

Structural and electronic properties of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ ternary and $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$ quaternary compounds

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Structural and electronic properties of ternary compounds $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ and quaternary compounds $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$ are investigated by using the density functional theory within full potential-linearized augmented plane wave method. The structural properties of compounds are examined using the Murnaghan equation of state, which also contains experimental data for comparison. Specifically, band structures exhibit very similar behaviour in total density of states of compounds which show narrow-gap semiconductor material characteristics. $\text{Bi}_{1.66}\text{Sb}_{0.33}\text{Te}_3$, $\text{Bi}_{1.33}\text{Sb}_{0.66}\text{Te}_3$, BiSbTe_3 , $\text{Bi}_{0.66}\text{Sb}_{1.33}\text{Te}_3$ and $\text{Bi}_{0.33}\text{Sb}_{1.66}\text{Te}_3$ are direct band gap materials and the band gap energies of these compounds are found to depend linearly on compound composition x . $\text{Bi}_{1.66}\text{Sb}_{0.33}\text{Te}_{2.66}\text{Se}_{0.33}$, $\text{Bi}_{1.33}\text{Sb}_{0.66}\text{Te}_{2.33}\text{Se}_{0.66}$, BiSbTe_2Se , $\text{Bi}_{0.66}\text{Sb}_{1.33}\text{Te}_{1.66}\text{Se}_{1.33}$, Sb_2TeSe_2 , $\text{Sb}_2\text{Te}_{0.66}\text{Se}_{2.33}$ and $\text{Sb}_2\text{Te}_{0.33}\text{Se}_{2.66}$ are direct band gap materials and the band gap energies of these compounds are found to depend non-linearly on compound composition x and y . This theoretical work will be of great interest in ternary and quaternary semiconductor research.

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Keywords: Bismuth telluride, Antimony telluride, Antimony triselenide, Structural properties, Electronic properties

1. Introduction

Topological insulators, which are Sb_2Te_3 , Bi_2Te_3 and Bi_2Se_3 [1–3], are one of the real hot topics. Chalcogenides (such as Sb_2Te_3 , Bi_2Te_3 and Bi_2Se_3) are narrow band semiconductors and their electronic properties have been widely studied for many years. Semiconductors are materials whose electronic properties depend on the energy gap (E_g) width or band gap and dopant concentration [4–5]. The presence of impurities even in very small proportions can have large effects on the electronic properties. Therefore, the conductivity of semiconductors may easily be modified by introducing dopants into their crystal structure. Sb_2Te_3 is a promising candidate for phase change random access memories (PRAM) [6] because of its outstanding properties, such as fast speed, excellent endurance, low-programming energy and nondestructive reading. Besides, Bismuth Telluride (Bi_2Te_3) and its alloy are currently the best thermoelectric materials known at room temperature and therefore used for portable solid-state refrigeration. Moreover, Bismuth Telluride and its p-type and n-type alloys have layered structures consisting of 5 atom thick Te-Bi-Te-Bi-Te sheets. Lithium ions are intercalated into the layered materials using liquid ammonia. Lithium intercalated Bi_2Te_3 has a higher conductivity and lower Seebeck coefficient than pristine Bi_2Te_3 due to electron transfer from the lithium [7].

Bi_2Te_3 , Sb_2Te_3 and Bi_2Se_3 have rhombohedral crystal

structure and space group of them are D_{3d}^5 ($R\bar{3}m$). The rhombohedral primitive unit cell contains two non-equivalent sites for the Te/Se atoms, Te1/Se1 and Te2/Se2, and one for the Bi/Sb atoms. The energy gap of Bi_2Te_3 is reported as 0.13 [8], 0.15 [9]. The energy gap of Sb_2Te_3 is pointed 0.09 eV [10] in nature.

In this study, structural and electronic properties of Bi_2Te_3 , Sb_2Te_3 and Sb_2Se_3 are investigated using density functional theory. In addition, in order to dope atom to binary compounds of Bi_2Te_3 , Sb_2Te_3 and Bi_2Se_3 , we used the chemical formula of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ and $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$. Electronic charge densities, density of states and band structure properties have been investigated using WIEN2k software within the FP-LAPW method. All materials are characterized as narrow band gap semiconductors.

