Calculations of DOS and electronic structure in $\text{Bi}_2\text{S}_3$ and $\text{Bi}_2\text{Se}_3$ by using FP-LAPW method

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Abstract

The electronic structures for $\text{Bi}_2\text{S}_3$ and $\text{Bi}_2\text{Se}_3$ have been investigated by first principles full potential- linearized augmented plane wave (FP-LAPW) method with Generalized Gradient Approximation (GGA). The calculated density of states (DOS) and band structures show semiconducting behavior of $\text{Bi}_2\text{S}_3$ and $\text{Bi}_2\text{Se}_3$ with a narrow indirect energy band gap of 1.4 eV in $\text{Bi}_2\text{S}_3$ and 0.8 eV in $\text{Bi}_2\text{Se}_3$.

Keywords: DFT, FP-LAPW, DOS, energy band structure, energy band gap.

PACS: 71.15.-m, 71.15.Dx, 71.15.Mb, 71.20.-b, 75.10.-b

1. INTRODUCTION

Today semiconductors can be grown with various compositions from monoatomic layer to nano-scale islands, rows, arrays, in the art of quantum technologies and the numbers of conceivable new electronic devices are manufactured [1]. Narrow gap semiconductors $\text{Bi}_2\text{S}_3$ and $\text{Bi}_2\text{Se}_3$ are classic room temperature thermoelectric materials [2]. These are the chalcogenides of poor metal having important technological applications in optoelectronic nano devices [3], field-emission electronic devices [4], photo-detectors and photo-electronic devices [5] and photovoltaic converters, thermoelectric cooling technologies based on the Peltier effect [6,7]. They have orthorhombic crystal structures at room temperature with x, y and z-positions of atoms [8] as given in Table 1 and space group Pnma (number 62). The crystal structures of $\text{Bi}_2\text{S}_3$ and $\text{Bi}_2\text{Se}_3$ are illustrated in Fig.1(a-b). In this report, we would like to present a systematic study of DOS and energy band structures of $\text{Bi}_2\text{S}_3$ and $\text{Bi}_2\text{Se}_3$ using FP-LAPW method.

Table 1: x, y and z-positions of atoms of $\text{Bi}_2\text{S}_3$ and $\text{Bi}_2\text{Se}_3$

<table>
<thead>
<tr>
<th>Atom (Bi$_2$S$_3$)</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi 1</td>
<td>0.0164</td>
<td>0.25</td>
<td>0.6745</td>
</tr>
<tr>
<td>Bi 2</td>
<td>0.3406</td>
<td>0.25</td>
<td>0.4661</td>
</tr>
<tr>
<td>S 1</td>
<td>0.0494</td>
<td>0.25</td>
<td>0.1311</td>
</tr>
<tr>
<td>S 2</td>
<td>0.3773</td>
<td>0.25</td>
<td>0.0604</td>
</tr>
<tr>
<td>S 3</td>
<td>0.2165</td>
<td>0.25</td>
<td>0.8069</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atom (Bi$_2$Se$_3$)</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi 1</td>
<td>0.012</td>
<td>0.25</td>
<td>0.328</td>
</tr>
<tr>
<td>Bi 2</td>
<td>0.343</td>
<td>0.25</td>
<td>0.534</td>
</tr>
<tr>
<td>Se 1</td>
<td>0.067</td>
<td>0.25</td>
<td>0.876</td>
</tr>
</tbody>
</table>
2. THEORY AND COMPUTATIONAL METHODS
First principles FP-LAPW [9] method based on density functional theory (DFT) is used for calculations of DOS and band structure of Bi₂S₃. The version of GGA as prescribed by Perdew, Burke and Ernzerhof [10] was used for the exchange and correlation potentials. The calculated total energy (E) within GGA as a function of the volume (V) were used for determination of theoretical lattice constants. Equilibrium lattice constants are calculated by fitting the calculated total energy to the Murnaghan’s equation of state [11]. A series of total energy calculations as a function of volume can be fitted to an equation of states according to Murnaghan.

\[ E(V) = E_0 + \frac{V_0}{B_0} \left( \frac{V}{V_0} \right)^{1/3} - \frac{1}{B_0} \left( \frac{V}{V_0} \right)^{4/3} + \frac{3}{2} B'_0 V_0 \left( \frac{V}{V_0} \right)^{2/3} \]

