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Calculations of DOS and electronic structure in Bi_2S_3 and Bi_2Se_3 by using FP-LAPW method

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Abstract
The electronic structures for Bi_2S_3 and Bi_2Se_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 Bi_2S_3 and Bi_2Se_3 with a narrow indirect energy band gap of 1.4 eV in Bi_2S_3 and 0.8 eV in Bi_2Se_3 .

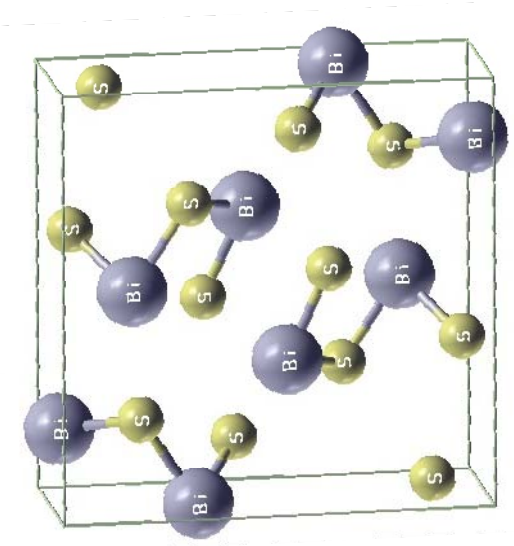
Keywords: *DFT, FP-LAPW, DOS, energy band structure, energy band gap.*
PACS: *71.15.-m, 71.15.Dx, 71.15.Mb, 71.20.-b, 75.10.-b*

1. INTRODUCTION

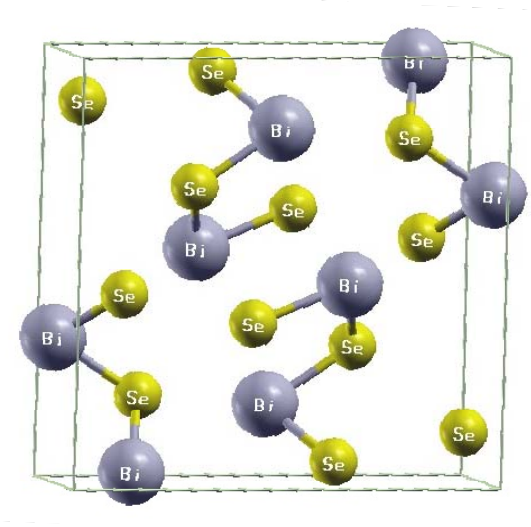
Today semiconductors can be grown with various compositions from monoatomic layer to nano-scale islands, rows, arrays, in the art of quantum technologies and the numbers of conceivable new electronic devices are manufactured [1]. Narrow gap semiconductors Bi_2S_3 and Bi_2Se_3 are classic room temperature 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 convertors, 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 Bi_2S_3 and Bi_2Se_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 Bi_2S_3 and Bi_2Se_3 using FP-LAPW method.

Table 1: x, y and z-positions of atoms of Bi_2S_3 and Bi_2Se_3

Atom (Bi_2S_3)	X	Y	Z
Bi 1	0.0164	0.25	0.6745
Bi 2	0.3406	0.25	0.4661
S 1	0.0494	0.25	0.1311
S 2	0.3773	0.25	0.0604
S 3	0.2165	0.25	0.8069
Atom (Bi_2Se_3)	X	Y	Z
Bi 1	0.012	0.25	0.328
Bi 2	0.343	0.25	0.534
Se 1	0.067	0.25	0.876
Se 2	0.870	0.25	0.556
Se 3	0.213	0.25	0.193



