Physics of semiconductor devices & renewable energies journal

Vol. 01 n. 01 (2023) ; ISSN 2992-040X
Journal homepage: www.psdrej.com

Theoretical insights into the structural and optoelectronic properties of the ternary cesium tetrafluoridobromate semiconductor $CsBrF_4$

Ishak Mebarkia * and Aïssa Manallah

Applied Optics Laboratory, Institute of Optics and Precision Mechanics, University of Setif 1, 19000, Setif, Algeria; aissa.manallah@univ-setif.dz
*Corresponding author *Email: ishak.mebarkia@gmail.com or ishak.mebarkia@univ-setif.dz*

Abstract

This work deals with the first theoretical study of structural, electronic, and optical properties of $CsBrF_4$ ternary compound by using first-principle calculations. The calculated structural parameters and atomic positions are in accordance with the experimental ones declared in the literature. The obtained electronic properties signalize that this compound is a semiconductor material with a direct energy band gap. According to the investigated optical properties, the vast optical absorption range in the ultraviolet region indicates that $CsBrF_4$ semiconductor could be useful for specific applications in ultraviolet optoelectronic devices; consequently, this theoretical study is the potential to support future experimental research.

Keywords: *first-principle calculations; structural properties; optoelectronic properties; Cesium tetrafluoridobromate; $CsBrF_4$ compound; semiconductor material*

1. Introduction

The ternary tetrafluoridobromates of alkali metals are a motivating category belonging to the fluoride single crystals family which is favorable for the optoelectronic technologies, owing to their wide ultraviolet optical absorption domain, large band gaps, and lower refractive indices compared to those of oxides [1]. These ternary compounds possess a general formula of $ABrF_4$, where A signifies some elements of group I from the periodic table such as Na, K, Rb and Cs.

Over the past century, several experimental researches have been performed to determine the crystal structure of $ABrF_4$ (A=Na, K, Rb, and Cs) ternary compounds, but their structures are still vague [2]. During the late years of this century, many researchers have been agreeing that $NaBrF_4$, $KBrF_4$ and $RbBrF_4$ crystallize in tetragonal space group type I4/mcm (No. 140) [3–5]. While $CsBrF_4$ crystallizes in orthorhombic structure space group type Immm (No. 71), where Ivlev et al. (2013) [6] executed the synthesis of $CsBrF_4$ crystal using powder X-ray diffraction data process, whereas Malin et al. (2020) [7] has been done the redetermination of this crystal structure using single-crystal X-ray diffraction data to improve the results of the fractional coordinates of the atoms and the anisotropic displacement parameters with high precision.

Since there is no research work reporting on the fundamental physical properties of the alkali metal tetrafluoridobromate materials, we carried out recently a theoretical study to foresee the structural, mechanical, electronic, and optical properties of the alkali metal tetrafluoridobromates that crystallize in tetragonal structure ($NaBrF_4$, $KBrF_4$, and $RbBrF_4$) [8].

Whereas until now neither experimental nor theoretical works were performed on the physical properties of the cesium tetrafluoridobromate $CsBrF_4$ ternary compound, which motivates us to remove the theoretical lacking in the present work and investigate its structural, electronic, and optical properties using ab-initio methods within the framework of density functional theory (DFT).

The rest of the present paper is orderly as follows: section 2 describes the used calculation methods. Thereafter, section 3 presents and discusses our obtained results of the total energy first-principles calculations. Finally, Section 4 summarizes the results of this work and draws conclusion.

2. Methods

The first-principle calculations of the optoelectronic properties were carried out within the framework of the density functional theory (DFT), using the planewave pseudopotential (PP-PW) method as implemented in Cambridge Serial Total Energy Package (CASTEP) code. To treat the electronic exchange potential, the generalized gradient approximation (GGA) was used with the Perdew-Burke-Ernzerhof in solids (PBEsol) exchange correlation function. The pseudoatomic computations were performed as the following valence states: $6s^1$ for Cs, $4s^2$ $4p^5$ for Br and $2s^2$ $2p^5$ for F. The cut-off energy of 60 Ry is taken for the plane-wave basis set, and a mesh of 4×3×2 special k-points corresponding to 4 irreducible points in the first Brillouin zone is used.