where \( E_0 \) is the minimum energy at \( V = 0 \), \( B_0 \) is the bulk modulus at the equilibrium volume and \( B'_0 \) is pressure derivative of the bulk modulus at the equilibrium volume. The equilibrium volume is given by the corresponding total energy minimum as shown in Fig.2(a-b) [12]. The equilibrium lattice constant was optimized using the experimental values of \( a=11.269 \text{\ Å}, b=3.9717 \text{\ Å} \) and \( c=11.129 \text{\ Å} \) for Bi₂S₃, and \( a=11.83 \text{\ Å}, b=4.09 \text{\ Å} \) and \( c=11.62 \text{\ Å} \) for Bi₂Se₃ [8]. The calculation was accomplished by using the WIEN2K code [13]. In the FP-LAPW procedure, wave functions, charge density and potential are expanded in spherical harmonics within non overlapping atomic spheres of radius \( R_{\text{MT}} \) and in the remaining space of the unit cell plane waves are considered. The maximum multi-polarity \( l \) for the waves inside the atomic spheres was confined within \( l_{\text{max}} = 10 \). The wave functions in the interstitial region were expanded in plane waves with a cut-off of to \( K_{\text{max}}=2.5 \text{\ a.u.}^{-1} \) (where \( K_{\text{max}} \) is the maximum value of the wave vector \( \mathbf{K} = \mathbf{k} + \mathbf{G} \)). For Bi: 6s, 6p, S: 3s, 3p and Se: 4s, 4p states were treated as valance state and all other lower states were treated as core state. The potential and charge density were expanded up to a cut-off \( G_{\text{max}} = 12 \text{\ a.u.}^{-1} \). The muffin-tin radii are set to \( R_{\text{MT}} = 2.4 \text{\ a.u.} \) for Bi and 2.2 a.u. for S in Bi₂S₃ and \( R_{\text{MT}} = 2.3 \text{\ a.u.} \) for Bi and 2.2 a.u. for Se in Bi₂Se₃. A mesh of 1500 k-points was used after doing k- optimization. The calculated lattice constants found by volume optimization are \( a=11.2263 \text{\ Å}, b=3.567 \text{\ Å} \) and \( c=11.0868 \text{\ Å} \) for Bi₂S₃, and \( a=11.4753 \text{\ Å}, b=3.9647 \text{\ Å} \) and \( c=11.2716 \text{\ Å} \) for Bi₂Se₃ which are shown in Fig.2(a-b).

Table 2: The parameters chosen for the computation of Bi₂S₃ and Bi₂Se₃

<table>
<thead>
<tr>
<th>PARAMETERS</th>
<th>VALUES USED</th>
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<tbody>
<tr>
<td>The plane-wave cut-off for the basis functions, ( R_{\text{MT}} \times K_{\text{max}} )</td>
<td>7</td>
</tr>
<tr>
<td>Expansion of wave functions, density, potentials inside the ( R_{\text{MT}} ), ( l_{\text{max}} )</td>
<td>10</td>
</tr>
<tr>
<td>The potential, charge density</td>
<td>12 a.u.^{-1}</td>
</tr>
</tbody>
</table>

Expanded up to cut-off \( G_{\text{max}} \)

| Number of plane waves generated | 729 |
| Wave vector, \( \mathbf{k} \) | |
| \( R_{\text{MT}} \) used | |
| Bi = 2.4 a.u., S = 2.2 a.u. (for Bi₂S₃) | |
| Bi = 2.3 a.u., Se = 2.2 a.u. (for Bi₂Se₃) | |

Fig. 2: Energy versus Volume curve using the volume optimization method for Bi₂S₃ and Bi₂Se₃

3. RESULTS AND DISCUSSIONS
In Fig.2(a-b), we show the total energy curve as a function of unit cell volume for Bi₂S₃ and Bi₂Se₃. The total and partial DOS plots of Bi₂S₃ and Bi₂Se₃ are shown in Figs.3,4,5 & 6. From Fig.3, we found that the contributions to total DOS were from Bi-6p and S-3p electron states in Bi₂S₃ and from Bi-6p and Se-4p electron states in Bi₂Se₃. The core region which is below -6eV is formed by 6s and 6p electron states of Bi and a sharp peak at around -10.5 eV is observed in Bi₂S₃ [Fig.4(a)] and a sharp peak at around -10.2 eV is observed in Bi₂Se₃ [Fig.4(b)]. The conduction region, which is above the Fermi level, is mainly contributed by Bi-6p, 6pα, 6pβ state electrons in Bi₂S₃ [Fig.5(a)]
and by Bi-6\(p\), 6\(p\) state electrons in \(\text{Bi}_2\text{Se}_3\) [Fig.5(b)]. In the valence region (below Fermi level), we have observed, S–3\(p\) electron state is mainly contributing to total DOS giving a sharp peak at around -0.8eV in \(\text{Bi}_2\text{S}_3\) [Fig.6(a)] and Se–4\(p\) electron state is mainly contributing to total DOS giving sharp peaks at around -0.5eV and -1.2eV in \(\text{Bi}_2\text{Se}_3\) [Fig.6(b)].
From the band structure plots, we observed an indirect band gap of the order of 1.4 eV in Bi$_2$S$_3$[Fig.7(a)] and an indirect band gap of the order of 0.8 eV in Bi$_2$Se$_3$[Fig.7(b)]. The band structure plots were also found with higher number of bands at the regions where peaks of the DOS were observed. In Fig.8 & 9 we have compared band structures with DOS plots of Bi$_2$S$_3$ and Bi$_2$Se$_3$, and found that higher DOS regions correspond to more bands.

4. CONCLUSIONS
In conclusion, we have observed a qualitative agreement between theoretical and experimental lattice constants. Calculated band
gap is very close to experimental value. Band gaps of the order of 1.4 eV and 0.8 eV suggest that Bi$_2$S$_3$ and Bi$_2$Se$_3$ are semiconductors with low energy gap. Since Fermi level is very close to valance band, it indicates that the semiconductors are p-type. The calculated band gaps also suggest that the compounds may be used as suitable candidate for thermoelectric applications. The semiconductor Bi$_2$S$_3$ with band gap 1.4eV belongs to a family of solid state materials with applications in thermoelectric cooling technologies based on the Peltier effect [14,15]. The semiconductor Bi$_2$Se$_3$ with band gap 0.8eV has useful applications in the field of thermoelectric devices as solid state coolers or generators [16,17]. However, the band gaps when checked with experimental values (1.3eV in Bi$_2$S$_3$ and 0.8eV in Bi$_2$Se$_3$) [14] seem to have differences. We propose to check these discrepancies with mBJ potential inclusion.

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REFERENCES