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The Structural and Electronic Properties of $TlGa_{1-x}In_xTe_2$ (x=0.00, 0.25, 0.50, 0.75) Alloys

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Abstract: In this study, the structural and electronic properties of $TlGa_{1-x}In_xTe_2$ alloys have been investigated using the full potential linearized augmented plane wave (FP-LAPW) method within the density functional theory (DFT). The $TlGa_{1-x}In_xTe_2$ (x=0.25, 0.50, 0.75) alloys have tetragonal structure as in $TlInTe_2$ and $TlGaTe_2$ alloys. We create the crystal structure of these alloys using the P1 (C_1^1) space group. We found that the value of the lattice parameter a and volume of unit cell increases with increasing In concentrations. These alloys have characteristics of semiconductors. Moreover, we show that the band gap energy is dependent on the alloy composition index x. The calculated band gap energies indicate that all the studied alloys here are characterized by narrow band-gap semiconductors. The finding of this study motivates further future studies for concerning quaternary $TlGa_{1-x}In_xTe_2$ for x=0.25, 0.50 and 0.75 alloys.

***Key words**:* DFT Method, Structural Properties, Electronic Properties.

$TlGa_{1-x}In_xTe_2$ (x=0.00, 0.25, 0.50, 0.75) Alaşımlarının Yapısal ve Elektronik Özellikleri

Özet: Bu çalışmada**,** yoğunluk fonksiyonel teorisi dahilinde lineer genişletilmiş düzlem dalga metodu kullanılarak $TlGa_{1-x}In_xTe_2$ alaşımlarının yapısal ve elektronik özellikleri incelendi. $TlGa_{1-x}In_xTe_2$ (x=0.25, 0.50, 0.75) alaşımları, $TlInTe_2$ ve $TlGaTe_2$ alaşımları gibi tetragonal yapıya sahiptir. Alaşımların Kristal yapıları P1 (C_1^1) uzay grubu kullanılarak elde edildi. Yapısal hesaplamalardan, birim hücre içerisindeki In konsantrasyonunun artışı ile örgü parametresi a ve birim hücre hacminin arttığı tespit edildi. Incelenen alaşımların, elektronik band yapı ve durum yoğunluğu hesaplamalarından, yarıiletken özellik sergilediğini bulundu. Ayrıca, alaşımların yasak band enerjisinin, x konsantrasyonuna bağlı olarak değiştiği tespit edildi. Hesaplanan yasak band enerjileri, alaşımların dar band aralıklı yarıiletken olduğunu göstermektedir. Bu çalışmanın bulguları dörtlü $TlGa_{1-x}In_xTe_2$ (x=0.25, 0.50, 0.75) alaşımları ile ilgilenen araştırmacılar için iyi bir referans çalışma olacaktır.

Anahtar kelimeler: DFT Metot, Yapısal Özellikler, Elektronik Özellikler.

1. Introduction

The family of compounds identified with the chemical formula $TlXY_2$ (X = In, Ga and Y = S, Se, Te) is known as thallium dichalcogenides [1–4]. The structural, electrical and

photoelectric properties of thallium-based semiconductors have been investigated in previous studies [5-9]. The ternary alloy $TlInTe_2$ and $TlGaTe_2$ have partially chain-like crystal structure. The space group of $TlInTe_2$ alloy, exactly the same as TlSe alloy, is D_{4h}^{18} (I4/mcm). There are four selenium ions around the indium trivalent ions (In^{3+}) they form negatively charged chains (In^{3+}-Te^{2-}) along the tetragonal z-axis. There are both covalent and ionic bonds between the atoms forming the chains, where covalent bonds are relatively stronger than ionic bonds [10]. The electrothermal properties of $TlInTe_2$ and $TlGaTe_2$ alloys have been studied experimentally in Ref [11]. The band gap energy of $TlGaTe_2$ is reported as 0.84 eV from experimental study [12]. The quaternary $TlGa_{1-x}In_xTe_2$ (x=0.25, 0.50, 0.75) alloys can be formed from the substitution of In and Ga atoms in $TlInTe_2$ crystal structure. In this paper, the electronic properties of ternary $TlInTe_2$, $TlGaTe_2$ and quaternary $TlGa_{0.75}In_{0.25}Te_2$, $TlGa_{0.50}In_{0.50}Te_2$, $TlGa_{0.25}In_{0.75}Te_2$ alloys are investigated the using the FP-LAPW method [13] within the DFT [14].

2. Material and Method

The calculations of alloys were performed using WIEN2k software package [15-17] within the framework of DFT. The required ground state of lattice parameters for the cases x=0.00, 0.25, 0.50, 0.75, 1.00 are obtained by fitting experimental lattice parameters [18]. We set the cut-off energy for separating core from valance states to -6 Ry. The exchange correlation energy are treated with the Perdew-Burke-Ernzerhof (PBE) generalized gradient approach (GGA) [19]. In order to improve band gap calculations and electronic structures, we used Tran-Blaha modification of the Beckee-Johnson potential (TB-mBJ) [20] in the SCF calculations. In our study, we take $R_{MT} * K_{MAX}$ parameter equal to 7.0. Here, R_{MT} is the smallest atomic sphere radius in the unit cell and K_{MAX} is the magnitude of the largest K vector. We have performed the calculations using a mesh of 100 k-points in the Brillouin zone. In addition, we perform Brillouin zone integrations on 4x4x5 k-points meshes for all alloys. The cutoff in the charge density Fourier expansion, G_{MAX}, is taken to be 12. In order to substitute In and Ga atoms, the crystal structure of these alloys are created using the P1 (C_1^1) space group and 1x1x1 supercell.

