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Study of density of states and energy band structure in Bi_2S_3

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Abstract

The electronic structures for Bi_2S_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 structure show semiconducting behavior of Bi_2S_3 with a narrow indirect energy band gap of 1.4 eV.

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

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 [Erbarut, 2003]. Narrow gap semiconductor Bi_2S_3 is a classic room temperature thermoelectric material [Mohan, 2001]. It is the chalcogenide of poor metal having important technological applications in optoelectronic nano devices [Bao et al., 2007], field-emission electronic devices [Yu et al., 2005], photo-detectors and photo-electronic devices [Li et al., 2009] and photovoltaic convertors, thermoelectric cooling technologies based on the Peltier effect [Miller and Heller, 1976; Robin et al., 2006]. It has orthorhombic crystal structure at room temperature with x, y and z- positions of atoms [Lundegaard et al., 2005] as given in Table I. and space group Pnma (number 62) . The crystal structure of Bi_2S_3 is illustrated in Figure.1. In this report, we would like to present a systematic study of DOS and energy band structures of Bi_2S_3 using FP-LAPW method.

Table I

X, Y and Z positions of atoms of Bi_2S_3 at room temperature

Atom	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

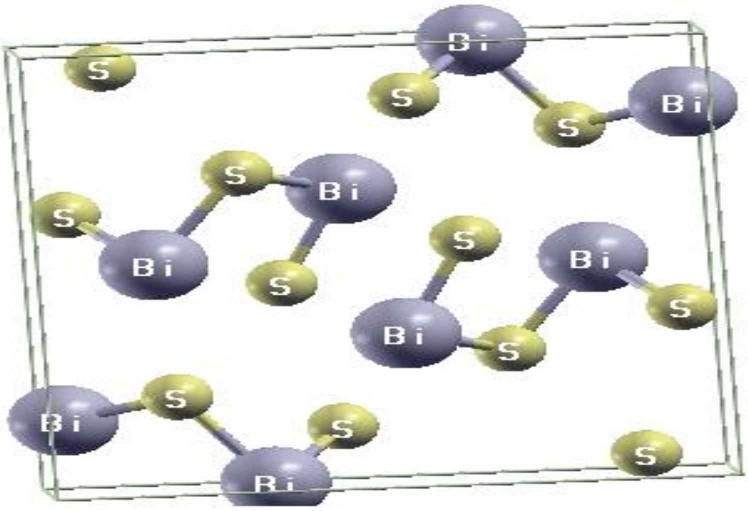

Figure 1: Unit cell structure of Bi_2S_3

2 Theory and computational methods

First principles FP-LAPW [Thapa et al., 2001] method based on density functional theory (DFT)) is used for calculations of DOS and band structure of Bi_2S_3. The calculated total energy (E) within GGA[Perdew , Burke and Ernzerhof, 1996] as a function of the volume (V) is 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 [Murnaghan, 1944]. A series of total energy calculations as a function of volume can be fitted to an equation of states according to Murnagha [1944.

$$E(V) = \quad + \quad \frac{(\frac{V_0}{V}}{B_0'}. + \frac{B_0}{B_0'} \tag{1}$$

where is the minimum energy at T = 0K, is the bulk modulus at the equilibrium volume and 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 Figure 2 [Schwartz and Blaha, 1903]. The equilibrium lattice constants are optimized using the experimental values of a= 11.269 Å, b=3.9717 Å and c= 11.129 Å [Lundegaard et al., 2005]. The calculation is accomplished by using the WIEN2K code [Blaha et al., 2001]. For exchange-correalation, we have used GGA. 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 are confined within l_{max}= 10. The wave functions in the interstitial region are 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* and Se: 4*s*, 4*p* states are treated as valance state and all other lower states are treated as core state. The potential and charge density are 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. A mesh of 1500 k-points is 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 which are shown in Figure 2.

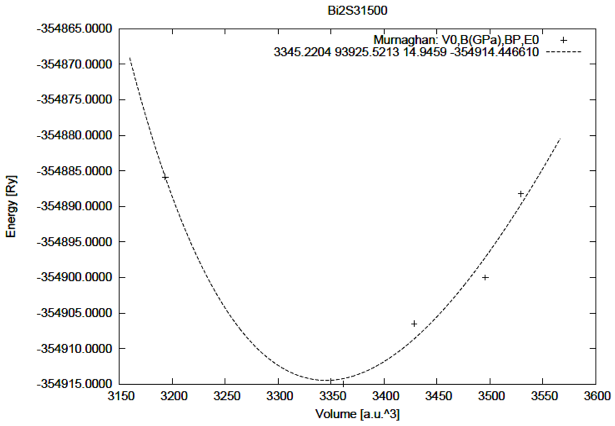

Figure 2: Energy versus Volume curve using the volume optimization method for Bi_2S_3

3 Results and Discussion

The total and partial DOS plots of Bi_2S_3 are shown in Figures.3,4,5 & 6. From the Figure 3 we have found that the contributions to total DOS are from Bi-6*p* and Se-4*p* electron states. 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 [Figure 4]. The conduction region, which is above the Fermi level, is mainly contributed by Bi-6*p*, 6*px*, 6*py* state electrons [Figure 5]. 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 [Figure 6].

