The elastic properties play a crucial role in clarifying the structural stability and stiffness of materials. Mechanical stability serves as a crucial metric for assessing the suitability of a material for various applications. The mechanical properties of solid materials are fundamentally influenced by the elastic constants, which dictate how the crystal responds to external forces that impose strain or stress on its atoms.

Table 2: Calculated Elastic constants and values of bulk, Young's, Shear modulus, Anisotropy and Poisson's ratio.

Parameters	$CsPbI_3$	Stability
C_{11}	22.13	$C_{11} - C_{12} > 0$
C_{12}	10.45	$C_{11} + 2C_{12} > 0$
C_{44}	9.08	$C_{44} > 0$
B(GPa)	12.411	
E(GPa)	15.522	
$\boldsymbol{G_v}$	6.009	
Y	0.29	
A	1.55	
$\boldsymbol{C_{11} - C_{12}}$	11.68	
$\boldsymbol{C_{11} + 2C_{12}}$	43.03	
B/G	2.065	

The mechanical properties of solid materials are fundamentally influenced by the elastic constants, which dictate how a crystal reacts to external forces that impose strain or stress on its atoms [7]. A trio of elastic constants (C_{11}, C_{12}, and C_{46}) is adequate for analyzing the mechanical behavior of any cubic system.

The numerical values of the three independent elastic coefficients, along with the bulk and shear moduli, Pugh ratio, Young's moduli, and Poisson's ratio for cubic, are presented in Table 2. The independent elastic coefficients C_{ij}, bulk modulus (B), shear modulus (G), and Young's modulus (E) are provided in GPa, with the anticipated numerical values for B, G, E, and v computed through Hill's averaging scheme. The data indicate that the material exhibits stiffness and resistance to compression, as shown by a bulk modulus value of 12.411 GPa. Additionally, a Young's modulus of 15.522 GPa suggests that the material is also resistant to shear deformation. The Poisson's ratio is measured at 0.29, suggesting that the longitudinal strain exceeds the transverse strain in this ternary mixture. The calculated values of the independent elastic coefficients listed in Table 2 meet the Born mechanical stability criteria for cubic systems [6] when applied to Equation (1), confirming that cubic is a mechanically stable material.

$$C_{11} - C_{12} > 0\ ,\ C_{11} + 2C_{12} > 0;\ C_{446} > 0 \qquad (1)$$

Table 2 presents an assessment of the material's ductility and brittleness, which are critical factors in cell manufacturing. Pugh's concept states that when the bulk-to-shear modulus (B/G) ratio falls below the critical threshold of 1.75, the material is classified as brittle; if it exceeds this value, it is considered ductile [7,8]. The computed ratio of B/G in Table 1 was determined to be 2.065, exceeding 1.75, which suggests that it is a ductile material based on its metallic characteristics.

1.1 3.3. *Optical Properties*

The optical properties of $CsPbI_3$ were investigated using density functional theory (DFT) to understand its potential for optoelectronic and photovoltaic applications. Figure 2 displays the computed real and imaginary components of these double perovskites' dielectric functions

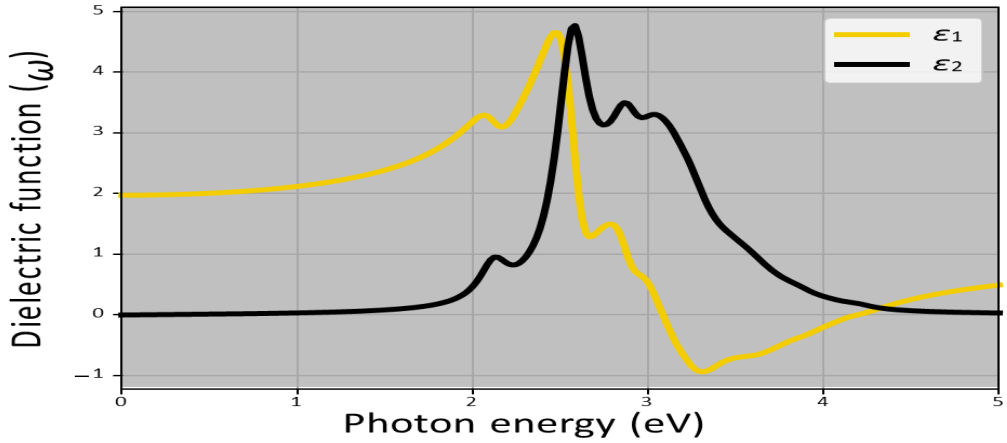

Figure 2: shows the Dielectric function of $CsPbI_3$

Figure 2 displays the dielectric function. In this context, the yellow line represents the real part and the black is the imaginarly part. At zero photon energy, the calculated dielectric function shows that $CsPbI_3$ has a dielectric constant of approximately 2. At higher photon energy, however, the imaginary part peaks at 2.5 eV, indicates enhanced absorption or energy loss as the imaginary part is analogous to the optical absorption [7].