3. Results

3.1. The structural properties of alloys

A typical thallium dichalcogenide alloy consists of two body centered tetragonal unit cells. There are four Tl atoms, four In atoms and eight Te atoms in each unit cell. The crystal structures of $TlGa_{1-x}In_xTe_2$ alloys for the cases x=0.00, 0.25, 0.50, 0.75 are shown in Figure 1. The ground state structural properties are investigated by fitting the total energy versus c/a graph (Figure 2). The lattice constants, bulk modulus, pressure derivatives of the bulk modulus and ground state energy values of the alloys are calculated at the ground state using Birch Murnaghan's equation of state [21]. The structural properties are presented in Table 1. From the table, we found that the value of the lattice parameter and volume of unit cell increases with increasing In concentrations. In addition, bond length of Tl-Tl, Ga-Te and In-Te increase depending on as In concentration. Because the atomic radius of In atoms are more greater than the atomic radius of Ga atoms.

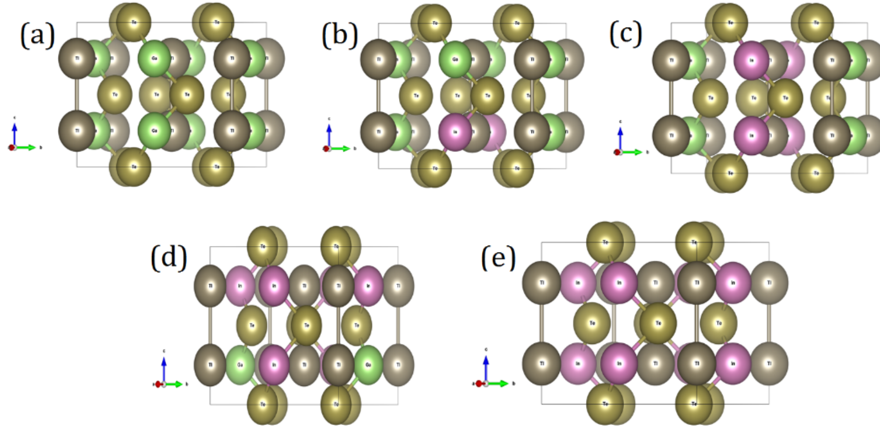

Figure 1. The crystal structures of alloys (a) $TlGaTe_2$, (b) $TlGa_{0.75}In_{0.25}Te_2$, (c) $TlGa_{0.50}In_{0.50}Te_2$, (d) $TlGa_{0.25}In_{0.75}Te_2$ and (e) $TlGaInTe_2$.

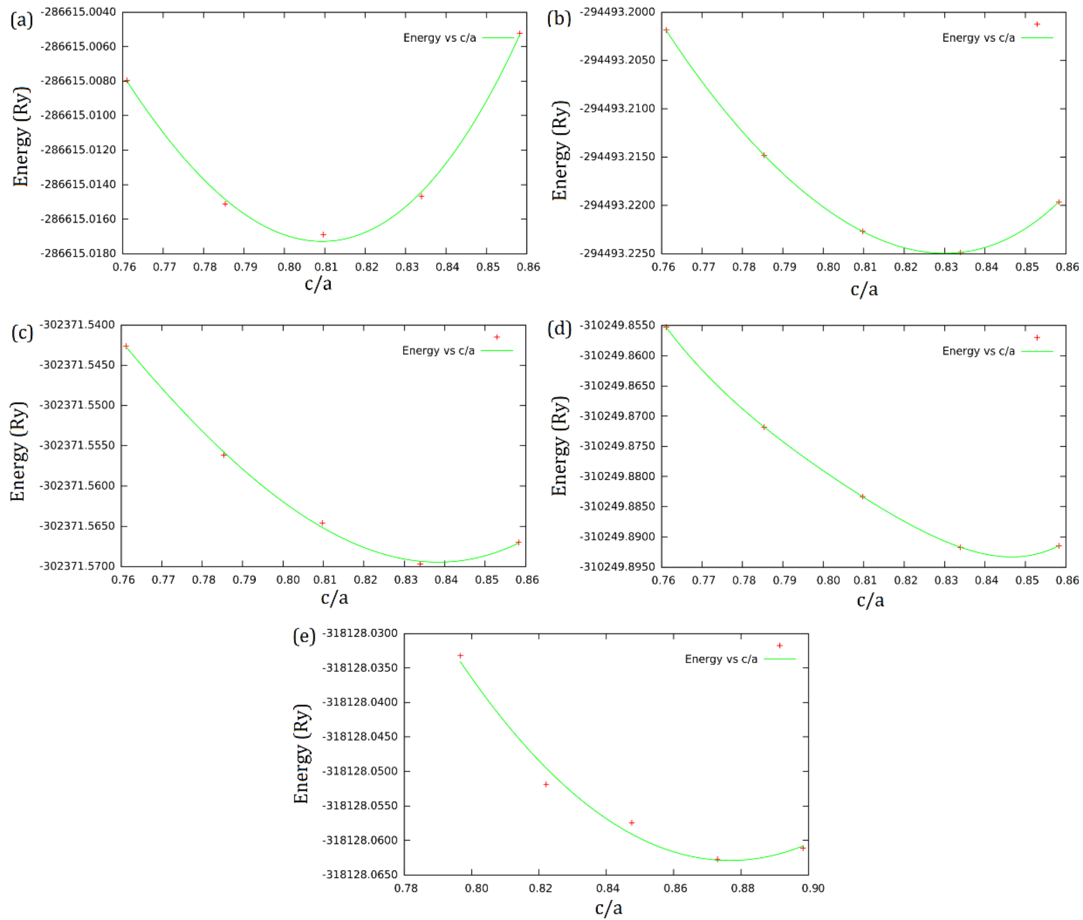

Figure 2. The total energy versus c/a graph for (a) $TlGaTe_2$, (b) $TlGa_{0.75}In_{0.25}Te_2$, (c) $TlGa_{0.50}In_{0.50}Te_2$, (d) $TlGa_{0.25}In_{0.75}Te_2$ and (e) $TlGaInTe_2$.