2. Computation details

The structural and electronic properties of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ and $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$ structures are investigated using the WIEN2k code within the framework of density functional theory [11–12]. The exchange correlation energy is treated using generalized gradient approximation (GGA) [13]. $R_{\text{mt}} * K_{\text{max}}$ parameter is taken equal to 7.0, where R_{mt} is the smallest atomic sphere radius in the unit cell and K_{max} is the magnitude of the largest K vector. Muffin-tin radii (a.u.) are selected to be 2.50 for $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ and

$\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$ structures. The crystal structures of all compounds are constructed using $1 \times 1 \times 1$ supercell. In order to add and substitute atoms, the space group is chosen P-1. The crystal structure of compound is shown in Fig. 1. The lattice parameters are $a = 4.38 \text{ \AA}$, and $c = 30.39 \text{ \AA}$, with the atomic positions of Te1 at $(0, 0, 0)$, Te2 at $(0, 0, 0.2069)$, and Bi at $(0, 0, 0.399)$ [14]. A mesh of 100 k-points in the range is taken for the Brillouin zone integrations in the corresponding irreducible wedge. The cut-off energy for separating core from valence states is set to -6 Ry .

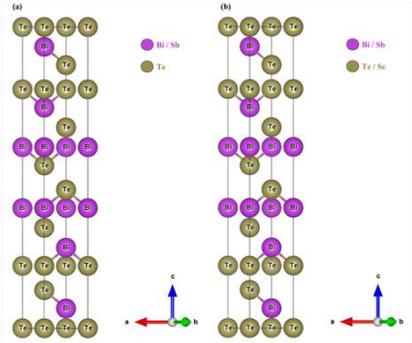


Fig. 1. The crystal structure of (a) $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ and (b) $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$

3. Results and discussion

3.1. Structural properties of compounds

$\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ and $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$

In order to investigate the ground states of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ and $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$, we firstly calculate the structural properties using FP-LAPW+lo approach. Using the optimized internal parameters, the total energy is calculated to obtain the absolute minimum in total energy for each structure at different volumes V . The calculated

total energies corresponding to volumes were fitted to the Murnaghan equation of state [15] in order to obtain the structural parameters; in other words, the equilibrium volume (V_0) of the unit cell, lattice constants, a and c , bulk modulus B as well as its first pressure derivative B' . The results are shown in Table 1, which also contains experimental data for comparison. The plots of calculated total energy versus reduced volume for binary (Bi_2Te_3 , Sb_2Te_3 and Sb_2Se_3) compounds are given in Fig. 2, for ternary ($\text{Bi}_{1.66}\text{Sb}_{0.33}\text{Te}_3$, $\text{Bi}_{1.33}\text{Sb}_{0.66}\text{Te}_3$, BiSbTe_3 , $\text{Bi}_{0.66}\text{Sb}_{1.33}\text{Te}_3$, $\text{Bi}_{0.33}\text{Sb}_{1.66}\text{Te}_3$) compounds are given in Fig. 3 and for quaternary ($\text{Bi}_{1.66}\text{Sb}_{0.33}\text{Te}_{2.66}\text{Se}_{0.33}$, $\text{Bi}_{1.33}\text{Sb}_{0.66}\text{Te}_{2.33}\text{Se}_{0.66}$, BiSbTe_2Se , $\text{Bi}_{0.66}\text{Sb}_{1.33}\text{Te}_{1.66}\text{Se}_{1.33}$ and $\text{Bi}_{0.33}\text{Sb}_{1.66}\text{Te}_{1.33}\text{Se}_{1.66}$) compounds are given in Figure 4. Our computed lattice parameters a , c are in good agreement with the available experimental data [16-21]. We note that the calculated lattice constant values are slightly lower than the measured ones while the GGA is generally known by its slight overestimation of the lattice constant value. This discrepancy may occur owing to the measurement conditions, such as the accuracy of measurement, temperature of measurement and so on.

