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Structural and Electronic Properties of Orthorhombic Phase Bi_2Se_3 Based on First-Principles Study

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ABSTRACT

Bi_2Se_3 is one of the promising materials in thermoelectric devices and is environmentally friendly due to its efficiency to perform in room temperature. Structural and electronic properties of Bi_2Se_3 were investigated based on the first-principles calculation of density functional theory (DFT) using CASTEP computer code. The calculation is conducted within the exchange-correlation of local density approximation (LDA) and generalised gradient approximation within the revision of Perdew-Burke-Ernzerhof (GGA-PBE) functional. A comparative study is carried out between the electronic properties of LDA and GGA-PBE. Lattice parameter and band gap are consistent with the other reports. Calculation from LDA is more accurate and has a better agreement than GGA-PBE in describing the lattice parameter of Bi_2Se_3. Band gap and density of states of LDA show higher electrical conductivity than GGA-PBE. Both LDA and GGA-PBE have same degree of thermal conductivity due to the occurrence of indirect band gap at same range of wave vector.

Keywords: *bismuth selenide, density functional theory, electronic*

INTRODUCTION

Bi_2Se_3 has been known as one of the best thermoelectric materials due to its high thermoelectric performance and unique near-gap electronic structure. It is also known as a topological insulator, in which, Bi_2Se_3 has a bulk similarity to insulator with conducting states on the surface [1]. Its bulk band gap is larger than room temperature energy scale which is suitable candidate of spintronic application [2]. Bi_2Se_3 is one of the most extensively studied topological insulator because of its surface state simplicity that is made up of a single Dirac cone at the point [3]. Bi_2Se_3 has received much attention due to its potential application in conversion of heat waste to electricity [4], power generation [5], energy harvesting [4], heat pumping [6], solid-state refrigeration [7] and solution to the environmental crisis because thermoelectric device can use waste heat that contributed to the global warming to generate electricity [4]. Thermoelectric performance is described by the dimensionless figure of merit, *ZT*.

$$ZT = \frac{S^2 \sigma T}{\kappa}$$

Where *S* represents thermopower, represents electrical conductivity, T represents temperature and represents heat conductivity. Good thermoelectric performance should have higher thermopower and electrical conductivity and lower heat conductivity [8]. Understanding of electronic structure is important to determine the suitability of thermoelectric material for applications. The performance of the thermoelectric material depends on its effective mass and anisotropy, band gap, carrier mobility, and band extremes degeneracy. Narrow band gap can increase electrical conductivity, and the sensitivity of the thermoelectric materials to operate at low temperature. Furthermore, direct band gap is desirable for thermoelectric efficiency compare to indirect band gap. Occurrence of indirect band gap increased thermal conductivity [9, 10].

The electronic structure of Bi_2Se_3 have been studied for its single Dirac cone formation located inside the bulk band gap. This properties is an essential for many optoelectronic devices [11]. Several experimental and theoretical studies have been conducted on the electronic properties of

Bi_2Se_3. However, most of those studies were conducted on the rhombohedral phase instead of orthorhombic phase. First principles calculation that was implemented in the CASTEP computer code was performed to determine structural and electronic properties of Bi_2Se_3. Comprehensive analysis of band structure and density of states was carried out. Comparative study was conducted between electronic properties from LDA and generalised gradient approximation (GDA). Despite many theoretical reports for band gap, the experimental report is absent [1, 12-14].

COMPUTATIONAL DETAILS

Orthorhombic structure of Bi_2Se_3 that belongs to the space group of *Pnma 62* was used. The initial structure was taken from the experimental study performed by Atabaeva *et al*. [16]. The calculation of structural optimisation was performed within LDA [17], and GGA-PBE exchange correlation functional [18] together with the employment of OTFG ultra soft pseudopotential [19]. Koelling-Harmon was applied as a relativistic treatment [20]. Then, electronic properties which are band structure and density of states were calculated. Convergence test for both LDA & GGA has been done and found that the suitable cut-off energy and k-point value were 350 eV and 1 x 3 x 1, respectively. The value above 350 eV and above 1 x 3 x 1 was not chosen as it would be time consuming due to the higher energy and dimension provided in the calculation. The total energy SCF tolerance and the maximum cycle of SCF was set at 1.0×10^{-6} eV/atom and 100, respectively. The maximum force, maximum stress, and maximum displacement was set at 0.03 eV/Å, 0.05 GPa, and 0.001 Å, respectively. The spin-polarised and formal spin as initial were applied within the calculation. All the calculations were performed using CASTEP computer code in the Material Studios [15].

STRUCTURAL PROPERTIES

The orthorhombic structure of Bi_2Se_3 was used directly from the experimental as an initial structure, and then optimisation is performed to stabilise the geometric cells. The structure belongs to the space group of Pnma 62 that consists of two types of atoms which are bismuth and selenium. The optimisation structure is shown in Figure 1.