Table 1. The calculated lattice constants (a and c), bulk modulus (B), pressure derivatives of the bulk modulus (B') and bond length *R-R* in unit Å

Alloy	a (Å)	c (Å)	B(GPa)	B'	R_{Tl}-R_{Tl}	R_{Ga}-R_{Te}	R_{In}-R_{Te}
$TlGaTe_2$	8.5454	6.9183	36.3758	4.6483	3.46	2.70	-
$TlGa_{0.75}In_{0.25}Te_2$	8.6344	7.0370	35.1219	4.5924	3.52	2.73	2.73
$TlGa_{0.50}In_{0.50}Te_2$	8.6694	7.1740	35.7022	4.1969	3.59	2.76	2.76
$TlGa_{0.25}In_{0.75}Te_2$	8.7130	7.3674	32.9751	4.3624	3.68	2.80	2.80
$TlInTe_2$	8.7535	7.3609	33.3824	4.3601	3.68	-	2.81

3.2. The electronic properties of alloys

We analyzed the electronic properties of $TlGaTe_2$, $TlGa_{0.75}In_{0.25}Te_2$, $TlGa_{0.50}In_{0.50}Te_2$, $TlGa_{0.25}In_{0.75}Te_2$ and $TlInTe_2$ alloys in this subsection. These include the band structure, the electronic total density of states (TDOS) and partial density of states (PDOS). The band structures of the alloys are calculated using mBJ methods and are shown along with high symmetry points in Figure 3. As can be seen from Figure 3, the top of the valance band and bottom of the conduction band are positioned at the same symmetry point Γ. This shows that the all alloys have characteristics of a direct band gap material, and hence can be considered as a future prospective material for optoelectronic devices. From the figure band gap energies (E_g), the antisymmetric gap (E_{AS}) between the two lowest valence bands and the total valance band width (E_{VB}) are obtained by using mBJ method are given in Table 2. The antisymmetric gap (E_{AS}) between the two lowest valence bands and the total valance band width (E_{VB}) are used to calculate ionicity parameter. The ionicity is directly associated with the characteristics of the chemical bond, which provides us with a means for explaining and classifying the properties of the alloys. We calculate the ionicity parameter for all crystals adopting the empirical formula used in ref. [22]. In this empirical formula, the ionicity parameter is defined as Equation 1. The calculated ionicity parameters show that $TlGaTe_2$ is more covalent than other alloys.

$$f_i = \frac{1}{2}\left[1 - \cos\left(\pi \frac{E_{AS}}{E_{VB}}\right)\right] \tag{1}$$

Table 2. The calculated band gap energies (E_g), the antisymmetric gap (E_{AS}), the total valance band width (E_{VB}) and ionicity parameters (f_i).

Alloys	E_g (eV)	E_{AS} (eV)	E_{VB} (eV)	f_i
$TlGaTe_2$	0.94	3.36	11.72	0.19
$TlGa_{0.75}In_{0.25}Te_2$	1.05	3.50	11.50	0.21
$TlGa_{0.50}In_{0.50}Te_2$	1.14	3.55	11.42	0.22
$TlGa_{0.25}In_{0.75}Te_2$	1.28	3.67	11.35	0.23
$TlInTe_2$	1.26	3.63	11.35	0.24