(a) Bi_2S_3



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(b) Bi_2Se_3

Fig.1 : Unit cell structures of Bi_2S_3 and bi_2Se_3

2. THEORY AND COMPUTATIONAL METHODS

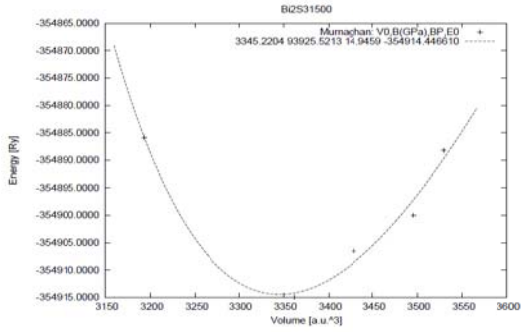
First principles FP-LAPW [9] method based on density functional theory (DFT)) is used for calculations of DOS and band structure of Bi_2S_3. The version of GGA as prescribed by Perdew, Burke and Ernzerhof [10] was used for the exchange and correlation potentials. The calculated total energy (E) within 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.

$$E(V) = E_0 + \frac{(\frac{V_0}{V})^{B_0'}}{B_0' - 1} + \frac{B_0 V_0}{B_0' - 1} \qquad (1)$$

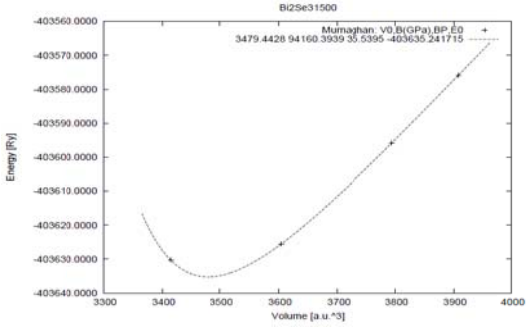
where E_0 is the minimum energy at T = 0K, B_0 is the bulk modulus at the equilibrium volume and B_0' is pressure derivative of the bulk modulus at the equilibrium volume. The equilibrium volume is given by the corresponding total energy minimum as shown in Fig.2(a-b) [12]. The equilibrium lattice constant was optimized using the experimental values of a=11.269 Å, b=3.9717 Å and c= 11.129 Å for Bi_2S_3, and a= 11.83 Å, b=4.09 Å and c=11.62 Å for Bi_2Se_3 [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_{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_{max}= 10. The wave functions in the interstitial region were expanded in plane waves with a cut-off of to K_{max}=2.5 a.u.$^{-1}$ (where K_{max} is the maximum value of the wave vector **K**=k+**G**). For Bi: 6*s*, 6*p*, S: 3*s*, 3*p* and Se: 4*s*, 4*p* states were treated as valance state and all other lower states were treated as core state. The potential and charge density were expanded upto a cut-off G_{max} = 12 a.u.$^{-1}$. The muffin- tin radii are set to R_{mt} = 2.4 a.u. for Bi and 2.2 a.u. for S in Bi_2S_3 and R_{mt} = 2.3 a.u. for Bi and 2.2 a.u. for Se in Bi_2Se_3. A mesh of 1500 k-points was used after doing k- optimization. The calculated lattice constants found by volume optimization are a= 11.2263 Å, b= 3.567 Å and c= 11.0868 Å for Bi_2S_3, and a=11.4753 Å, b= 3.9647 Å and c= 11.2716 Å for Bi_2Se_3 which are shown in Fig.2(a-b).

Table 2: The parameters chosen for the computation of Bi_2S_3 and Bi_2S_3

PARAMETERS	VALUES USED
The plane-wave cut-off for the basis functions , R_{MT} x K_{max}	7
Expansion of wave functions,density, potentials inside the R_{MT} , l_{max}	10
The potential, charge density expanded upto cut-off ,G_{max}	12 a.u.$^{-1}$.
Number of plane waves generated	729
Wave vector, k	1500
R_{MT} used	Bi = 2.4 a.u., S = 2.2 a.u. (for Bi_2S_3) Bi = 2.3 a.u.,Se= 2.2 a.u. (for Bi_2Se_3)



(a) Bi_2S_3



(b) Bi_2Se_3

Fig. 2: Energy versus Volume curve using the volume optimization method for $Bi_2S_3$and Bi_2Se_3

