OPTOELECTRONIC STUDY OF DOUBLE PEROVSKITE Rb₂SnBr₆: A FIRST PRINCIPLES CALCULATIONS

MD. ABDUR RAZZAQ ¹, TARIKUL ISLAM ²

ABSTRACT

The aim of this research work is to investigate the structural, mechanical, electronic and optical properties of double perovskite Rb₂SnBr₆ by density functional theory (DFT) calculations. The calculated lattice parameter is in sensible agreement with the on the market experimental information. From Paugh’s ductility index (B/G), it shows that Rb₂SnBr₆ is brittle at ambient conditions. The Zener anisotropy factor confirms the anisotropic nature of this compound. The calculated energy band structures indicate that Rb₂SnBr₆ is a direct band gap semiconductor, with the band gap of 1.228 eV using PBE potentials. In this work, the optical properties such as dielectric constants, refractive index, conductivity, extinction coefficient, loss function, and reflectivity have been studied and reported for radiation up to 20 eV. It is found that the reflectivity is about 50% in the ultraviolet (UV) region regions up to ~11 eV of incident radiation.

Keywords: Elastic anisotropy, Electronic properties, First principles study, Optical properties, Rb₂SnBr₆.

1. INTRODUCTION

In recent years, the Organic–inorganic halide perovskites have fascinated significant attention to the researcher due to their dynamic properties such as high optical absorption potential low-cost, tunable band gap, manufacturability and high conversion efficiency for the photovoltaic applications [1–3]. In the visible energy range the materials, MAPbX₃ (MA = CH₃NH₃, X = Br, I) display the strong absorption [4–8]. In 2009 to 2019, the power conversion efficiency (PCE) is quickly elevated from 3.8% to 25.2% of lead-based perovskite solar cells [9, 10]. But the main problem of the lead is pernicious to life and nature. Searching new materials for chemically stable and lead-free perovskite solar cells has become an emergent mission to solve these problems [11–15]. The inorganic halide perovskites, which are also called double perovskites, draw great research interest due to their effective application as light-absorbing materials in perovskite solar cells [16, 17]. Liu et al. have discussed the structural, mechanical, electronic, and optical properties of double perovskites Cs₂TiI₆Br [18]. The optical absorption coefficient and environmental stability of mixed halide double perovskites Cs₂TiIₓBrₓ (x = 0, 2, and 6) as shown by Yan et al. [19]. The structural, electronic, optical properties of Double Perovskites K₂SnX₆ (X = Br, I) [21]. They have also shown the semiconducting nature of these compounds. Tsuyama et al. have discussed the electronic and optical properties of Cs₂TiX₆ (X = Br, I) [21]. The elastic, electronic and optical properties for A₂PtX₆ (A = K, Rb and Cs) have been studied by Bouras et al. [21]. Using the periodic DFT code the analysis of the inelastic neutron scattering (INS) spectrum of Rb₂PtH₆ and Rb₂PtD₆ have been deliberated by Parker et al. [22].

In this work, the structural, electronic and optical properties of Rb₂SnBr₆ has been investigated by using first-principles calculations based on the density functional theory. Optoelectronic properties such as band structures, density of states, dielectric constants, refractive index, conductivity, absorption, loss function, and reflectivity have been studied.

2. METHODOLOGY

The geometry optimization was performed using the plane wave pseudopotential method in the Cambridge Serial Total Energy Package (CASTEP) code [23]. In these calculations, generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) in the framework of DFT was used [24]. For the best convergence Monkhorst-Pack points of 15×15×15 grid and plane wave cut-off energy of 500 eV have been employed in this study of the computed structures and energies. The valence states are: Rb- 4p°, 5s¹; Br- 4s², 4p°; Sn 5s², 5p² for Rb₂SnBr₆. Geometrical optimization was obtained using cutoff energy change per atom less than 5×10⁻⁶ eV, residual force less than 0.01 eV/Å.
3. RESULTS & DISCUSSION

3.1. Structural Properties

Rb$_2$SnBr$_6$ crystallized in face-centered cubic crystal with space group Fm-3m (#225) is shown in Figure 1. The optimized lattice parameter is 10.75 Å which is near to the investigational (Å [25]).

![Crystal structure of Rb$_2$SnBr$_6$](image)

Figure 1. Crystal structure of Rb$_2$SnBr$_6$

Table 1. Occupied Wyckoff positions for Rb, Sn, and Br atoms of Rb$_2$SnBr$_6$.

<table>
<thead>
<tr>
<th>k</th>
<th>Atom</th>
<th>Position</th>
<th>k</th>
<th>Atom</th>
<th>Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sn</td>
<td>(0, 0, 0) a0</td>
<td>6</td>
<td>Br</td>
<td>(0, u, 0) a0</td>
</tr>
<tr>
<td>2</td>
<td>Rb</td>
<td>(0.25, 0.25, 0.25) a0</td>
<td>7</td>
<td>Br</td>
<td>- (0, u, 0) a0</td>
</tr>
<tr>
<td>3</td>
<td>Rb</td>
<td>- (0.25, 0.25, 0.25) a0</td>
<td>8</td>
<td>Br</td>
<td>(0, 0, u) a0</td>
</tr>
<tr>
<td>4</td>
<td>Br</td>
<td>(u, 0, 0) a0</td>
<td>9</td>
<td>Br</td>
<td>- (0, 0, u) a0</td>
</tr>
<tr>
<td>5</td>
<td>Br</td>
<td>- (u, 0, 0) a0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Where a0/Å=lattice parameter of Rb$_2$SnBr$_6$ and u=0.245 (Å).

