


Theoretical Computation of Structural Properties and Electronic Band Gap of CsGeCl₃ Perovskite: A DFT-based Simulation

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This study aimed to explore the structural properties and electronic band gap of CsGeCl₃ with cubic structure (Pm-3m space group, No.221). Based on the density functional theory (DFT), all calculations were performed using Ultra Soft Pseudo Potential (USPP) type potential in generalized gradient approach (GGA) with Perdew-Burke-Ernzerhof (PBE) for exchange-correlation function, as implemented in the QUNATUM ESPRESSO code. The primitive cell was used in all calculations for predicting physical properties of solid. The computation results were compared with available literature data. It was found that structural properties of the compound were compatible with other reported results. To understand the nature bond of the chemical bond, the bond lengths of Cs-Cl and Ge-Cl atoms were calculated. The electronic band structure was calculated along the high symmetry points (Γ -X-M-R- Γ) using optimized geometry structure.

1. Introduction

The halide perovskites have recently emerged as potential materials for high efficiency solar cells. Especially lead-free halide perovskites have been widely studied due to toxicity problem of lead. It has been reported that while the efficiency of perovskite based solar cells is 3.8 % in 2009, this rate has increased rapidly to 19.3 % in 2014 [1]. Inorganic metal halide perovskites exhibit excellent physical properties such as optical absorption, tunable band gap, and high charge carrier mobility [2,3]. Generally, lead-free metal halide perovskites exhibit high absorption coefficient and high optical conductivity. In the hybrid organic-inorganic perovskite structure with common formula ABX₃, where A-site is a cation, B is metal ion such as Pb, Sn, Ge, and X is halogen [4]. The ideal crystal structure of ABX₃ is cubic symmetry with space group Pm-3m (No. 221). Recently, lead-free perovskites have been widely studied theoretically because toxicity problems caused by Pb. Sn-based halide perovskite has a susceptibility problem due to tin oxidation. Thus, there are fewer studies that focused on the Sn-based perovskites [5]. Recently, theoretical studies have focused on Ge-based perovskites for their potential use in photovoltaic applications. Roknuzzaman et al. studied the non-toxic

perovskites which Pb is replaced with a non-toxic metal cation in a detailed way using theoretical methods. They focused on the structural, mechanical, electronic, and optical properties of CsBX₃ (B=Ge, Sn and X=Cl, Br, I). It was also reported that CsGeI₃ semiconductor was the best promising lead-free material [6]. The electronic, optical, thermodynamic and lattice dynamical properties of CsGeCl₃ were studied by Erdinç et al using DFT calculations [7]. It is reported that CsGeCl₃ is a wide band gap with 3.67 eV [8-10]. Jong et al. calculated that AGeX₃ (A=Cs, Rb; X=I, Br, Cl) structure [5]. However, most of halide perovskites have not yet been synthesized experimentally. This lack of experimental results makes theoretical approaches important for understanding the nature of these perovskites. Density functional theory (DFT) is one of the quantum mechanical approaches that has important role for understanding geometric and electronic structures of solid. DFT based on the Hohenberg-Kohn-Sham formula aims to solve the Schrödinger equation of the system. In this study, first principles calculations were performed to determine structural parameters and electronic band structure and electronic band gap of Ge-based CsGeI₃ perovskite. To explore the nature bond of the

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Keywords: lead-free perovskite, CsGeCl₃, structural, electronic, DFT

Received: 19 September 2023 | Accepted: 11 October 2023 | Published: 22 December 2023

J.NanoSci.Adv.Mater. 2023, 2 (2), 31

chemical bond in a detailed way, the bond lengths Cs-Cl and Ge-Cl atoms were calculated.

2. Results and Discussion

2.1. Structural properties

The primitive cell of CsGeCl₃ perovskite is depicted in Figure 1. This structure has five atoms in unit cell and its crystal structure has cubic symmetry with the Pm-3m space group, No.221. The lattice parameters and atomic positions of compound were determined by geometric optimization at ambient pressure. While Cs atoms are positioned on the corner of cube, Ge and Cl atoms are positioned body center and face center, respectively. In the primitive cell, fractional coordinates are (0,0,0), (0.5,0.5,0.5) and (0,0.5,0.5) for Cs, Ge and Cl atoms, respectively.