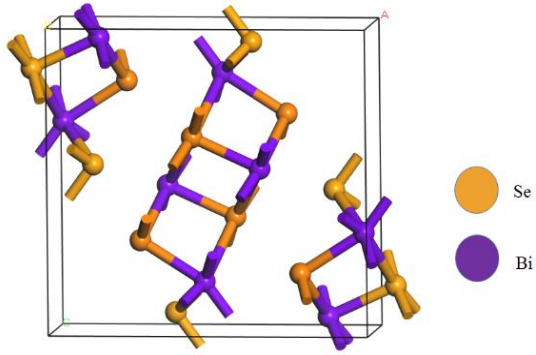

Figure 1: Orthorhombic Structure of Bi_2Se_3

Structural properties consist of lattice parameters and bond length. The calculated lattice parameter is shown in Table 1. The results were compared with other theoretical and experimental works for verification.

Table 1: Structural Properties of Bi_2Se_3

Method	a (Å)	b (Å)	c (Å)	Reference
LDA	11.823	4.079	11.231	This Work (CASTEP)
GGA-PBE	13.087	4.186	11.952	This Work (CASTEP)
LDA	11.767	4.141	11.491	Theory (Quantum Espresso) [13]
LAPW + lo	11.830	4.090	11.620	Theory (WIEN2K) [20]
LDA	11.763	4.106	11.476	Theory (SIESTA) [1]

LDA	11.505	4.079	11.302	Theory (VASP) [1]
-	11.830	4.090	11.620	Experimental [1]
-	11.706	4.142	11.608	Experimental [16]

LDA result for experimental values of lattice parameter a = 11.830 Å, b = 4.090 Å, c = 11.620 Å is consistent with other theoretical values calculated by SIESTA, VASP and QUANTUM ESPRESSO. However, for the of lattice parameter c, our result was underestimated by 3.3%. Compared to other experimental studies, our LDA result was overestimated by 1% for lattice parameter a, underestimated by 1.5% for lattice parameter b, and underestimated by 3.2% for lattice parameter c. Result from GGA-PBE result shows that lattice parameter a was overestimated value by 11% and 12%, lattice parameter b was overestimated by 2.3% and 1%, and lattice parameter c was overestimated by 2.9% and 3%. Overall, our results are consistent with experimental studies except for GGA-PBE that have overestimation more than 10%. This indicates LDA is a reliable method of calculation for structural properties of orthorhombic Bi_2Se_3.

ELECTRONIC PROPERTIES

The band structure calculation Bi_2Se_3 within LDA and GGA-PBE were plotted with Fermi level at 0 eV on energy scale in band gap plots as shown in Figure 2 and Figure 3, respectively to observe the band gap for each method of calculation. Both calculations were performed with Koelling-Herman relativistic pseudopotentials. The blue mark in the diagram represents the minimum conduction band and the green mark represents the maximum valence band. Both diagrams show an indirect band gap.

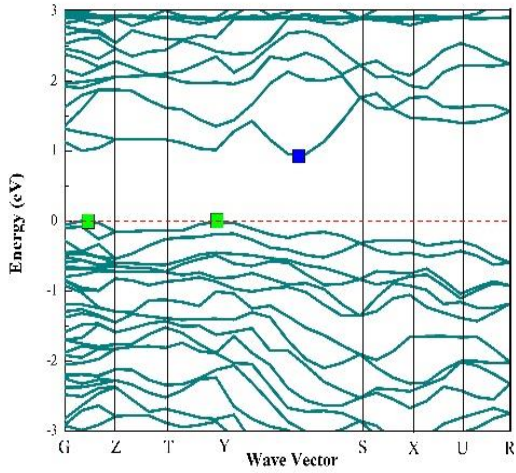

Figure 2: Band Structure of Bi_2Se_3 within LDA Functional

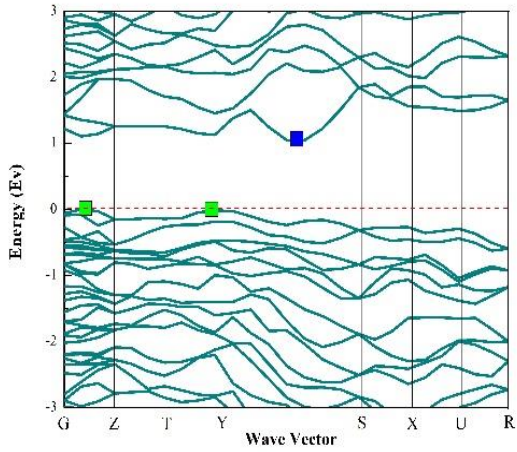

Figure 3: Band Structure of Bi_2Se_3 within GGA-PBE Functional

From the calculations, we got the band gap of 0.95 eV within LDA and 1.05 eV within GGA-PBE. The results obtained are consistent with other theoretical studies as shown in Table 2 [1, 14, 19, 21]. GGA-PBE result shows a close result with LAPW + Io result of 1.1 eV. LDA result was similar with that from SISTA calculation. This shows that LDA is a reliable method to calculate the energy gap of Bi_2Se_3.