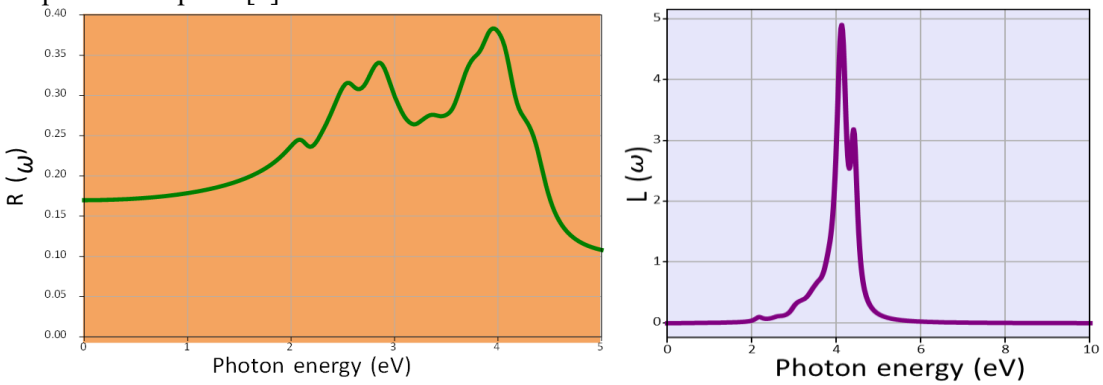

Figure 3: Reflectivity(a) and, Loss function(b), of $CsPbI_3$

Figure 3 illustrates that at a photon energy of 0 eV, the material begins to reflect 17% of the incoming solar radiation from the sun. At the peak, the material reflects 37% of the incoming solar radiation, indicating its efficiency. This suggests a high charge transfer or real conductivity at this photon energy. Figure 3(a) presents the reflectivity spectra as a function of photon energy; the highest peak is observed at 3.8 eV, indicating that perovskites have the potential to function as an outstanding coating material. Furthermore, the peak reflectivity value was observed when the real part of the dielectric function was negative, indicating that the material behaves as metallic within this energy range. The energy loss function characterizes the energy dissipation experienced by a high-velocity electron as it traverses a material. The peaks observed in Figure 3(b) of the loss function spectra indicate the characteristics linked to plasma resonance. The observed resonant energy loss occurs at 4.1 eV. The spectra indicate that the energy of the refractive index is determined by the degree to which light is bent or refracted upon entering a material.

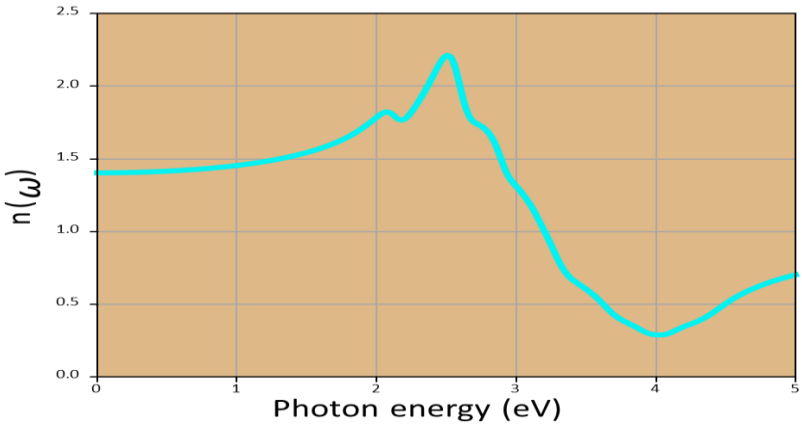

Figure 4: Calculated Optical Refractive of double perovskite $CsPbI_3$

The refractive indices are illustrated in Figure 4 as a function of photon energy. From this data, we established that the static refractive index attained a peak value of 2.3 at 2.5 eV, while at zero photon energy, the static refractive index was approximately 1.40. In this scenario, the refractive index of all the computed compounds exceeds one, as photons experience a delay upon entering a material due to their interactions with electrons.

3.4. Thermal properties

The thermodynamic properties of $CsPbI_3$ were calculated using first-principles density functional theory (DFT), emphasizing the changes in free energy, entropy, and heat capacity (Cv) as functions of temperature. The evaluation of these properties is essential for assessing the thermal stability and energy conversion efficiency of perovskite-based materials in optoelectronic applications.