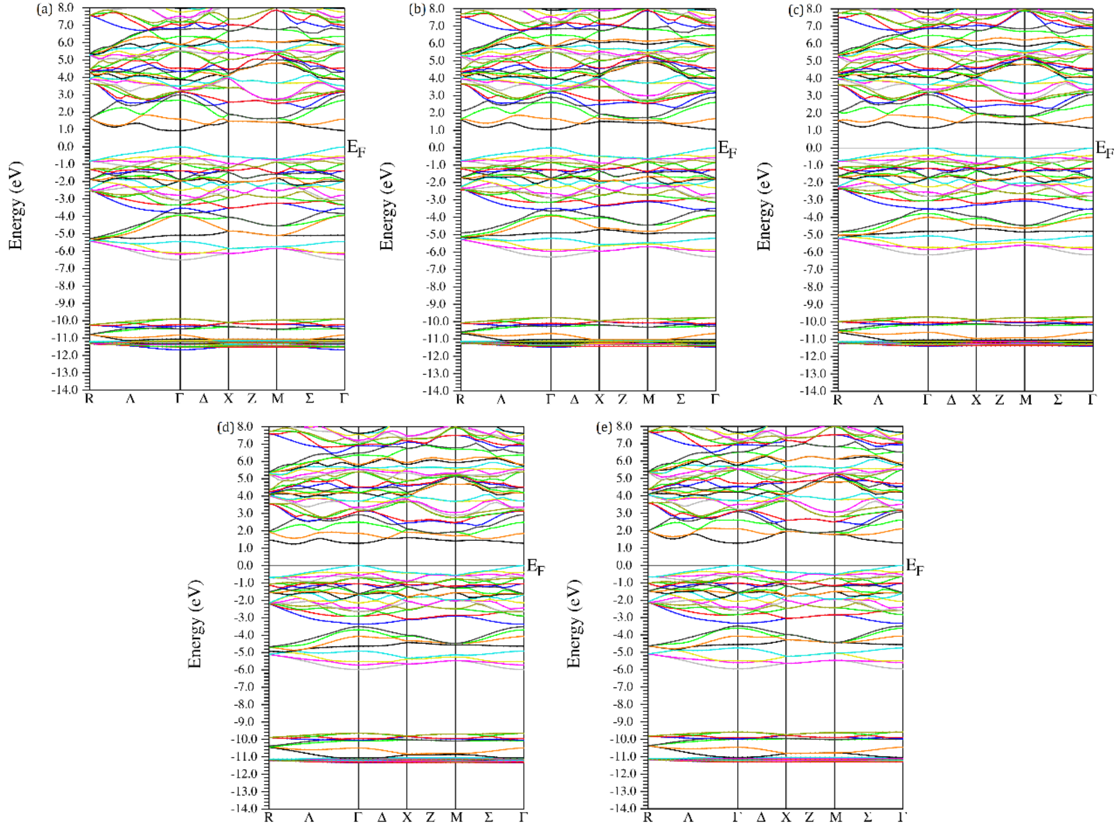

Figure 3. The obtained band structures for (a) $TlGaTe_2$, (b) $TlGa_{0.75}In_{0.25}Te_2$, (c) $TlGa_{0.50}In_{0.50}Te_2$, (d) $TlGa_{0.25}In_{0.75}Te_2$ and (e) $TlGaInTe_2$.

Figure 4 we illustrate the TDOS and PDOS of $TlGaTe_2$ crystal system using mBJ method. As can be seen from the Figure that TDOS exhibits very similar behaviour to that of the band structure. From figure, we see that the valence band is divided into two sub-bands. The low energy sub-band extends from -10.98 eV to -9.83 eV. The d-states of Tl atoms and the s-states of Te atoms mainly create these bands. The high energy sub-band extends from -6.57 eV to Fermi level. The s-states of Tl atoms, the s and p-states of Ga atoms and p-states of Te atoms mainly create this band. Moreover, the d and p-states of Tl atoms and d-states of Ga atoms rarely appears in this band. This results shows that the high energy sub-band located between -6.57 eV and Fermi levels mainly dominated by Tl and Ga atoms. In addition, the peaks in conduction band between 0.91 eV and 16.20 eV mainly result from p states of Tl atoms, s and p-states of Ga atoms. The d-states of Tl, Te, Ga atoms and s-states of Tl atoms rarely effect formation of conduction band.

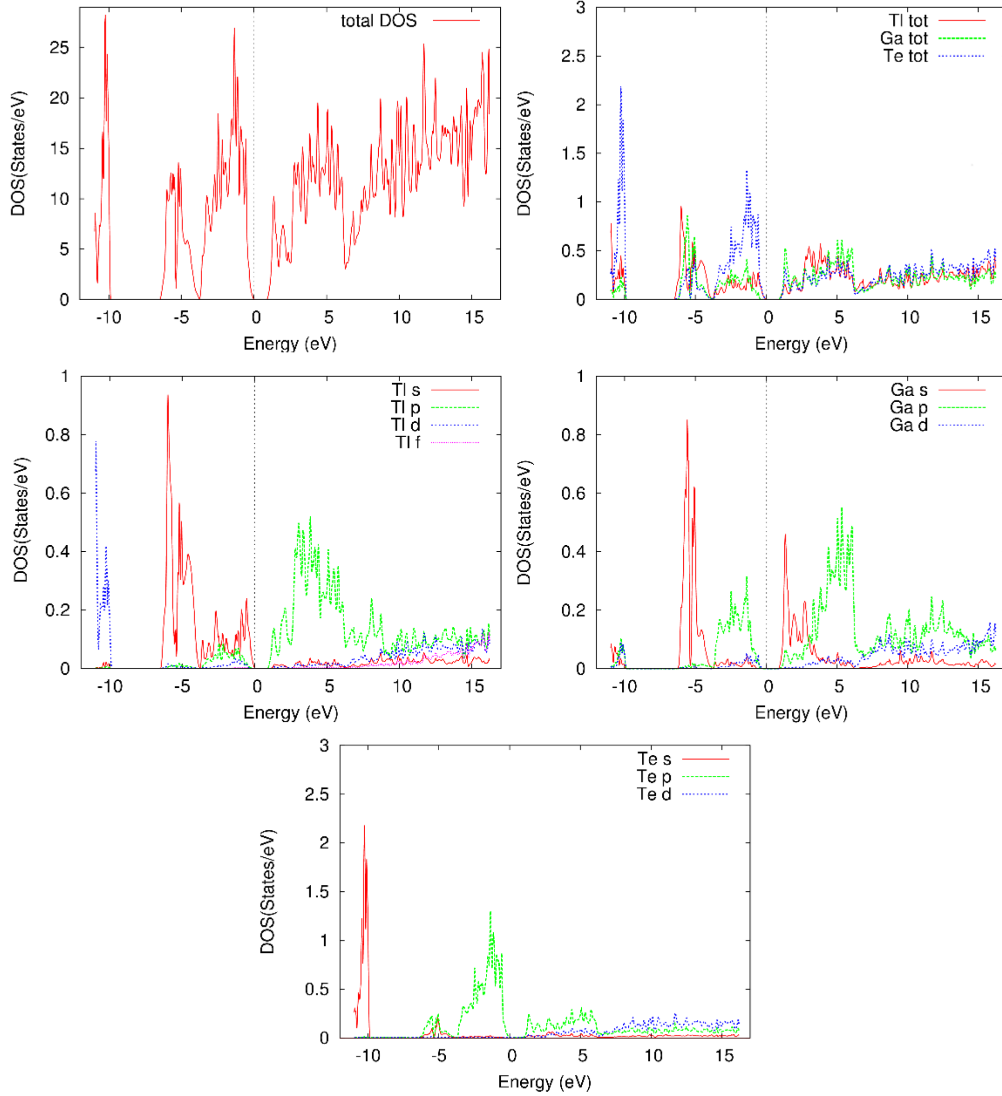

Figure 4. The TDOS and PDOS of $TlGaTe_2$ alloy.