3.2 Mechanical Properties

The elastic constants are essential for defining the mechanical properties that make a link with the forces operating in solids [26, 27]. The Young’s modulus (Y) reflects the resistance of materials against uniaxial tension. The Bulk modulus (B) is a measure of the resistance of a material against volume change under hydrostatic pressure, while the shear modulus (G) describes the resistance to shape change caused by a shearing force.

Table 2. Calculated and experimental lattice constants a (Å), elastic constants Cij (GPa), Bulk moduli B (GPa), Shear moduli G (GPa), Young’s moduli Y (GPa), B/G values, anisotropy factor A, Poisson’s ratio σ of Rb$_2$SnBr$_6$.

<table>
<thead>
<tr>
<th>Structures</th>
<th>a (Å)</th>
<th>C11 (GPa)</th>
<th>C12 (GPa)</th>
<th>C44 (GPa)</th>
<th>B (GPa)</th>
<th>G (GPa)</th>
<th>Y (GPa)</th>
<th>B/G</th>
<th>A</th>
<th>σ</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rb$_2$SnBr$_6$</td>
<td>10.75</td>
<td>28.7</td>
<td>10.99</td>
<td>13.2</td>
<td>16.89</td>
<td>11.15</td>
<td>22.62</td>
<td>1.51</td>
<td>1.47</td>
<td>0.23</td>
<td>[Thio]</td>
</tr>
<tr>
<td>Rb$_2$Br$_6$</td>
<td>10.64</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[25]</td>
</tr>
</tbody>
</table>

Hence, it has been calculated the elastic constants of Rb$_2$SnBr$_6$ at ambient condition. There are three independent elastic constants for a cubic crystal, and the well-known mechanical stability criteria [28] are as follows:

\[ C_{11} > 0, \quad C_{44} > 0, \quad C_{11} - C_{12} > 0 \quad \text{and} \quad C_{11} + 2C_{12} > 0 \]  

The elastic anisotropy (A) is defined by Zener [29], which has been calculated using Table 2. The calculated values show the anisotropic nature of this compound. The Cauchy’s pressure (C$_{12} - C_{44}$) is negative which indicates the material’s brittle behavior [30]. The Pugh’s ratio B/G also confirms the brittle behavior of Rb$_2$SnBr$_6$ [31]. The Poisson’s ratio σ is another essential property to describe the mechanical properties of a material [32]. By using this ratio the ductility/brittleness of any material can be tested. If the value σ < 0.26 the material is called ductile, otherwise it is characterized as brittle material [33]. According to this criterion, it assumes that Rb$_2$SnBr$_6$ is a ductile material, which is also confirmed by the Pugh’s ratio’s calculation.

3.3 Electronic Properties

The electronic band structures at ambient conditions along with high symmetry directions in the Brillouin zones are depicted in Figure 2.

![Band Structure along with high symmetry direction in the Brillouin zones of Rb$_2$SnBr$_6$](image)

Figure 2. Band Structure along with high symmetry direction in the Brillouin zones of Rb$_2$SnBr$_6$

![Total and partial DOS of Rb$_2$SnBr$_6$](image)

Figure 3. Total and partial DOS of Rb$_2$SnBr$_6$
The analysis of the band structures reveal that Rb\textsubscript{2}SnBr\textsubscript{6} is direct band gap with the valence band maximum (VBM) and conduction band minimum (CBM) located at G point. Thus, indicates semiconducting behavior and the value of band gap is 1.228 eV.

From Figure 3, it shows that the total density of states (TDOS) and partial density of states (PDOS). The hybridization above the Fermi level at 4.1 eV comes between Sn-5s and Br-4p orbitals. On the other-hand hybridization above the Fermi level at ~7.0 eV comes from Br-4s, Rb-4p. On the other-hand the upper peak in the density of states below the Fermi level ~0.0 eV to -4.02 eV comes from the strong hybridization between Sn-4p and Br-4p orbitals. The Hybridization below the Fermi level at ~5.8 to -8.23 eV comes from Sn-4s, Br-4s. The peak at around ~14.16 eV comes from the strong hybridization between Sn-4s, Sn-4p and Br-4p orbitals. The density of states gives further confirmation that Rb\textsubscript{2}SnBr\textsubscript{6} is a semiconductor.