3. RESULTS AND DISCUSSIONS

In Fig.2(a-b), we show the total energy curve as a function of unit cell volume for Bi_2S_3 and Bi_2Se_3. The total and partial DOS plots of Bi_2S_3 and Bi_2Se_3 are shown in Figs.3,4,5 & 6. From Fig.3, we found that the contributions to total DOS were from Bi-6*p* and S-3*p* electron states in Bi_2S_3 and from Bi-6*p* and Se-4*p* electron states in Bi_2Se_3. The core region which is below -6eV is formed by 6*s* and 6*p* electron states of Bi and a sharp peak at around -10.5 eV is observed in Bi_2S_3[Fig.4(a)] and a sharp peak at around -10.2 eV is observed in Bi_2Se_3[Fig.4(b)]. The conduction region, which is above the Fermi level, is mainly contributed by Bi-6*p*, 6p_x, 6p_y state electrons in Bi_2S_3[Fig.5(a)]

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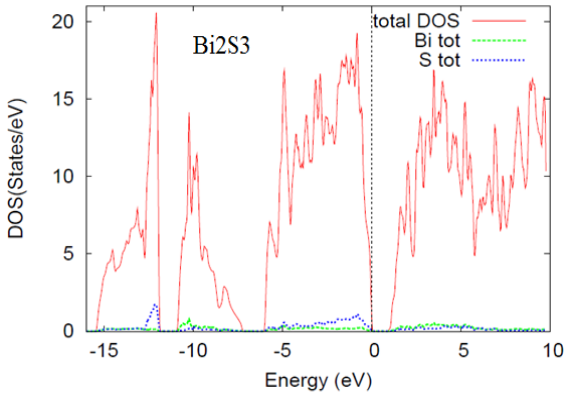
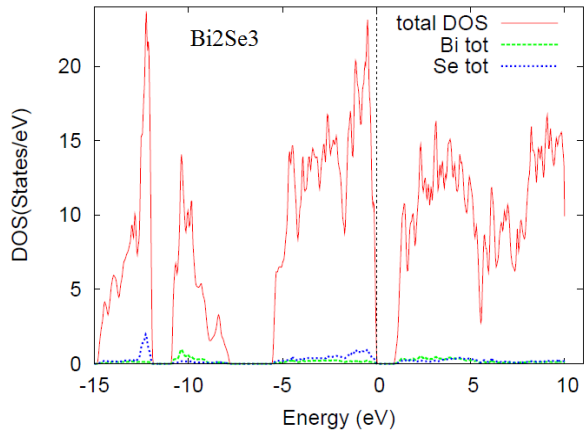
and by Bi-6*p*, 6p_x state electrons in Bi_2Se_3[Fig.5(b)]. In the valence region (below Fermi level), we have observed, S–3*p* electron state is mainly contributing to total DOS giving a sharp peak at around -0.8eV in Bi_2S_3 [Fig.6(a)] and Se–4*p* electron state is mainly contributing to total DOS giving sharp peaks at around -0.5eV and -1.2eV in Bi_2Se_3 [Fig.6(b)].

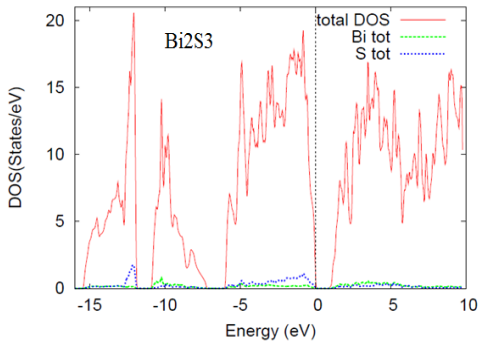


(a) Bi_2S_3

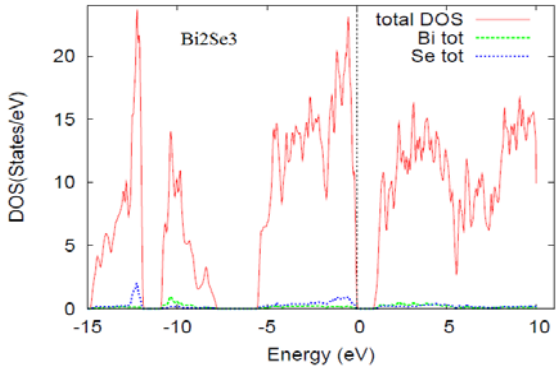


(b) Bi_2Se_3

Fig. 3: Bi_2S_3 -total, Bi-total and S-total and Bi_2Se_3 -total, Bi-total and Se-total (Energy= 0 eV, corresponds to Fermi level)