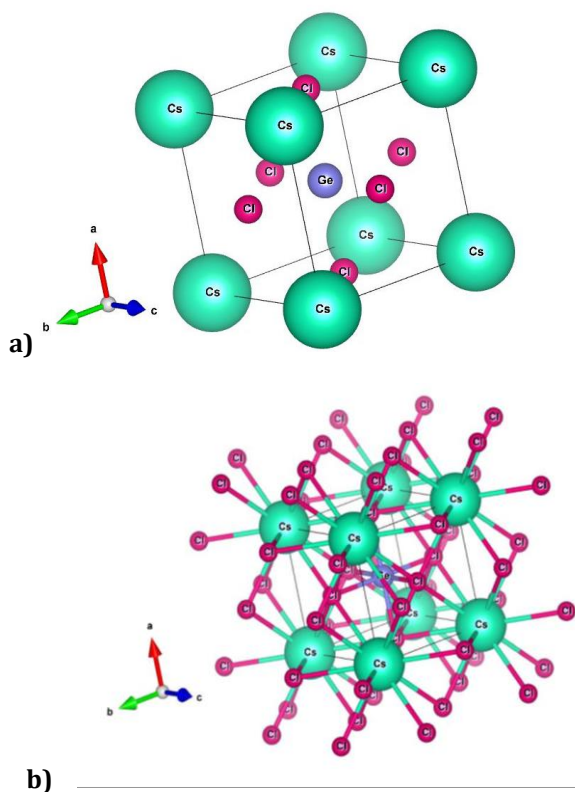


Figure 1. Geometric structure of CsGeCl₃ a) unit cell b) with bonds.

The optimized lattice parameters were calculated as USPP functional and given in Table 1 after achieving full lattice and atomic positions relaxations. Also, the minimum total energy was obtained. As can be seen Table 1, these calculated results are compatible with theoretical and experimental results.

Table 1. The lattice parameters of of CsGeCl₃

a(Å)	V ₀ (Å ³)
5.33*	151.530*
5.33 ^a (Calc., GGA, PBEsol)	-
5.43 ^b (Experimental)	-
5.54 ^c (Calc., GGA, PBE)	-
5.53 ^d (Calc., GGA, PBE)	-

*This study, [5]^a [11]^b [12]^c [13]^d

2.2. Bond lengths

In the ABX₃ halide perovskite structure, A-X and B-X bond type have been characterized by different nature bond [14]. Thus, these bonding between atoms should be separately analyzed. Two kinds of chemical bondings are given in Figure 2.

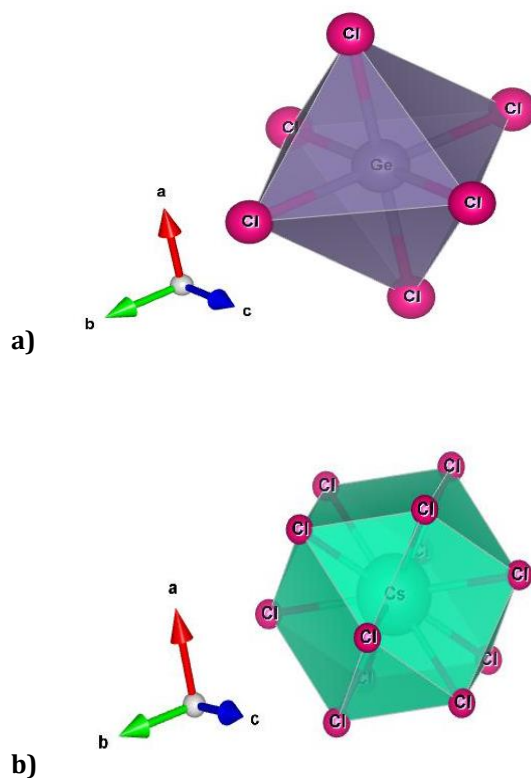


Figure 2. CsCl₁₂ and GeCl₆ chemical bondings

To understand the nature bond of the chemical bonds, compound has a key role determining of physical properties such as electronic, optical, and mechanical. In Figure 2, the occurred chemical bondings causes to form GeCl₆ and CsCl₁₂. Ge metal ion is centered in the distorted octahedron with Ge-Cl chemical bonds. Electric polarization which evolves the separation of charge carriers arises from the octahedral distortion. It means that it allows the photovoltage to exceed the electronic band gap [15, 16]. Table 2 shows that calculated bond lengths.