3.4 Optical Properties

To understand better the application of materials the optical properties are necessary to know. The dielectric function is expressed as \( \varepsilon = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \) is a crucial parameter to describe the optical properties of any homogeneous medium. The imaginary part \( \varepsilon_2(\omega) \) is obtained from the momentum matrix elements between the occupied and the unoccupied electronic states and calculated directly by using Equation 1 [34]. The knowledge of both \( \varepsilon_1(\omega) \) and \( \varepsilon_2(\omega) \) allows the calculation of important optical constants. The optical refractive index, loss function, absorption spectrum, reflectivity, and conductivity can be calculated by using Equation 49 to 54 in reference [34]. There are two contributions of \( \varepsilon(\omega) \): interband and intraband transition. The real part of dielectric function \( \varepsilon_1(\omega) \) can be equated using the kramers-kronig relation from the imaginary part. The optical functions of photon energy up to 20 eV for polarization vectors [100] of Rb\textsubscript{2}SnBr\textsubscript{6} are displayed in Figure 4. The calculations have been performed using Gaussian smearing. It is to be noted that there are no experimental or theoretical studies on optical properties on our studied compounds. It is shown in Figure 4 (a), that there is a single peak of the real part of dielectric function \( \varepsilon_1(\omega) \), but it starts with 3.12 at 0 eV which is known as static dielectric constant in the zero frequency limit, (excluding any contributions from lattice vibrations). It starts increasing form zero frequency, then falls down after that it reaches the highest value of 4.41 at 4.48 eV. Then it decreases. The \( \varepsilon_1(\omega) \) spectra minimum is at about 8.44 eV. It is also observed that the real part of \( \varepsilon_1(\omega) \) goes through zero from below at about 11.46 eV and the imaginary part approaches zero from above at about 11.46 eV. The imaginary part of the dielectric constant shows a single peak.

The change of refractive index (n) and extinction coefficient (k) with photon energy is shown in Figure 4 (b). The calculated static refractive index n (0) is found to be 1.746. The refractive index is found to have the maximum value of 2.09 at 4.40 eV. The greater refractive index shows, when the photons are travelling through a material it slowed down more. Usually, when the electron density increases, the refractive index in a material also increases. Interestingly, the covalent compounds have a higher refractive index than ionic compounds. Few electrons are shared by ions in ionic bonds than in covalent bonding. It is illustrated in Figure 4 (c), the optical conductivity starts at about 1.22 eV, and that indicates the semiconducting nature of Rb\textsubscript{2}SnBr\textsubscript{6} which is consistent with the band structure presented in Figure 2. An indistinguishable style is observed in the manner of imaginary dielectric function \( \varepsilon_2(\omega) \) and extinction coefficient k that is in Figure 4 (a) and Figure 4 (b). The highest optical conductivity was observed at photon energy of ~3.80 eV. It is shown in Figure 4 (d), that the absorption spectrum with a single peak at 8.16 eV for Rb\textsubscript{2}SnBr\textsubscript{6}, which decreases slowly in the high-energy region. The absorption range predicts the usefulness of the compound for optoelectronic devices. The optical reflectivity is shown in Figure 4 (e). It is found the maximum reflectivity when the real dielectric function goes below zero. The maximum value of reflectivity is about 10 eV in the ultraviolet region. Consequently, this compound can be used as a potential candidate for coating material to avoid solar heating in the ultraviolet region. When a fast electron crosses a material, the loss function becomes an important factor. The peak of the loss function is known as the plasma frequency \( \omega_p \) which is associated with the plasma resonance. The relation of \( \omega_p \) is directly proportional with electron density of the material. The peak of L(\( \omega \)), is shown at 11.6 eV from Figure 4 (f). Regrettably, non experimental data has been reported to compare with found results of Rb\textsubscript{2}SnBr\textsubscript{6} for the optical properties.

**Figure 4.** Energy-dependent (a) dielectric function, (b) refractive index, (c) conductivity, (d) absorption, (e) reflectivity, (f) loss function of Rb\textsubscript{2}SnBr\textsubscript{6} along [100] direction.

4. CONCLUSIONS

At the end, from the mechanical and optoelectronic study of double Perovskite Rb\textsubscript{2}SnBr\textsubscript{6}, it is cleared that the Paugh’s ductility index (B/G) is calculated which shows that Rb\textsubscript{2}SnBr\textsubscript{6} is brittle at ambient condition. The Zener anisotropy factor confirms the anisotropic nature of this compound. The electronic band structures and DOS are calculated. The electronic band structures show semi conducting characteristics of the compound and the band gap is 1.228 eV. Finally, optical properties are calculated and discussed for the first time. The reflectivity is found to be 50% in the UV regions up to ~11 eV, thus showing promise as good coating materials.

**ABBREVIATIONS**

- DFT-Density Functional Theory
- UV- Ultraviolet
- eV- Electron Volt
- Å-Angstrom
- PCE- Power Conversion Efficiency
- CASTEP- Cambridge Serial Total Energy Package
- GGA- generalized gradient approximation
- PBE- Perdew-Burke-Ernzerhof
Cij - elastic constants
GPa - Giga Pascal
Y - Young’s modulus
B - Bulk modulus
G - Shear modulus
A - Anisotropy factor
σ - Poisson’s ratio
DOS - Density of States
UV - Ultraviolet

CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest related to the publication of this article.

REFERENCES