We illustrate the TDOS and PDOS of $TlGa_{0.75}In_{0.25}Te_2$ crystal system using mBJ method Figure 5. As can be seen from the Figure that TDOS exhibits very similar behavior to that of the band structure. From figure we see that the valence band is divided into two sub-bands. The low energy sub-band extends from -10.69 eV to -9.72 eV. The d-states of Tl atoms and In atoms, s-states of Te atoms mainly create these bands. The high energy sub-band extends from -6.57 eV to Fermi level. The s-states of Tl, Ga, In atoms and p-states of Ga, In, Te atoms mainly create this band. Moreover the d -states of Tl and In atoms and p-states of Tl atoms rarely appears in this band. This results shows that the high energy sub-band located between -6.57 eV and Fermi level is mainly dominated by Tl, In, Te and Ga atoms. In addition, the peaks in conduction band between 0.95 eV and 16.49 eV mainly result from p states of Tl, Ga, In atoms and s-states of Ga, In atoms. The d-states of Tl, Te, Ga, In atoms, s-states of Tl atoms and p-states of Te atoms rarely effect formation of conduction band.

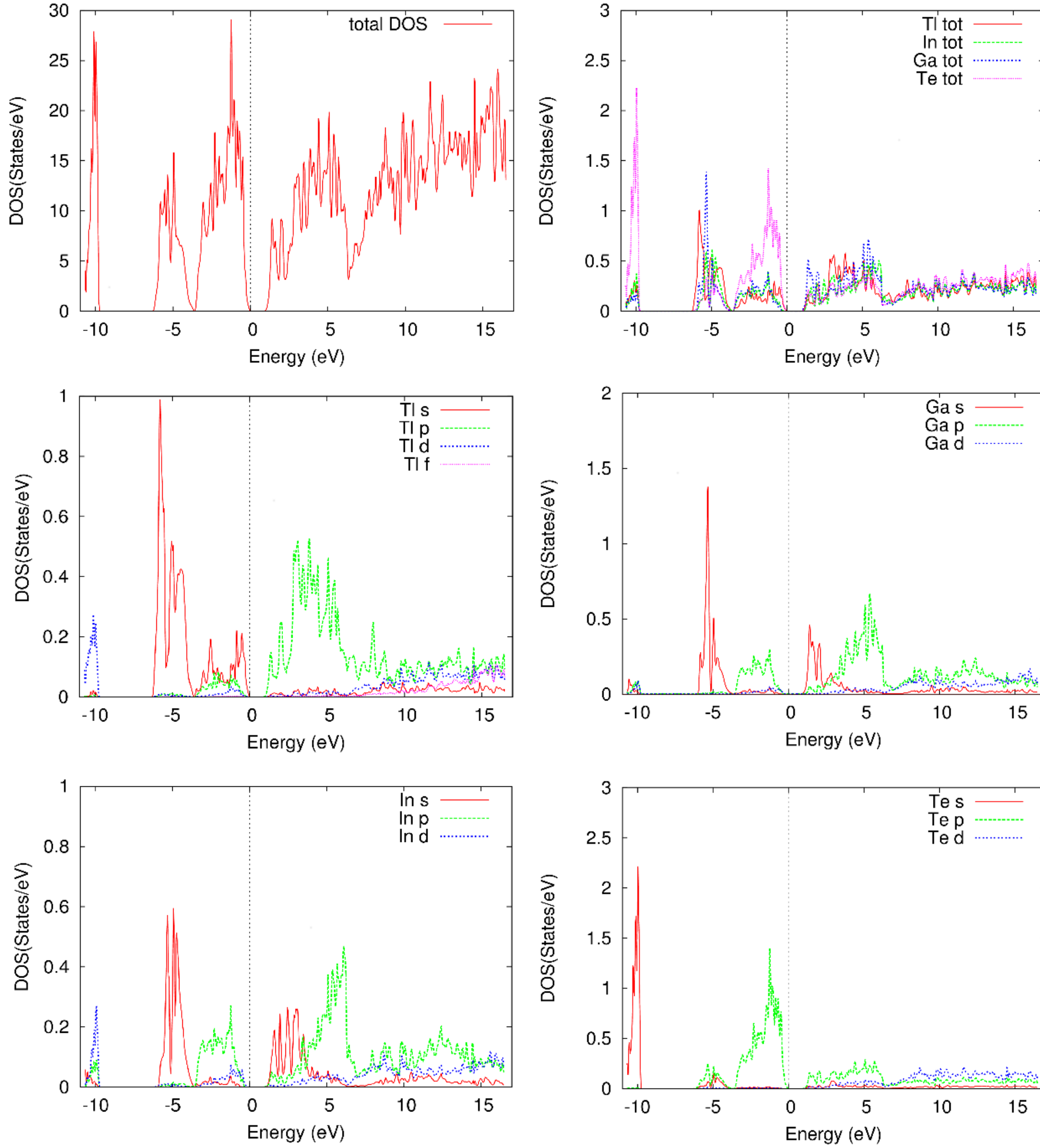

Figure 5. The TDOS and PDOS of $TlGa_{0.75}In_{0.25}Te_2$ alloy.