3. Results

3.1. Structural properties

At ambient conditions, $CsBrF_4$ crystallizes in the orthorhombic structure, space group Immm (No. 71). As shown in Figure 1, the conventional cell contains four formula units (Z = 4) in which the Cesium atom “Cs” located at 4i (0.5, 0.5, z_{CS}), the Bromine atoms “Br1” at 2d (0.5, 0, 0.5), “Br2” at 2b (0.5, 0, 0), and the Fluorine atoms “F1” at 4j (0.5, 0, z_{F1}), “F2” at 8l (0.5, y_{F2}, z_{F2}) and “F3” at 4g (0.5, y_{F3}, 0.5) Wyckoff sites; z_{CS} is the internal z-coordinate of the Cesium atom, whereas z_{F1}, y_{F2}, z_{F2} and y_{F3} correspond to the indicating internal coordinates of the Fluorine atoms.

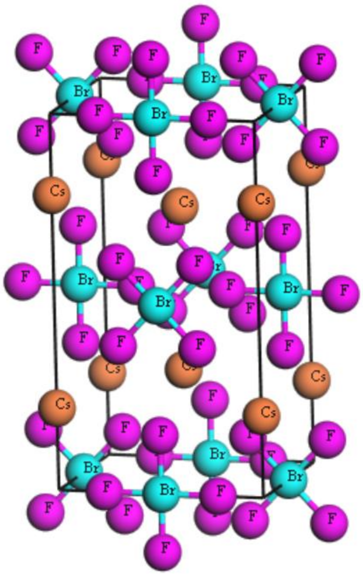


Figure 1: The conventional cell of $CsBrF_4$ ternary compound

After building the initial crystal structure based on the experimental parameters, the relaxation of both ratios b/a and c/a provides the equilibrium volume, and the forces minimization predicts the atomic positions. Table 1 mentions the calculated equilibrium structural parameters include the lattice constants (a, b and c) and the internal coordinates z_{CS}, z_{F1}, y_{F2}, z_{F2} and y_{F3} for $CsBrF_4$ ternary compound using GGA PBE-sol approximation alongside with the available experimental data to make the comparison.

Table 1: The equilibrium lattice constants a, b and c (in Å) and the internal coordinates z_{CS}, z_{F1}, y_{F2}, z_{F2} and y_{F3} for $CsBrF_4$ ternary compound

	a	**b**	**c**	z_{CS}	z_{F1}	y_{F2}	z_{F2}	y_{F3}
calc.	5.6296	6.9018	12.2901	0.71648	0.34304	0.19348	0.11244	0.27773
Expt. [2]	9.828	9.828	7.166	-	-	-	-	-
Expt. [6]	5.6413	6.8312	12.2687	-	-	-	-	-
Expt. [7]	5.5075	6.7890	12.2572	0.71714	0.34482	0.19339	0.11100	0.27770

We can notice the accordance between our calculated values of the equilibrium structural parameters and the latest experimental ones obtained by single crystal x-ray diffraction data, where the highest relative deviation (2.22%) confirms the reliability of our performed calculations. We note also the absence of any theoretical data on structural properties of $CsBrF_4$ except some values of interatomic distances and angles [6].

3.2. Electronic properties

The electronic band structure along the Brillouin zone high symmetry lines is shown in Figure 2 alongside the total density of states (Total DOS) of $CsBrF_4$ ternary compound, as well as the density of states of each separate element Cs, Br and F. The Fermi level E_f positioned at 0 eV and indicated by the horizontal dashed line.