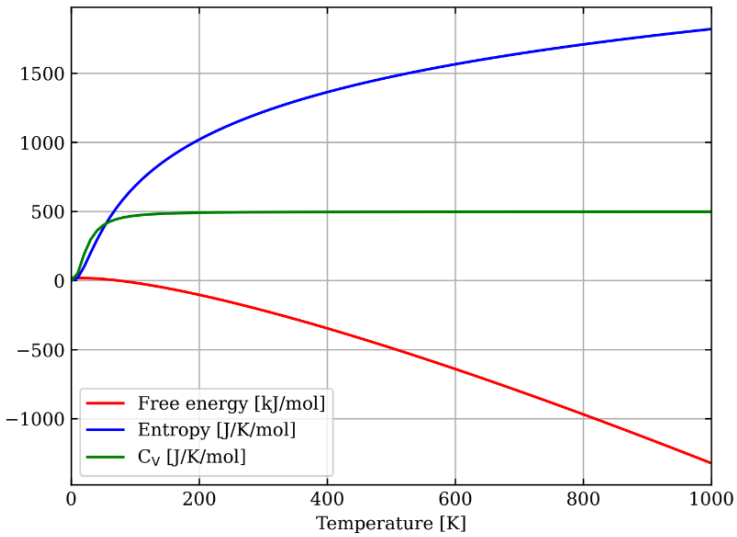

Figure 5: Thermal properties of $CsPbI_3$

The graph illustrates the changes in free energy, entropy, and heat capacity (Cv) of $CsPbI_3$ in relation to temperature, derived from density functional theory (DFT) calculations. As the temperature rises from 0 K to 1000 K, there is a notable decrease in the free energy of $CsPbI_3$, which exemplifies the characteristics of thermodynamically stable materials. This decline suggests that the system attains greater energetic favorability as temperatures increase. The material's entropy shows a consistent increase throughout the temperature range, indicating a rise in disorder within the crystal structure as atomic vibrations become more pronounced. This gradual increase is consistent with core

thermodynamic principles, as entropy is anticipated to rise alongside temperature. Furthermore, the heat capacity (Cv) of $CsPbI_3$ demonstrates a trend of increase with temperature, initially escalating quickly and subsequently nearing a saturation point at approximately 600 K. This behavior indicates that the material attains a threshold in its capacity to absorb further thermal energy for each degree of temperature rise, aligning with the Dulong–Petit law noted in solid-state materials.

4. Conclusion

First-principles calculations were utilized to explore the structural, optical, and mechanical properties of perovskites $CsPbI_3$. The optical characteristics of this material exhibit low reflectance, indicating potential applications in enhancing the overall efficiency of solar cells and various optoelectronic energy devices. The mechanical stability of $CsPbI_3$ indicates that the material is capable of preserving its structure when subjected to mechanical stress. The material exhibited ductility, evidenced by a bulk to shear quotient (B/G) of 2.065, surpassing the critical threshold of 1.75. This inherent ductility was further corroborated by the calculated values of Pugh's ratio and Poisson's ratio. The thermodynamic analysis of $CsPbI_3$ demonstrates its thermal stability and consistent behavior as temperature rises, supported by the observed trends in free energy, entropy, and heat capacity. The characteristics confirm its appropriateness for applications in high-temperature optoelectronics and photovoltaics.

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References

1. Mahmood, Q., Alhossainy, M. H., Rashid, M. S., Flemban, T. H., Althib, H., Alshahrani, T., ... & Laref, A. (2021). First-principles study of lead-free double perovskites Rb2TeX6 (X= Cl, Br, and I) for solar cells and renewable energy. *Materials Science and Engineering: B*, *266*, 115064.
2. Albalawi, H., Nazir, G., Younas, M., Al-Qaisi, S., Ashiq, M. G. B., Alzahrani, J., ... & Ghrib, T. (2022). Study of lead-free vacancy ordered double perovskites Cs2TeX6 (X= Cl, Br, I) for solar cells, and renewable energy. *Physica Scripta*, *97*(9), 095801.
3. Maleka, P. M., Dima, R. S., Ntwaeaborwa, O. M., & Maphanga, R. R. (2022). Study of inorganic lead halide perovskites properties using first-principles density functional theory for photovoltaic and optoelectronic devices. *Materials Today: Proceedings*, *62*, S12-S22.
4. Maleka, P. M., R. S. Dima, O. M. Ntwaeaborwa, and R. R. Maphanga. "Density functional theory study of Br doped $CsPbI_3$ perovskite for photovoltaic and optoelectronic applications." Physica Scripta 98, no. 4 (2023): 045505.
5. Ranwaha, T. S., Maluta, N. E., & Maphanga, R. R. DFT Study of selected croconate dye molecules for application in dye sensitized solar cells.
6. Ranwaha, T., Elegbeleye, I., Maluta, N., & Maphanga, R. (2020). Optical and electronic properties of croconates dye molecules adsorbed on TiO2 brookite nanocluster for dye sensitized solar cells application. *Materials Express*, *10*(11), 1917-1924.
7. Rugut, E. K., Maluta, N. E., Maphanga, R. R., Mapasha, R. E., & Kirui, J. K. (2024). A Density Functional Theory Insight into Structural, Mechanical, and Optical Properties of Rb_2LiTlF_6 Double Perovskite. *Advanced Engineering Materials*, *26*(5), 2300995.
8. Pei, Z., & Zeng, Q. (2023). Density functional theory predictions of the mechanical properties of crystalline materials. *CrystEngComm*.