Considering to Table 1, it is clear that the calculated bulk modulus value increases from Bi_2Te_3 to Sb_2Te_3 , suggesting that the compressibility decreases from Bi_2Te_3 to Sb_2Te_3 . Besides, the lattice parameter reduction and the enlargement in bulk modulus indicate the tightening tendency of lattice on decreasing size of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ structures. Bi and Sb atoms ratio could be responsible for the lattice constant decreasing from Bi_2Te_3 to Sb_2Te_3 . Considering table values, the results of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$ structures are similar to $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$. Consequently, in both $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ structures and $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$ structures, the contraction occurs in bulk modulus due to increasing of Antimony and Selenium atoms.

Table 1. Lattice constant $a(\text{\AA})$, $c(\text{\AA})$, bulk modulus $B(\text{GPa})$ and its first derivative B' , equilibrium volume V_0 for binary, ternary and quaternary compounds

System	$a(\text{\AA})$	$c(\text{\AA})$	$B(\text{GPa})$	B'	V_0
Binary					
Bi_2Te_3					
This work	4.43	30.9	43.35	9.33	3548.7179
Expt. [Ref.16,17]	4.38	30.5	-	-	-
Sb_2Te_3					
This work	4.37	29.79	47.82	4.21	3328.3142
Expt. [Ref.18]	4.26	30.45	-	-	-
Sb_2Se_3					
This work	4.082	28.16	61.95	5.39	2742.3609
Theory. [Ref.19]	4.076	29.83	-	-	-
Ternary					
$\text{Bi}_{1.66}\text{Sb}_{0.33}\text{Te}_3$					
This work	4.46	30.27	46.59	4.18	3521.8409
$\text{Bi}_{1.33}\text{Sb}_{0.66}\text{Te}_3$					
This work	4.44	30.3	46.79	4.154	3485.5617
BiSbTe_3					
This work	4.42	30.17	47.02	4.148	3448.1594
Expt. [Ref.20]	4.32	30.49	-	-	-

$\text{Bi}_{0.66}\text{Sb}_{1.33}\text{Te}_3$ This work	4.41	30.04	46.91	3.99	3409.7099
$\text{Bi}_{0.33}\text{Sb}_{1.66}\text{Te}_3$ This work	4.39	29.97	47.47	4.29	3369.0962
Quaternary					
$\text{Bi}_{1.66}\text{Sb}_{0.33}\text{Te}_{2.66}\text{Se}_{0.33}$ This work	4.43	30.01	47.25	4.6	3452.8626
$\text{Bi}_{1.33}\text{Sb}_{0.66}\text{Te}_{2.33}\text{Se}_{0.66}$ This work	4.39	29.73	49.17	4.47	3351.7043
BiSbTe_2Se This work	4.35	29.38	51.09	4.61	3252.3175
Expt. [Ref.21]	4.16	29.41	-	-	-
$\text{Bi}_{0.66}\text{Sb}_{1.33}\text{Te}_{1.66}\text{Se}_{1.33}$ This work	4.29	29.26	53.20	4.74	3055.0412
$\text{Bi}_{0.33}\text{Sb}_{1.66}\text{Te}_{1.33}\text{Se}_{1.66}$ This work	4.25	28.93	54.52	4.52	2942.4191