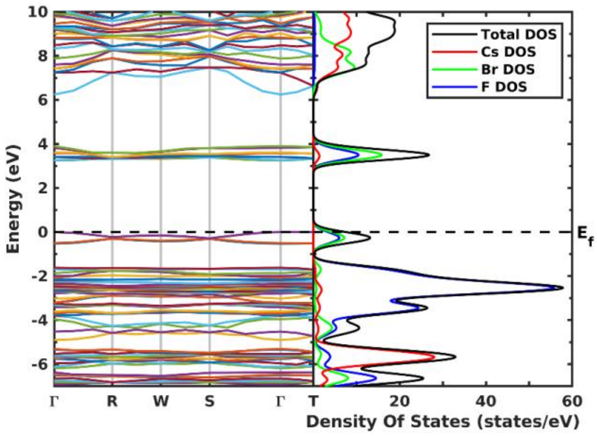


Figure 2: The band structure and the density of states for $CsBrF_4$ ternary compounds.

The calculated value of the energy gap is 3.246 eV, which gives $CsBrF_4$ the property to become a semiconductor material with a wide band gap. Furthermore, it is clear from the band structure shape of the herein studied compound that it has a direct band gap, owing to its valence band maximum (VBM) and its conduction band minimum (CBM) are situated at Γ point.

According to the plotted densities of states, we can confirm that the lower part of the valence band situated from -7 eV to -1 eV consists mainly of Cs and F like states, whereas the VBM originates only from Br and F states. On the other hand, the CBM dominated by the states of Br and F elements with a small contribution of the states of Cs, while the states of Cs and Br contribute to the upper part of the conduction band.

3.3. Optical properties

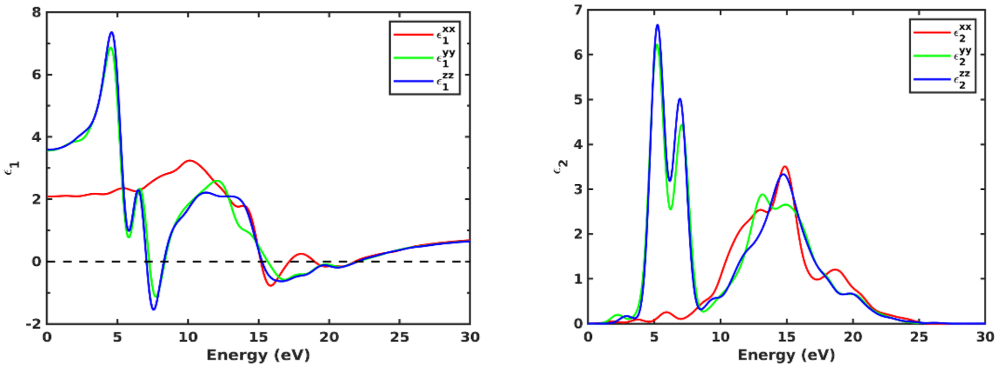
The main optical parameters such as the refractive index n and the absorption coefficient α that describe the optical behavior of the material when it interacts with an external electromagnetic field can be computed from the dielectric permittivity ε, which is a complex function depends of the angular frequency ω of the applied electric field, given as:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\,\varepsilon_2(\omega) \qquad (1)$$

Where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are respectively the real part and the imaginary part of the dielectric function. The Kramers-Kronig relation employed to estimate $\varepsilon_1(\omega)$ from $\varepsilon_2(\omega)$ using the principal part of the Cauchy integral P as follows:

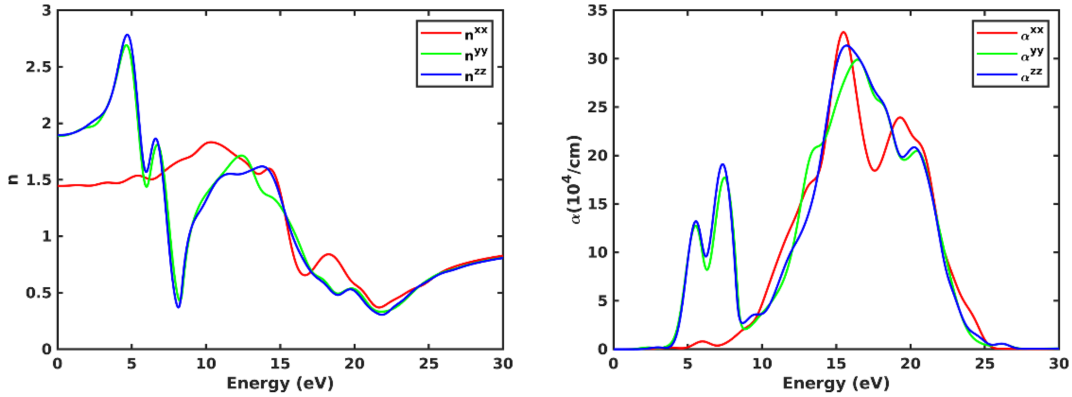
$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^{+\infty} \frac{\omega'\varepsilon_2(\omega')}{\omega'^2 - \omega^2}\, d\omega' \qquad (2)$$