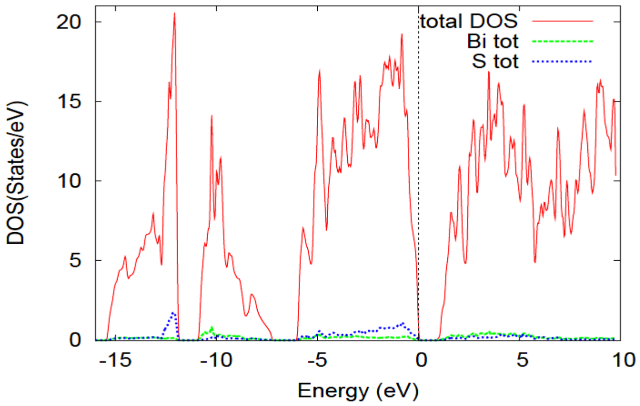

Figure 3: Bi_2S_3 -total, Bi-Total and S-total, Energy= 0 eV, corresponds to Fermi level

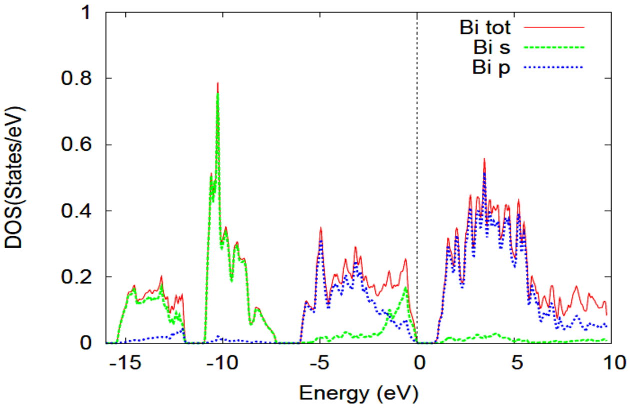

Figure 4: Bi-total, Bi-*s* & Bi-*p* states of Bi_2

From the band structure plot [Figure 7] we have observed an indirect band gap of the order of 1.4 eV. The band structure plot is also found with higher number of bands at the regions where peaks of the DOS are observed. In Figure 8, we have compared band structure with DOS plot of Bi_2S_3 and found that higher DOS regions correspond to more bands.