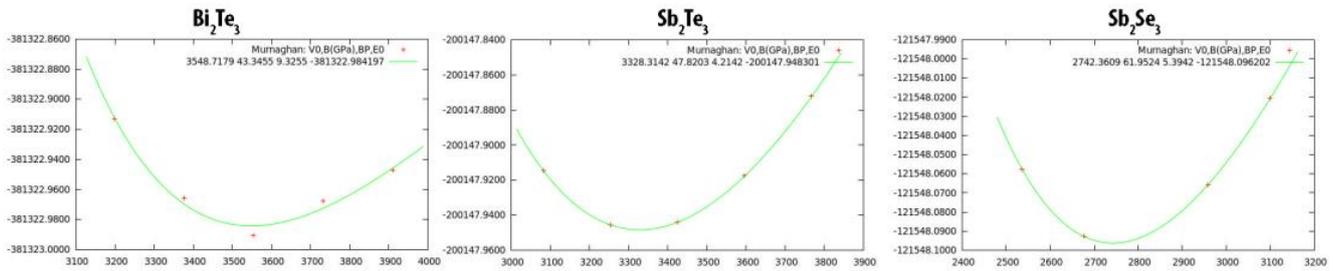


Fig. 2. Optimization graphics of binary compounds (Bi_2Te_3 , Sb_2Te_3 and Sb_2Se_3)

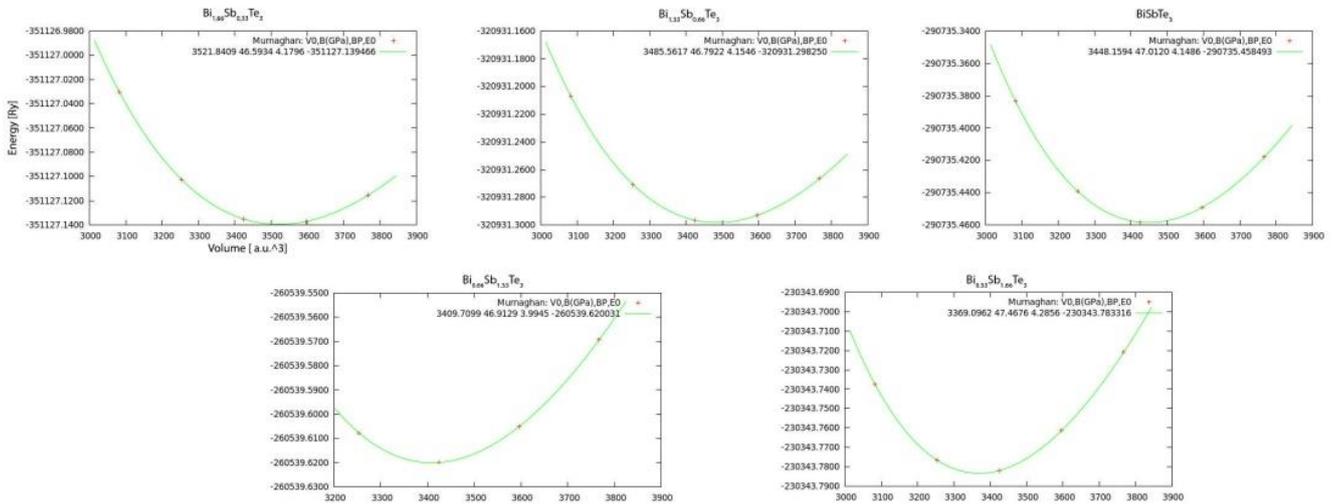


Fig. 3. Optimization graphics of ternary compounds ($\text{Bi}_{1.66}\text{Sb}_{0.33}\text{Te}_3$, $\text{Bi}_{1.33}\text{Sb}_{0.66}\text{Te}_3$, BiSbTe_3 , $\text{Bi}_{0.66}\text{Sb}_{1.33}\text{Te}_3$ and $\text{Bi}_{0.33}\text{Sb}_{1.66}\text{Te}_3$)