Table 2. The bond lengths of CsGeCl₃

atom-atom	number of bonds	bond length (Å ^o)
Cs-Cl	12	3.768 [*]
Ge-Cl	6	2.665 [*]
		2.35 ^a

^{*}This study, [17]^a

The calculated bond length of Cs-Cl is larger than Ge-Cl due to electronegativity difference. It can indicate covalent bond existing between Ge metal ion and Cl halogen.

3. Electronic band structure

The electronic band structure has a key role on understanding physical properties such as crystal structures and nature of bond. The electronic band gap was calculated using the primitive cell of CsGeCl₃. Using the optimized structural geometry, the electronic band gap was obtained along the high symmetry points (Γ -X-M-R- Γ), which are shown in Figure 2. The band gap was calculated as a 1.050 eV with USPP functional. In Figure 3, the Fermi level (E_f) was indicated by horizontal black line at 4.65 eV. The valance band maximum and conduction band minimum were occupied at same point. Therefore, direct band gap was formed at R->R point. The valance band and conduction band were illustrated different color, pink and blue, respectively. Table 3 shows calculated band gap with available literature results.

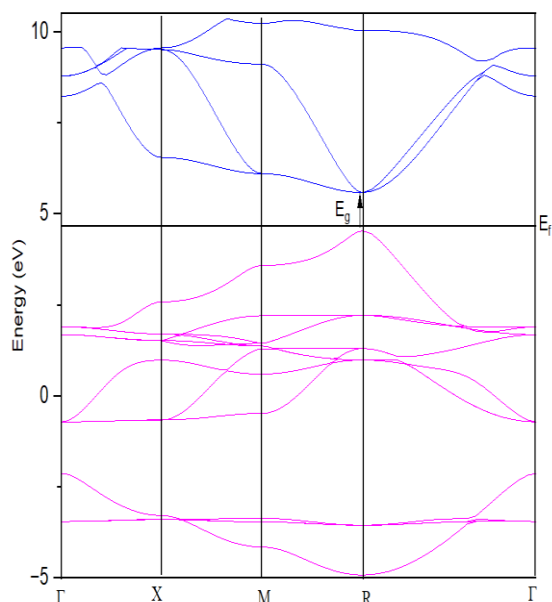


Figure 3. The electronic band structure of CsGeCl₃.

As can be clearly seen in Table 3, the different approximations remarkably influence the electronic band gap value. It is well-known that

Table 3. The band gap of CsGeCl₃

Band gap (eV)	Band type and point
1.050 [*]	direct (R->R)
2.12 ^a (GGA-PBE)	direct (Z->Z)
2.05 ^a (GGA-PBE+SOC)	direct (Z->Z)
2.81 ^a (HSE)	direct (Z->Z)
4.01 ^a (GW)	direct (Z->Z)
2.28 ^b (HSE06+SOC)	direct (Z->Z)
2.13 ^b (GGA-PBEsol)	direct (Z->Z)
2.08 ^b (GGA-PBEsol+SOC)	direct (Z->Z)
3.24 ^b (HSE06)	direct (Z->Z)
2.28 ^b (HSE06+SOC)	direct (Z->Z)
0.997 ^c (GGA-PBE)	direct (R->R)
3.67 ^d (Exp.)	-
1.03 ^e (GGA-PBE)	direct

^{*}This study, [13]^a, [5]^b, [18]^c, [19]^d, [20]^e

hybrid functionals accurately predict the electronic band gap of materials. Hybrid potentials can calculate the band gap close to experimental results. Theoretical studies predicted that band gap of CsGeX₃ semiconductor compounds reveals direct band gap between 0.82 and 7.91 eV [7,8,10,21,22]. These results change depending on used approximations in calculations. Rahaman et al. focused on the investigation of band structure of CsGeCl₃ with pristine and metal doping. They reported the effect of metal doping on the band structure investigation [23]. Jong et al. calculated the electronic band gap of CsGeCl₃ as a 2.13 eV using PBEsol functional. However, this band gap was calculated as 3.24 eV using hybrid functional (HSE) in same study [5]. Han et al. studied CsGeCl₃ electronic and optical properties using GGA-PBE, with/without Spin-orbit coupling (SOC), Hybrid functional and Green (GW) method. They obtained that the electronic band gap reveals direct band gap at Z point for CsGeCl₃ structure for all different methods [13]. Qian et al. performed comprehensive theoretical study on a series of halide perovskites ABX₃ [24]. Idrissi et al. studied inorganic metal halide cubic perovskites CsBX₃ (B=Sn, Ge; X=I, Br, Cl) using DFT calculations. These investigated compounds exhibit semiconductor behavior with direct band gap. They reported that CsXCl₃ (X=Sn, Pb or Ge) can be defined as a promising photovoltaic candidate [25].