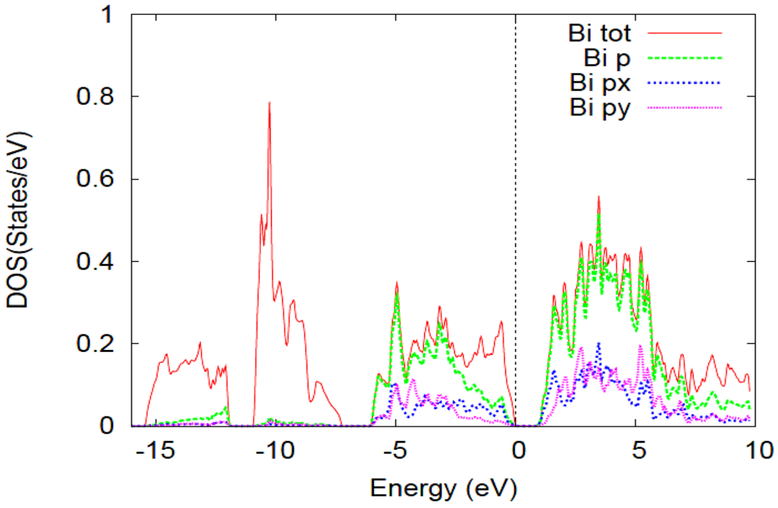

Figure 5: Bi-total, Bi-*p*, *px* & *py* states of Bi_2S_3

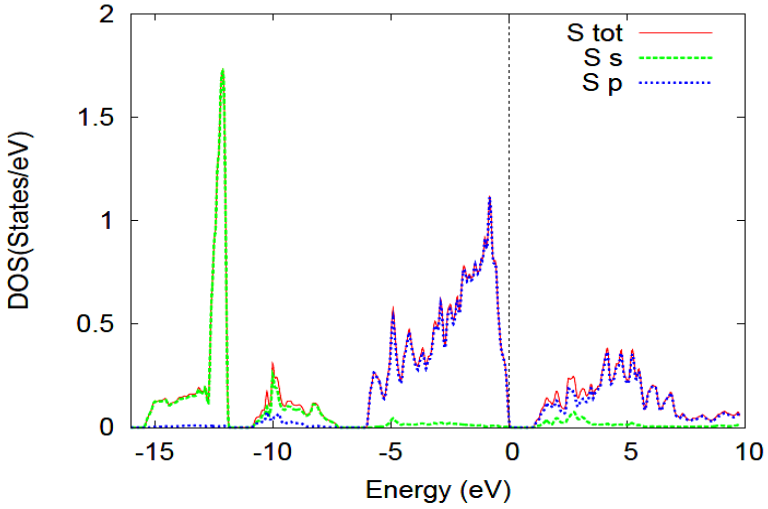

Figure 6: S-total, S-*s* & S-*p* States of Bi_2S_3

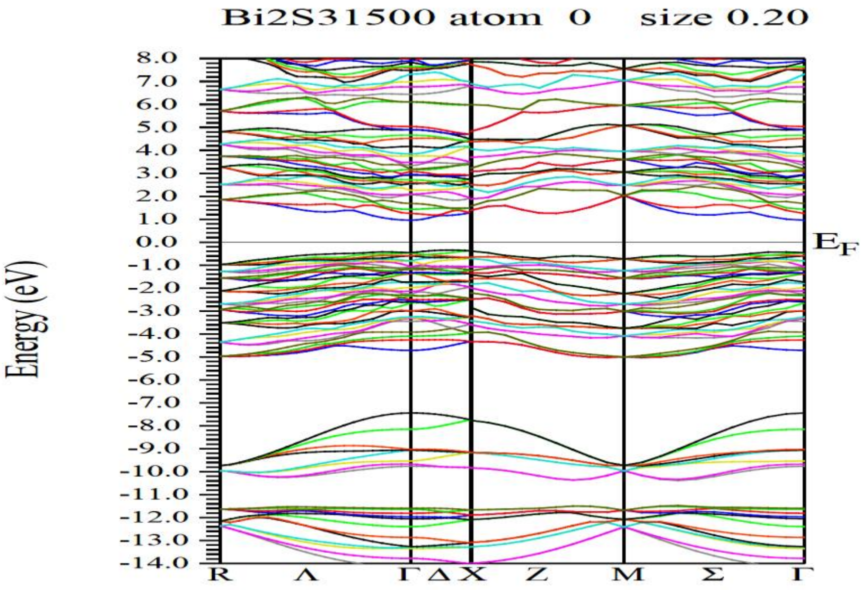

Figure 7: The plot of band structure of Bi_2S_3.

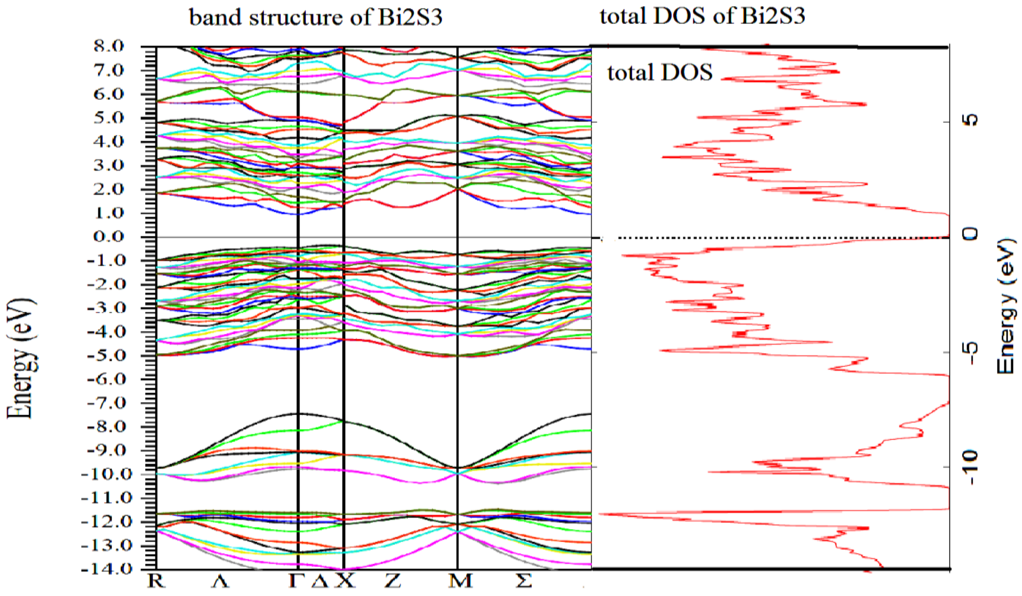

Figure 8: Band structure combined with DOS plot (Energy=0eV corresponds to Fermi Level.

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 gap of the order of 1.4 eV suggests that Bi_2S_3 is a semiconductor with low energy gap. The calculated band gap also suggests that the compound may be used as suitable candidate for thermoelectric applications. However, the band gap when checked with experimental value (1.3eV) [Black et al., 1957] seems to have differences. We propose to check these discrepancies with mBJ potential inclusion.

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