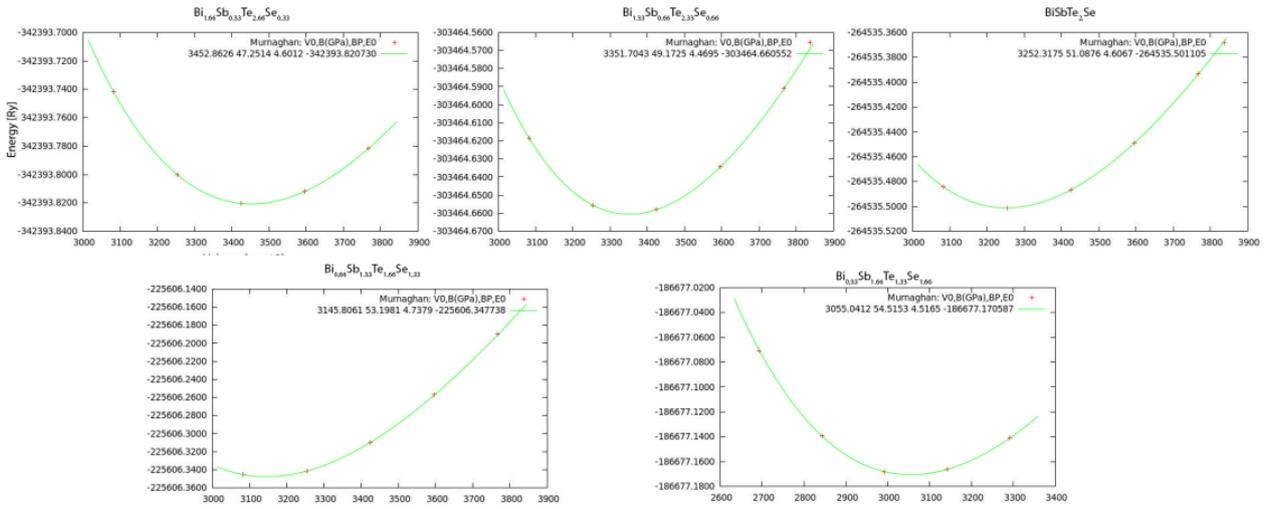


Fig. 4. Optimization graphics of quaternary compounds ($Bi_{1.66}Sb_{0.33}Te_{2.66}Se_{0.33}$, $Bi_{1.33}Sb_{0.66}Te_{2.33}Se_{0.66}$, $BiSbTe_2Se$, $Bi_{0.66}Sb_{1.33}Te_{1.66}Se_{1.33}$ and $Bi_{0.33}Sb_{1.66}Te_{1.33}Se_{1.66}$)

3.2. Electronic properties of compounds $Bi_{2-x}Sb_xTe_3$ and $Bi_{2-x}Sb_xTe_{3-y}Se_y$

3.2.1 Electronic properties of binary compounds Bi_2Te_3 , Sb_2Te_3 and Sb_2Se_3

The electronic properties of binary compounds Bi_2Te_3 , Sb_2Te_3 and Sb_2Se_3 are discussed by calculating the band structures and the electronic total density of states (TDOS). The band structures of the alloys using GGA exchange potential are shown along with high symmetry points in Fig. 5. It can be observed in Fig. 5 (a) and Fig. 5 (b) that the top of valence band and the bottom of conduction band are positioned at same symmetry points Γ

for Bi_2Te_3 and Sb_2Te_3 , respectively. However, it can be observed in Fig. 5 (c) that top of the valance band is positioned between symmetry points Γ and M, whereas the bottom of conduction band is positioned between symmetry points Γ for Sb_2Se_3 . Bi_2Te_3 and Sb_2Te_3 compounds show direct band gap material characteristics which enables them to be considered as a future prospect material for optoelectronic devices; on the other hand, Sb_2Se_3 compound shows indirect band gap material characteristics. Total density of states of alloys exhibits very similar behavior in band structures, which show narrow-gap semiconductor material characteristics. The calculated band gap energies are given in Table 2 for binary compounds Bi_2Te_3 , Sb_2Te_3 and Sb_2Se_3 .