We illustrate the TDOS and PDOS of $TlGa_{0.50}In_{0.50}Te_2$ crystal system using mBJ method Figure 6. As can be seen from the Figure that TDOS exhibits very similar behavior to that of the band structure. From figure, we see that the valence band is divided into two sub-bands. The low energy sub-band extends from -10.54 eV to -9.64 eV. The d-states of Tl atoms and In atoms, s-states of Te atoms mainly create these bands. The d-states of Tl atoms rarely appears in this band. The high energy sub-band extends from -6.21 eV to Fermi level. The s-states of Tl, Ga, In atoms and p-states of Ga, In, Te atoms mainly create this band. Moreover the d -states of In atoms and p-states of Tl atoms rarely appears in this band. This results shows that the high energy sub-band located between -6.21 eV and Fermi level is mainly dominated by Tl, In, Te and Ga atoms. In addition, the peaks in conduction band between 1.02 eV and 16.65 eV mainly result from p states of Tl, Ga, In atoms and s-states of Ga, In atoms. The d-states of Tl, Te, Ga, In atoms, s-states of Tl atoms and p-states of Te atoms rarely effect formation of conduction band.

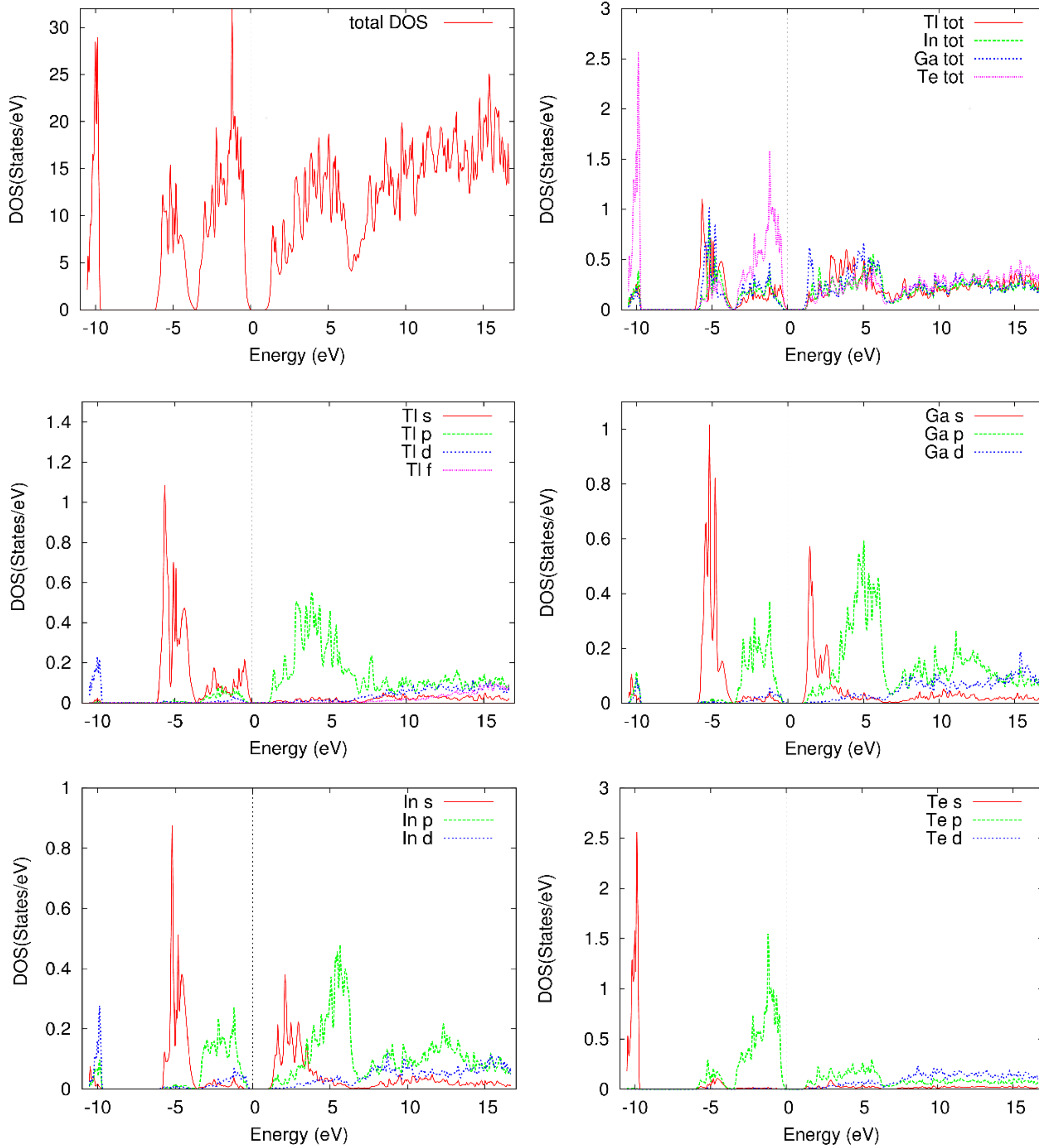

Figure 6. The TDOS and PDOS of $TlGa_{0.50}In_{0.50}Te_2$ alloy.