3. Conclusion

The halide perovskite materials are defined as a promising candidate for solar cell applications due to optoelectronic properties. To summarize, density functional theory (DFT) was performed to calculate the lattice parameters, bond lengths and electronic band gap of CsGeCl₃ in the cubic structure at ambient pressure to understand its potential use in the solar cell applications. The obtained structural parameters in this study are in good agreement with

theoretical and experimental results. The bond characterization of Cs-Cl and Ge-Cl exhibited different bonding behavior. However, the calculated band gap value (1.050 eV) slightly differs from the other literature data due to different potentials used. However, it was found that semiconductor behavior with direct band gap was as expected from halide perovskite materials group.

4. Method

The structural properties and electronic band gap of CsGeCl₃ with cubic structure was investigated using Ultra Soft Pseudo Potential (USPP) type potential in Generalized Gradient Approach (GGA) with Perdew-Burke-Ernzerhof (PBE) scheme for exchange-correlation function [26]. All calculations were performed based on Density Functional Theory (DFT) as implemented in the QUANTUM ESPRESSO code [27]. Firstly, cut-off energy and Monkhorst-Pack [28] kPoints sample values were determined by optimizing. The cut-off energy and kPoints convergence were determined at 55 Ry and 8x8x8. The convergence criterion was set at 10⁻⁸ Ry during convergence calculations. Based on the geometrical optimization calculations, the lattice parameters and relaxation atomic positions were obtained algorithm. Using these optimized parameters, electronic band structure was calculated and plotted. The VESTA [29] program was used to visualize and calculate the bond lengths of compound.

Acknowledgements

"Not applicable"

Authors' contributions:

Merve Özcan: Conceptualization, Methodology, Visualization, Investigation, Computation, Validation, Writing-original draft.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

[1] Yin W-J., Yang J-H., Kang J., Yan Y., Wei S-H. Halide perovskite materials for solar cells: a theoretical review. *Journal of Materials Chemistry A*, **3**, 8926-8942 (2015).

[2] Zhang W., Eperon G., Snaith H. J. Meta halide perovskites for energy applications. *Nature Energy* **1**(6), 16048 (2016).

[3] Yin W-J., Shi T., Yan Y. Unique properties of halide perovskites as possible origins of the superipr solar cell performance. *Advanced Materials* **26** (27), 4653-4658 (2014).

[4] Schileo G., Grancini G. Halide perovskites: current issues and new strategies to push material and device stability. *Jphys Energy* **2**, 021005 (2020).

[5] Jong U-G., Yu C-J., Kye Y-H., Choe Y-G., Hao W., Li S. First-principles study on structural, electronic, and optical properties of inorganic Ge-based halide perovskites. *Inorganic Chemistry* **58** (7), 4134-4140 (2019).

[6] Roknuzzaman Md., Ostrikov K. K., Wang H., Du A., Tesfamichael T. Towards lead-free perovskite photovoltaics and optoelectronics by ab-initio simulations. *Scientific Reports* **7** (1), 14025 (2017).

[7] Erdinç B., Secuka M. N., Aycibina M., Gülebaganb S. E., Doğan E. K., Akkusa H. Ab-initio study of CsGeCl₃ compound in paraelectric and ferroelectric phases. *Ferroelectrics* **494** (1), 138-149 (2016).

[8] Seo D. K., Gupta N., Whangbo M.H., Hillebrecht H., Thiele G. Pressure-induced changes in the structure and band gap of CsGeX₃ (X=Cl, Br) studied by electronic band structure calculations. *Inorganic Chemistry* **37** (3), 407-410 (1998).

[9] Huang D., Zhao Y-J., Ju Z-P., Gan L-Y., Chen X-M., Li C-S, Yao C-M., Guo J. First-principles prediction of a promising p-type transparent conductive material CsGeCl₃. *Applied Physics Express* **7** (4), 041202 (2014).

[10] Tang L-C., Chang Y-C., Huang J. Y., Lee M-H., Chang C-S. First principles calculations of linear and second-order optical responses in rhombohedrally distorted perovskite ternary halides, CsGeX₃ (X=Cl, Br, and I). *Japanese Journal of Applied Physics* **48**(11R), 112402 (2009).