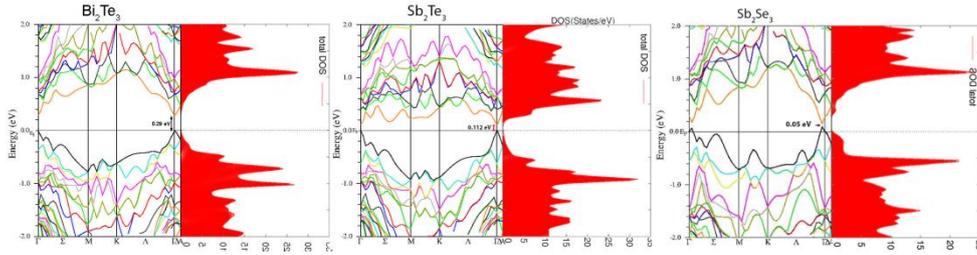


Fig. 5. Band Structures of binary compounds (Bi_2Te_3 , Sb_2Te_3 and Sb_2Se_3)

Table 2. Band Gap Energies for Binary Compounds (Bi_2Te_3 , Sb_2Te_3 , Sb_2Se_3)

Binary			
Compounds	Bi_2Te_3	Sb_2Te_3	Sb_2Se_3
$E_g(eV)$	0.29	0.112	0.05

3.2.2 Electronic properties of ternary compounds $Bi_{2-x}Sb_xTe_3$ for $x=0.33, 0.66, 1.00, 1.33, 1.66$

The electronic properties of ternary compounds $Bi_{1.66}Sb_{0.33}Te_3$, $Bi_{1.33}Sb_{0.66}Te_3$, $BiSbTe_3$, $Bi_{0.66}Sb_{1.33}Te_3$ and

$Bi_{0.33}Sb_{1.66}Te_3$ are discussed by calculating the band structures and the electronic total density of states (TDOS). The band structures of the alloys using GGA exchange potential are shown along with high symmetry points in Fig. 6. All compounds are characterized direct band gap materials which show narrow-gap semiconductor material characteristics. The band gap energy is found to depend linearly on compound composition x . The changes of band gap energy are caused by substitution of Sb with Bi. The calculated band gap energies are given in Table 3 for ternary compounds $Bi_{1.66}Sb_{0.33}Te_3$, $Bi_{1.33}Sb_{0.66}Te_3$, $BiSbTe_3$, $Bi_{0.66}Sb_{1.33}Te_3$ and $Bi_{0.33}Sb_{1.66}Te_3$.