As $CsBrF_4$ ternary compound crystallizes in the orthorhombic structure, the optical spectra of the dielectric function $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are plotted in Figure 3. Furthermore, the refractive index $n(\omega)$ and the absorption coefficient $\alpha(\omega)$ are plotted in Figure 4 for three components indicating by the superscripts *xx*, *yy* and *zz*, which concerning the polarization of the applied electric field along the *x*, *y* and *z* directions, respectively.



(a) (b)

Figure 3: The dielectric function spectra of CsBrF$_4$ ternary compound (**a**) The real part spectrum; (**b**) The imaginary part spectrum



(a) (b)

Figure 4: The optical spectra of CsBrF$_4$ ternary compound (**a**) The refractive index profile; (**b**) The absorption spectrum.

It is clear from the different spectra that the polarized components are not identical when the energy less than 20 eV, indicating that the CsBrF$_4$ material having an optical anisotropy behavior in this energy region.

According to the spectra of the real part $\varepsilon_1(\omega)$ (called also the dispersive part) we can affirm that the herein studied compound shows a Drude like behavior, which ε_1 crosses the zero frequency and represents the dielectric response to a static electric field. The calculated values of the zero-frequency limit for the different polarized components ($\varepsilon_1^{xx}(0)$, $\varepsilon_1^{yy}(0)$, and $\varepsilon_1^{zz}(0)$) are mentioned in Table 2. Furthermore, we can notice that $\varepsilon_1^{zz}(\omega)$ is the dominant component owing to its prominent peak located at about 4.6 eV.

Table 2: The calculated values of the static dielectric constant $\varepsilon_1(0)$, the energy values (in eV) correspond to the maximum peaks of $\varepsilon_2(\omega)$, and the static refractive index $n(0)$.

$\boldsymbol{\varepsilon_1^{xx}(0)}$	$\boldsymbol{\varepsilon_1^{yy}(0)}$	$\boldsymbol{\varepsilon_1^{zz}(0)}$	$\boldsymbol{\varepsilon_2^{yy}(\omega)}$	$\boldsymbol{\varepsilon_2^{zz}(\omega)}$	$\boldsymbol{n^{xx}(0)}$	$\boldsymbol{n^{yy}(0)}$	$\boldsymbol{n^{zz}(0)}$

2.09	3.55	3.59	5.21	5.25	1.455	1.88	1.89

As shown in Figure 4, the refractive index profile $n(\omega)$ takes the shape of the dispersive part spectrum $\varepsilon_1(\omega)$, where $n^{zz}(\omega)$ is the dominant component of the refractive index that possess a significant peak situated at about 4.7 eV. Moreover, the obtained values of the static refractive index for the different polarized components ($n^{xx}(0)$, $n^{yy}(0)$, and $n^{zz}(0)$) are mentioned in Table 2, which are close to the values obtained by the following semi-empirical relation:

$$n(0)=\sqrt{\varepsilon_1(0)} \tag{3}$$

These consequences confirm the reliability of the obtained results for $CsBrF_4$ ternary compound.

The imaginary part of the dielectric function $\varepsilon_2(\omega)$ (called also the absorptive part) shows an anisotropy between its polarized components, where $\varepsilon_2^{yy}(\omega)$ and $\varepsilon_2^{zz}(\omega)$ have prominent peaks at the lower energy region, whereas there is no peak in this energy region for $\varepsilon_2^{xx}(\omega)$. The energy values correspond to these peaks mentioned in Table 2, which principally originate from the optical transition between the highest occupied valence band and the lowest unoccupied conduction band.