Table 2: Band Gap of Bi_2Se_3

Method	Band Gap (eV)	Reference
LDA	0.95	This Work (CASTEP)
GGA-PBE	1.05	This Work (CASTEP)
LDA	0.90	Theory (ABINIT) [14]
LDA	0.99	Theory (QUANTUM ESPRESSO) [19]
LAPW + lo	1.10	Theory (WIEN2K) [21]
LDA	0.95	Theory (SIESTA) [1]

The band gap for LDA was 10% smaller than that of GGA-PBE. This indicates that LDA has higher electrical conductivity compare to GGA-PBE. Electron needs small energy to jump to the conduction band in LDA. Both LDA and GGA-PBE have indirect band gap with both valence band at wave vector Y. This indicates that band gaps for both LDA and GGA-PBE have the same degree of thermal conductivity. The occurrence of thermal conductivity is undesirable for thermoelectric performance. A partial density of states (PDOS) shows the nature and origin of the band gap. The PDOS results for Bi_2Se_3 within LDA is shown in Figure 4, whereby, the p-orbital and s-orbital for Se contribute the most states to the valence band. At conduction band, orbital-p of Bi and s-orbital for Se contributed the most.

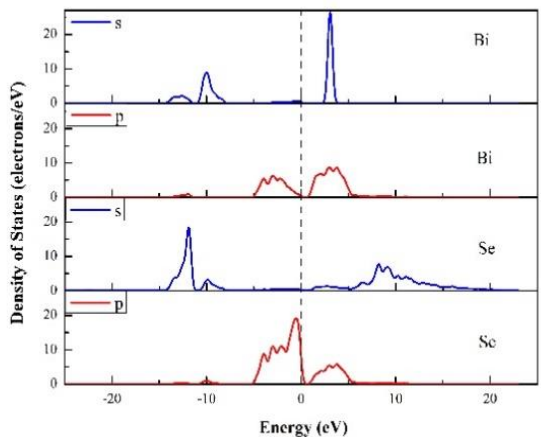

Figure 4: Partial Density of States of Bi_2Se_3 within LDA Functional

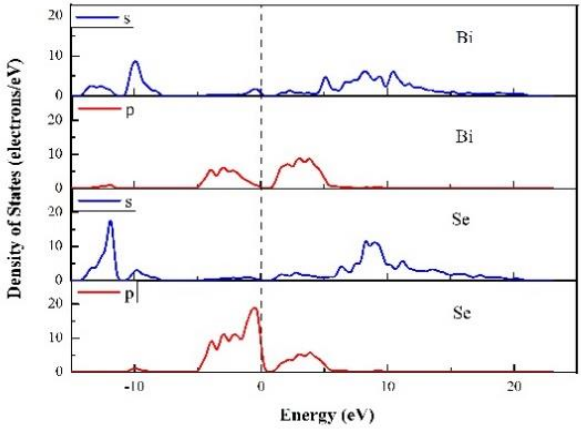

Figure 5: Partial Density of States of Bi_2Se_3 within GGA-PBE Functional

Bi_2Se_3 PDOS within GGA-PBE (Figure 5) shows s-orbital for Bi shows slight contribution compare to the s-orbital within LDA functional. This shows that it does not contributes the states to the core bands. The p-orbital for Bi and p-orbital for Se contributed the most states to the valence band, and the conduction band was similar with PDOS within LDA functional. Conduction band for LDA shows higher occupation of electron compare to the conduction band for GGA-PBE. This shows that Bi_2Se_3 that was calculated using the LDA functional has higher electrical conductivity than that of GGA-PBE functional.

CONCLUSION

In summary, we provided consistent theoretical results of structural and electronic properties of Bi_2Se_3 by using LDA and GGA-PBE of exchange-correlation functional. On structural properties, our results indicated that results from LDA was more accurate than that of GGA-PBE in the experimental works by a difference of < 5%. On electronic properties, results from LDA were consistent with those from other theoretical works. While GGA-PBE was most consistent with the work from the computer code of WIEN2k. LDA is the most consistent and accurate results and is reliable for the electronic calculation of Bi_2Se_3. However, there is no experimental works have been reported to support our band gap finding. From the band gap, LDA has higher electrical conductivity due to the smaller band gap,

compared to the band gap of GGA-PBE. This result is supported by PDOS finding that LDA has higher occupation of electrons compared to GGA-PBE. Both LDA and GGA-PBE has the same degree of thermal conductivity due to the indirect band gap that occurred between minimum conduction band at range Y – S and maximum valence band at Y.

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