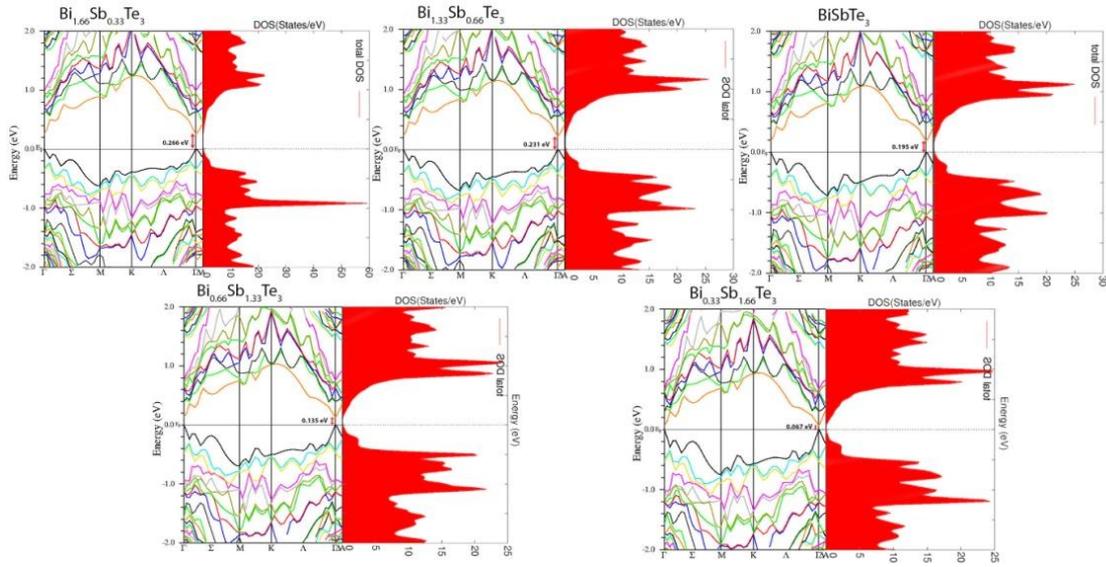


Fig. 6. Band Structures of ternary compounds ($\text{Bi}_{1.66}\text{Sb}_{0.33}\text{Te}_3$, $\text{Bi}_{1.33}\text{Sb}_{0.66}\text{Te}_3$, BiSbTe_3 , $\text{Bi}_{0.66}\text{Sb}_{1.33}\text{Te}_3$ and $\text{Bi}_{0.33}\text{Sb}_{1.66}\text{Te}_3$)

Table 3. Band Gap Energies for Ternary Compounds ($\text{Bi}_{1.66}\text{Sb}_{0.33}\text{Te}_3$, $\text{Bi}_{1.33}\text{Sb}_{0.66}\text{Te}_3$, BiSbTe_3 , $\text{Bi}_{0.66}\text{Sb}_{1.33}\text{Te}_3$ and $\text{Bi}_{0.33}\text{Sb}_{1.66}\text{Te}_3$)

Ternary	$\text{Bi}_{1.66}\text{Sb}_{0.33}\text{Te}_3$	$\text{Bi}_{1.33}\text{Sb}_{0.66}\text{Te}_3$	BiSbTe_3	$\text{Bi}_{0.66}\text{Sb}_{1.33}\text{Te}_3$	$\text{Bi}_{0.33}\text{Sb}_{1.66}\text{Te}_3$
$E_g(\text{eV})$	0.266	0.231	0.195	0.135	0.067

3.2.3 Electronic properties of quaternary compounds $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$ for $x=y=0.33, 0.66, 1.00, 1.33, 1.66$

The electronic properties of quaternary compounds $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$ are discussed by calculating the band structures and the electronic total density of states (TDOS). The band structures of the alloys using GGA

exchange potential are shown along with high symmetry points in Fig. 7. All compounds are characterized by direct band gap materials which show narrow-gap semiconductor material characteristics. The band gap energy is found to depend non-linearly on compound composition x and y . The changes in band gap energy are caused by substitution of Sb with Bi and Te with Se. The calculated band gap energies are given in Table 4 for quaternary compounds.