As mentioned in Figure 4, the absorption profile $\alpha(\omega)$ takes the shape of the absorptive part spectrum $\varepsilon_2(\omega)$, where represents the maximum absorbance in the ultraviolet (UV) optical range, which the first main peak located at about 5.5 eV, signifies that this ternary compound can be used for producing specified UV optoelectronic devices. Furthermore, the absorption threshold situated at 3.25 eV. These results confirm the reliability of the obtained electronic properties results for this semiconductor compound with an energy gap of 3.246 eV.

Since there are no experimental or theoretical investigations of the optoelectronic properties for $CsBrF_4$ ternary compound. Our results can be considered as a source for future research works.

4. Conclusion

In this study, the optoelectronic properties of $CsBrF_4$ ternary compound were investigated in details using the pseudopotential planewave method within the generalized gradient approximation. The obtained results can be summarized as follow:

- The results of the equilibrium structural parameters are in good agreement with the experimental ones.
- Based on the results of electronic properties,

it can be concluded that $CsBrF_4$ ternary compound is a semiconductor material with direct band gap.

- The outcome of our investigation in the optical properties suggests that $CsBrF_4$ could be useful material for specific applications in UV optoelectronic devices owing to its wide absorption in the UV region.

Author Contributions: I. M.: visualization, methodology, software, investigation, data curation, writing—original draft preparation. A. M.: validation, supervision. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Stevenson, A.J.; Serier-Brault, H.; Gredin, P.; Mortier, M. Fluoride Materials for Optical Applications: Single Crystals, Ceramics, Glasses, and Glass–Ceramics. *J. Fluor. Chem.* **2011**, *132*, 1165–1173, doi:10.1016/J.JFLUCHEM.2011.07.017.
2. Popov, A.I.; Kiselev, Y.M.; Sukhoverkhov, V.F.; Chumaevskij, N.A.; Krasnyanskaya, O.A.; Sadikova, A.T. Investigation of Thermal Stability of Alkali Metal Tetrafluorobromates (3). *Zh. Neorg. Khim.;* **1987**, *32:5*.
3. Ivlev, S.I.; Ostvald, R. V.; Kraus, F. A New Look at NaBrF4: The Most BrF3-Rich Tetrafluoridobromate(III) by Mass. *Monatshefte fur Chemie* **2016**, *147*, 1661–1668, doi:10.1007/s00706-016-1799-2.
4. Ivlev, S.I.; Kraus, F. Redetermination of the Crystal Structure of K[BrF 4] from Single-Crystal X-Ray Diffraction Data . *IUCrData* **2018**, *3*, doi:10.1107/s2414314618006466.
5. Malin, A. V.; Ivlev, S.I.; Ostvald, R. V.; Kraus, F. Rubidium Tetrafluoridobromate(III): Redetermination of the Crystal Structure from Single-Crystal X-Ray Diffraction Data. *IUCrData* **2019**, *4*, doi:10.1107/s2414314619015955.
6. Ivlev, S.; Woidy, P.; Sobolev, V.; Gerin, I.; Ostvald, R.; Kraus, F. On Tetrafluorobromates(III): Crystal Structures of the Dibromate CsBr 2F7 and the Monobromate CsBrF4. *Zeitschrift fur Anorg. und Allg. Chemie* **2013**, *639*, 2846–2850, doi:10.1002/zaac.201300290.
7. Malin, A. V.; Ivlev, S.I.; Ostvald, R. V.; Kraus, F. Redetermination of the Crystal Structure of Caesium Tetrafluoridobromate(III) from Single-Crystal X-Ray Diffraction Data. *IUCrData* **2020**, *5*, 3–8, doi:10.1107/s2414314620001145.
8. Mebarkia, I.; Manallah, A.; Belghit, R. The First Foreseen of Structural, Mechanical, Electronic and Optical Properties of Novel Alkali Metal Tetrafluoridobromate ABrF4 (A=Na, K and Rb). *Phys. B Condens. Matter* **2022**, *624*, 413450, doi:10.1016/j.physb.2021.413450.