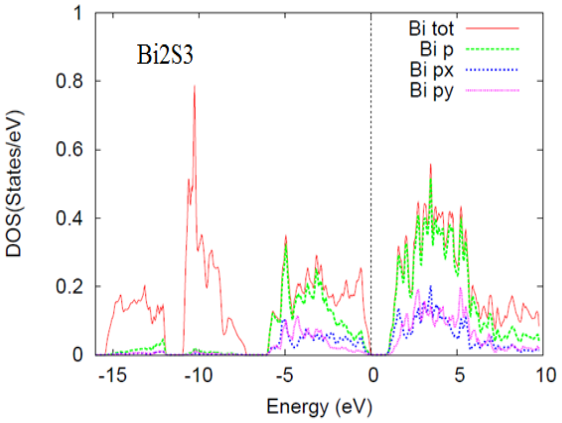


(a) Bi_2S_3

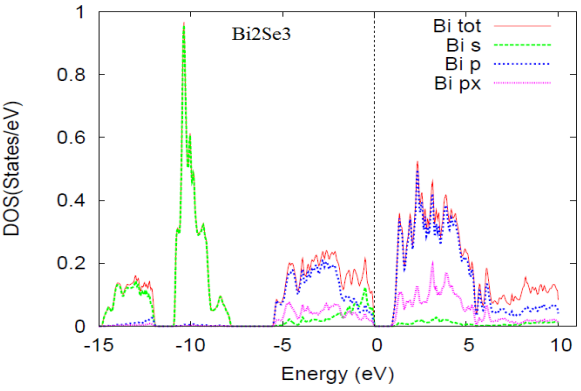


(b) Bi_2Se_3

Fig. 4 : Total DOS, Bi-total & S-total states of Bi_2S_3 and Total DOS, Bi-total & Se-total states of Bi_2Se_3



(a) Bi_2S_3



(b) Bi_2Se_3

Fig.5: Bi-total, Bi-*p*, *px* & *py* states of Bi_2S_3 and Bi-total, Bi-*s*, *p* & *px* states of Bi_2Se_3

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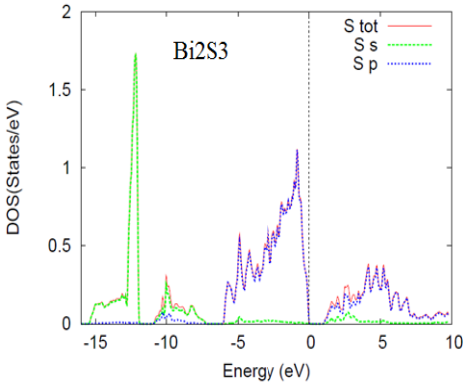
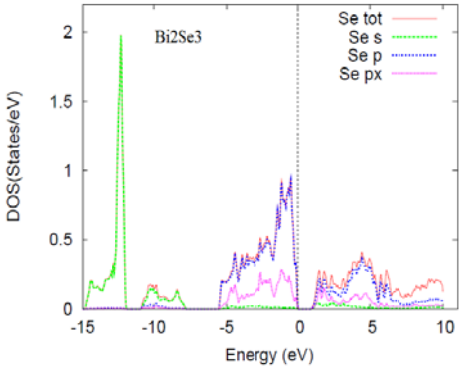