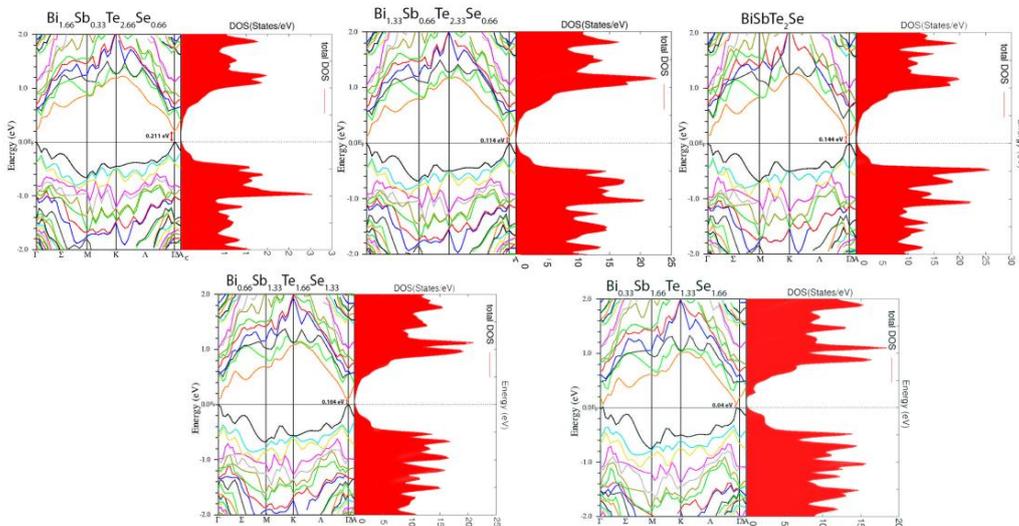


Fig. 7. Band Structures of quaternary compounds ($\text{Bi}_{1.66}\text{Sb}_{0.33}\text{Te}_{2.66}\text{Se}_{0.66}$, $\text{Bi}_{1.33}\text{Sb}_{0.66}\text{Te}_{2.33}\text{Se}_{0.66}$, BiSbTe_2Se , $\text{Bi}_{0.66}\text{Sb}_{1.33}\text{Te}_{1.66}\text{Se}_{1.33}$ and $\text{Bi}_{0.33}\text{Sb}_{1.66}\text{Te}_{1.33}\text{Se}_{1.66}$)

Table 4. Band Gap Energies for Quaternary Compounds ($Bi_{1.66}Sb_{0.33}Te_{2.66}Se_{0.33}$, $Bi_{1.33}Sb_{0.66}Te_{2.33}Se_{0.66}$, $BiSbTe_2Se$, $Bi_{0.66}Sb_{1.33}Te_{1.66}Se_{1.33}$, Sb_2TeSe_2 , $Sb_2Te_{0.66}Se_{2.33}$ and $Sb_2Te_{0.33}Se_{2.66}$)

Compounds	$Bi_{1.66}Sb_{0.33}Te_{2.66}Se_{0.33}$	$Bi_{1.33}Sb_{0.66}Te_{2.33}Se_{0.66}$	$BiSbTe_2Se$
$E_g(eV)$	0.211	0.114	0.144
Compounds	$Bi_{0.66}Sb_{1.33}Te_{1.66}Se_{1.33}$	$Bi_{0.33}Sb_{1.66}Te_{1.33}Se_{1.66}$	
$E_g(eV)$	0.104	0.04	

4. Conclusion

Structural and electronic properties of ternary compounds $Bi_{2-x}Sb_xTe_3$ and quaternary compounds $Bi_{2-x}Sb_xTe_{3-y}Se_y$ are presented by using the DFT within FP-LAPW method. The exchange correlation energy is treated by using GGA. The ternary compounds $Bi_{2-x}Sb_xTe_3$ and quaternary compounds $Bi_{2-x}Sb_xTe_{3-y}Se_y$ have rhombohedral crystal structure. The lattice parameters are optimized using the Murnaghan equation of state, which also contains experimental data for comparison. Both $Bi_{2-x}Sb_xTe_3$ structures and $Bi_{2-x}Sb_xTe_{3-y}Se_y$ structures the contraction occurs in bulk modulus due to increasing Antimony and Selenium atoms. Specifically, band structures exhibit very similar behaviour in total density of states of compounds, which show semiconductor material characteristics. $Bi_{1.66}Sb_{0.33}Te_3$, $Bi_{1.33}Sb_{0.66}Te_3$, $BiSbTe_3$, $Bi_{0.66}Sb_{1.33}Te_3$ and $Bi_{0.33}Sb_{1.66}Te_3$ are direct band gap materials and the band gap energies of these compounds are found to depend linearly on compound composition x. $Bi_{1.66}Sb_{0.33}Te_{2.66}Se_{0.33}$, $Bi_{1.33}Sb_{0.66}Te_{2.33}Se_{0.66}$, $BiSbTe_2Se$, $Bi_{0.66}Sb_{1.33}Te_{1.66}Se_{1.33}$, Sb_2TeSe_2 , $Sb_2Te_{0.66}Se_{2.33}$ and $Sb_2Te_{0.33}Se_{2.66}$ are direct band gap materials and the band gap energies of these compounds are found to depend non-linearly on compound composition x and y. The changes of band gap energy are caused by substitution of Sb with Bi and Te with Se. All ternary and quaternary compounds are characterized by narrow-gap semiconductors according to the band gap energies. Band gap energies of compounds correspond to the infrared region in the electromagnetic spectrum. Therefore, these alloys could be used for infrared detectors. This theoretical work will be of great interest in ternary and quaternary semiconductor research.

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