In figure 7, we illustrate the TDOS and PDOS of $TlGa_{0.25}In_{0.75}Te_2$ crystal system using mBJ method. As can be seen from the Figure that TDOS exhibits very similar behavior to that of the band structure. From figure, we see that the valence band is divided into two sub-bands. The low energy sub-band extends from -10.28 eV to -9.57 eV. The s-states of Te atoms mainly create these bands. The d-states of Tl and In atoms rarely appears in this band. The high energy sub-band extends from -6.03 eV to Fermi level. The s-states of Tl, Ga, In atoms and p-states of Ga, In, Te atoms mainly create this band. Moreover the d -states of In atoms and p-states of Tl atoms rarely appears in this band. This results shows that the high energy sub-band located between -6.21 eV and Fermi level is mainly dominated by Tl, In, Te and Ga atoms. In addition, the peaks in conduction band between 1.09 eV and 16.91 eV mainly result from p states of Tl, Ga, In atoms and s-states of Ga, In atoms. The d-states of Tl, Te, Ga, In atoms, s-states of Tl atoms and p-states of Te atoms rarely effect formation of conduction band.

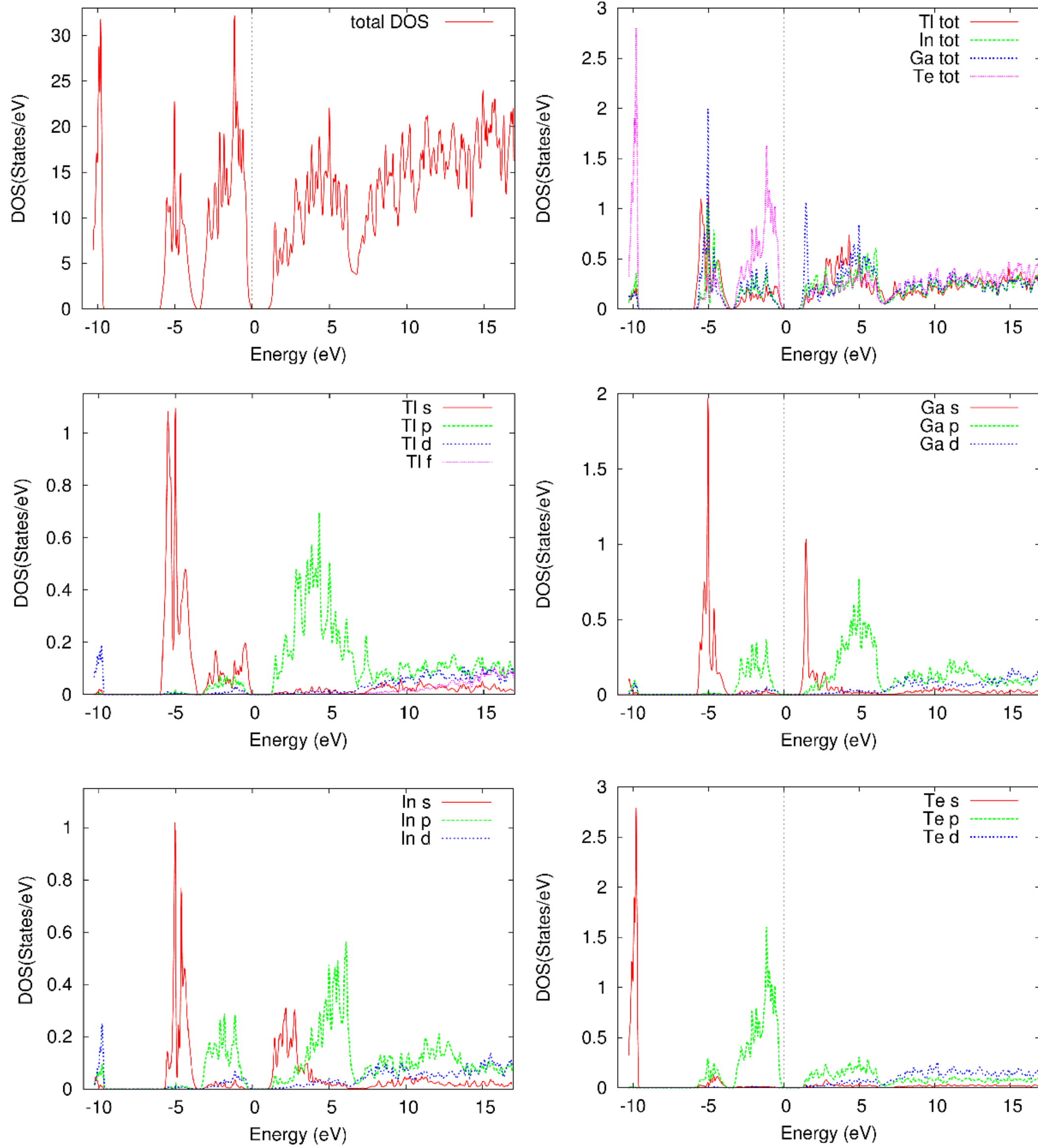

Figure 7. The TDOS and PDOS of $TlGa_{0.25}In_{0.75}Te_2$ alloy.

Finally, we illustrate the total and partial density of states of $TlInTe_2$ crystal system using mBJ method in Figure 8. As can be seen from the Figure that TDOS exhibits very similar behavior to that of the band structure. From figure we see that the valence band is divided into two sub-bands. The low energy sub-band extends from -10.25 eV to -9.52 eV. The s-states of Te atoms mainly create these bands. The d-states of Tl and In atoms rarely appears in this band. The high energy sub-band extends from -6.01 eV to Fermi level. The s-states of Tl, In atoms and p-states of In, Te atoms mainly create this band. Moreover the d -states of In atoms and p-states of Tl atoms rarely appears in this band. This results shows that the high energy sub-band located between -6.01 eV and Fermi level is mainly dominated by Tl, In and Te atoms. In addition, the peaks in conduction band between 1.23 eV and 16.93 eV mainly result from p states of Tl, In atoms and s-states of In atoms. The d-states of Tl, Te, In atoms, s-states of Tl atoms and p-states of Te atoms rarely effect formation of conduction band.