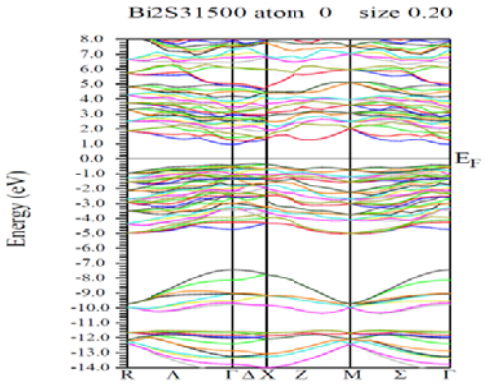
(a) Bi_2S_3



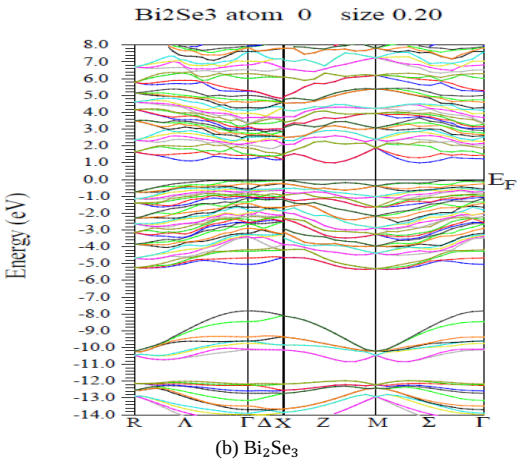
(b) Bi_2Se_3

Fig.6: S-total, S-*s* & S-*p* States of Bi_2S_3 and Se-total, Se-*s*, Se-*p* & Se-p_x States of Bi_2Se_3

From the band structure plots, we observed an indirect band gap of the order of 1.4 eV in Bi_2S_3[Fig.7(a)]and an indirect band gap of the order of 0.8 eV in Bi_2Se_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_2S_3 and Bi_2Se_3, and found that higher DOS regions correspond to more bands.



(a) Bi_2S_3



(b) Bi_2Se_3

Fig.7: The plots of band structures of Bi_2S_3 and Bi_2Se_3

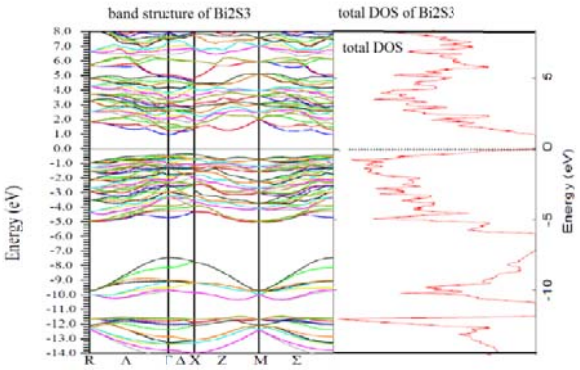


Fig.8: Band structure of Bi_2S_3 combined with DOS plot (Energy=0eV corresponds to Fermi Level, E_F)

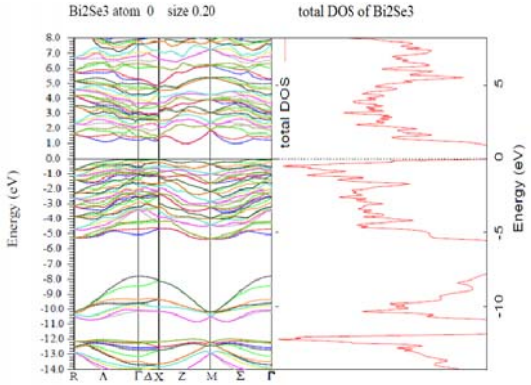


Fig.9: Band structure of Bi_2Se_3 combined with DOS plot (Energy=0eV corresponds to Fermi Level, E_F)

4. CONCLUSIONS

In conclusion, we have observed a qualitative agreement between theoretical and experimental lattice constants. Calculated band

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gap is very close to experimental value. Band gaps of the order of 1.4 eV and 0.8eV suggest that Bi_2S_3 and Bi_2Se_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_2S_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_2Se_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_2S_3 and 0.8eV in Bi_2Se_3) [14] seem to have differences. We propose to check these discrepancies with mBJ potential inclusion.

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