[11] Krishnamoorthy T., Ding H., Yan C., Leong W. L., Baikie T., Zhang Z., Sherburne M., Li S., Asta M., Mathews N., Mhaisalkar S. G. Lead-free germanium iodide perovskite materials for photovoltaic applications. *Journal of Materials Chemistry A*, **3**, 23829-23832 (2015).

[12] Walters G., Sargent E. H. Electro-optic response in germanium halide perovskites. *The Journal of Physical Chemistry Letters* **9** (5), 1018-1027 (2018).

[13] Han N. T., Dien V. K., Lin M-F. Electronic and optical properties of CsGeX₃ (X=Cl, Br, and I) compounds. *ACS Omega* **7**, 25210-25218 (2022).

[14] Wuttig M., Schön C-F., Schumacher M., Robertson J., Golub P., Bousquet E., Gatti C., Raty J-Y. Halide perovskites: Advanced photovoltaic materials empowered by a unique bonding mechanism. *Advanced Functional Materials* **32** (2) 2110166 (2021).

[15] Zhao Z., Li Z., Zou Z. Electronic structure, and optical properties of monoclinic clinobisvanite BiVO₄. *Physical Chemistry Chemical Physics* **13**, 4746-4753 (2011).

[16] Inoue Y., Kubokawa T., Sato K. Photocatalytic activity of alkali-metal titanates combined with ruthenium in the decomposition of water. *The Journal of Physical Chemistry*, **95**(10), 4059-4063 (1991).

[17] Winkler B. Pressure-induced change of the stereochemical activity a lone electron pair. *The Journal of Chemical Physics* **108** (13) 5506-5509 (1997).

[18] Nik Y. R., Reyhani A., Farjami-Shayesteh S., Mortazavi S. Z. Photocurrent enhancement of hybrid perovskite CsGeBr₃ assisted two-dimensional WS₂ nano-flakes based on electron-hole mobility improvement. *Optical Materials* **112**, 110754 (2021).

[19] Tag L-C., Chang Y-C., Huang J-Y., Lee M-H, Chang C-S. First principles calculations of linear and second-order optical responses in rhombohedrally distorted perovskite ternary halides, CsGeX₃ (X=Cl, Br and I). *Japanese Journal of Applied Physics* **48**, 112403 (2009).

[20] Dias A. C., Lima M. P., Silva J. L. F. Role of structural phases and octahedra distortions in the optoelectronic and excitonic properties of CsGeX₃ (X=Cl, Br, I) perovskites. *The Journal of Physical Chemistry* **125** (35), 19142-19155 (2021).

[21] Brik M. G. Comparative first-principles calculations of electronic, optical, and elastic anisotropy properties of CsXBr₃ (X=Ca, Ge,Sn) crystals. *Solid State Communications* **151**, 1733-1738 (2011).

[22] Körbel S., Marques M. A. L., Botti S. Stability and electronic properties of new inorganic perovskites from high throughput: Ab initio calculations. *Journal of Materials Chemistry* **4**, 3157-3167 (2016).

[23] Rahaman Md. Z., Hossain A. K. M. A. Effect of metal doping on the visible light absorption, electronic structure and mechanical properties of non-toxic metal halide CsGeCl₃. *RSC Advances* **8**, 33010 (2018).

[24] Qian J., Xu B., Tian W. A comprehensive theoretical study of halide perovskites ABX₃. *Organic Electronics* **37**, 61-73 (2016).

[25] Idrissi S., Ziti S., Labrim H., Bahmad L. Band gaps of the solar perovskites photovoltaic CsXCl₃ (X=Sn, Pb or Ge). *Materials Science in Semiconductor Processing* **122**, 10548 (2021).

[26] Perdew J. P., Burke K., Ernzerhof M. Generalized Gradient Approximation Made Simple. *Physical review Letters* **78**, 1396 (1996).

[27] Giannozzi P., Baroni S., Bonini N., Calandra M. Car R. et al. QUANTUM ESPRESSO: a modular and open-source software project for quantum-simulations of materials. *Journal of Physics: Condensed Matter* **21**(39), 395502 (2009).

[28] Monkhorst H. J., Pack J. D. Special points for Brillouin-zone integrations. *Physical Review B* **13**, 5188 (1976).

[29] Momma K. And Izumi F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *Journal of Applied Crystallography* **44**, 1272-1276 (2011).