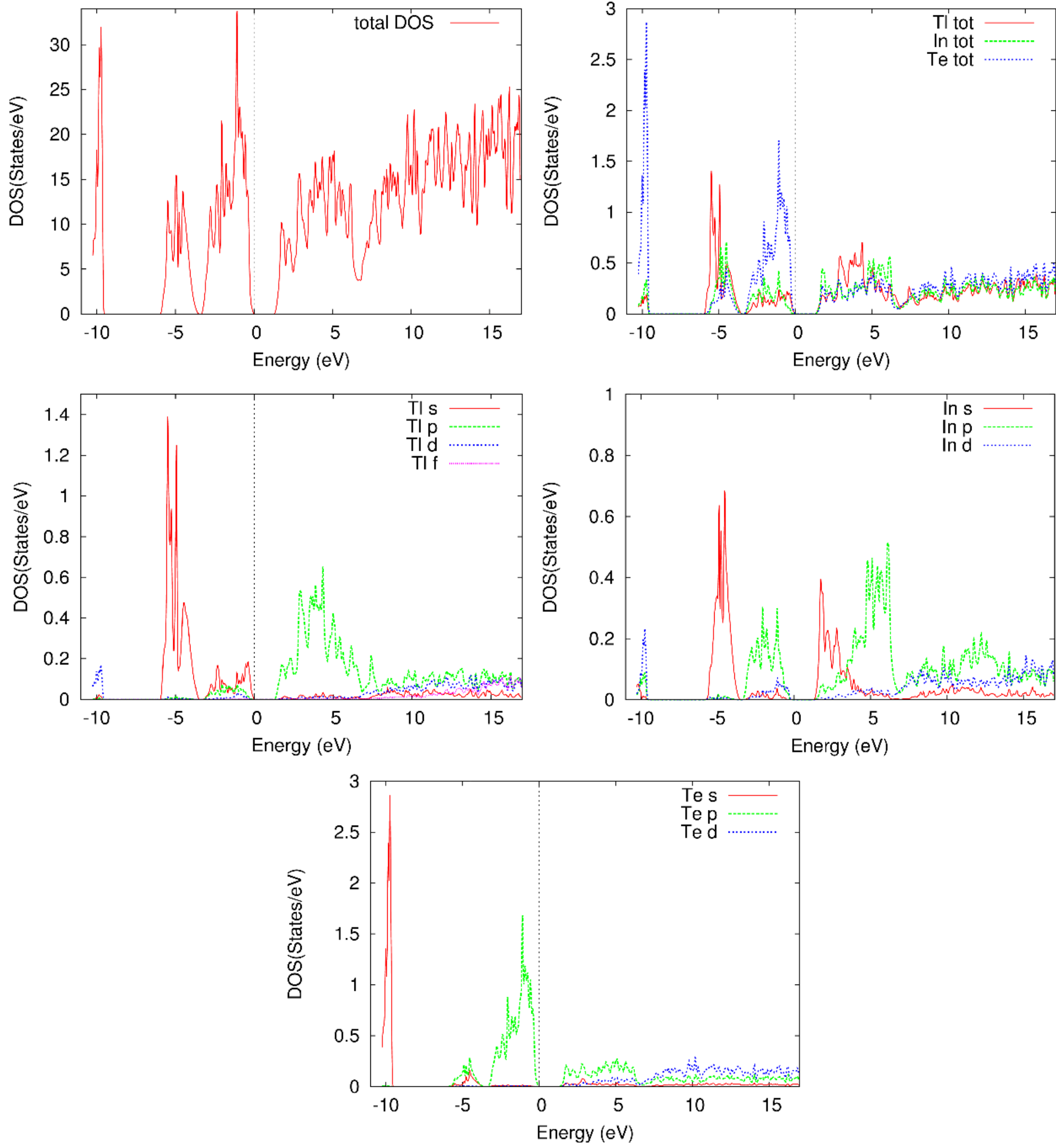

Figure 8. The TDOS and PDOS of $TlInTe_2$ alloy.

4. Conclusion and Comment

In this work, the electronic properties of $TlGa_{1-x}In_xTe_2$ alloys are studied using the DFT method. The exchange correlation energy is treated using GGA method. In order to improve band gap calculations and electronic structures, we used Tran-Blaha modification of the Beckee Johnson potential (TB-mBJ) in the SCF calculations. We found from structural properties that the value of the lattice parameter a and volume of unit cell increases with increasing In concentrations. We have shown that $TlGaTe_2$, $TlGa_{0.75}In_{0.25}Te_2$, $TlGa_{0.50}In_{0.50}Te_2$, $TlGa_{0.25}In_{0.75}Te_2$ and $TlInTe_2$ alloys have characteristics of indirect band gap materials. In addition, the band gap energies of all alloys depend on the germanium, silicon and tin concentrations. All the studied alloys here are characterized by narrow band-gap semiconductors. Therefore, band gap energies of these alloys lie in the ultraviolet region of the electromagnetic spectrum. The most important properties of the narrow band gap semiconductor has been used as infrared

sources and detectors. This theoretical work is of great interest for quaternary semiconductor research and motivates further future studies.

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