Süleyman Demirel Üniversitesi Fen Edebiyat Fakültesi Fen Dergisi https://dergipark.org.tr/sdufeffd
Süleyman Demirel University Faculty of Arts and Sciences Journal of Science e-ISSN: 1306-7575
Research Article, 2023, 18(2): 76-87, DOI: 10.29233/sdufeffd.1207660

The effect of Na Atom on $TlInSe_2$ and $TlInTe_2$ Compounds

İsmail Yücel[*1]

[1]Independent Scholar, 32100, Isparta, TÜRKİYE
https://orcid.org/0000-0002-8660-3931
* *corresponding author*: ismaillyucell@gmail.com

(*Alınış / Received*: 21.11.2022, *Kabul / Accepted*: 03.03.2023, *Yayımlanma / Published*: 22.06.2023)

Abstract: Thermoelectric materials have widely used applications in technological areas such as electronic devices and data storage. $TlInSe_2$ and $TlInTe_2$ compounds are among these thermoelectric materials. In this study, while the structural, electronic, and optical properties of $TlInSe_2$, $TlInTe_2$, $Tl_{0.75}Na_{0.25}InSe_2$ and $Tl_{0.75}Na_{0.25}InTe_2$ compounds have been examined with the WIEN2k program based on DFT, their thermoelectric properties have been calculated with another program BoltzTrap. The electronic calculations show that, all compounds exhibit indirect band gap properties. In addition, the band gap energy of $Tl_{0.75}Na_{0.25}InSe_2$ is shifted in the electromagnetic spectrum. The optical properties are found to change depending on the direction for all compounds. Finally, the thermoelectric parameters have been calculated depending on temperature. It is thought that especially the results for Na-doped compounds will be a leading reference for experimental studies.

Key words: WIEN2k, Electronic, Thermoelectric, Optic

Na Atomunun $TlInSe_2$ ve $TlInTe_2$ Bileşikleri Üzerindeki Etkisi

Öz: Termoelektrik malzemeler, elektronik cihazlar ve veri depolama gibi teknolojik alanlarda yaygın olarak kullanılan uygulamalara sahiptir. $TlInSe_2$ ve $TlInTe_2$ bileşikleri bu termoelektrik malzemeler arasında yerini almaktadır. Bu çalışmada $TlInSe_2$, $TlInTe_2$, $Tl_{0.75}Na_{0.25}InSe_2$ ve $Tl_{0.75}Na_{0.25}InTe_2$ bileşiklerinin yapısal, elektronik ve optik özellikleri DFT tabanlı WIEN2k programı ile incelenirken, başka bir program olan BoltzTrap ile termoelektrik özellikleri hesaplanmıştır. Band yapısı hesabından tüm bileşiklerin dolaylı bant aralığı özellikleri gösterdiği bulunmuştur. $Tl_{0.75}Na_{0.25}InTe_2$ bileşiğinin bant aralığı enerjisinin elektromanyetik spektrumda yer değiştirdiği tespit edilmiştir. Optik özelliklerin tüm bileşikler için yöne bağlı olarak değiştiği bulunmuştur. Son olarak sıcaklığa bağlı olarak termoelektrik parametreler hesaplanmıştır. Özellikle Na katkılı bileşikler için elde edilen sonuçların deneysel çalışmalar için öncü bir referans olacağı düşünülmektedir.

Anahtar kelimeler: WIEN2k, Elektronik, Termoelektrik, Optik

1. Introduction

Increasing global energy demand day by day, it is desired to convert wasted thermal energy into useful electrical power. One of the important factors in obtaining efficient thermoelectric materials (TE materials) is low thermal conductivity [1, 2]. Materials with low thermoelectric properties have widely used applications in technological areas such as electronic devices and data storage [3, 4]. In this study, $TlInSe_2$ and $TlInTe_2$ compounds have been investigated in terms of electronic, optic, and thermoelectric properties. Ding et al. emphasized that $TlInTe_2$ compound could be one of the promising materials with thermoelectric efficiency [5]. Moreover, $TlInSe_2$ compound is a widely studied compound due to its superior thermoelectric properties [6]. Isik and Gasanly have

reported that, there is a decrease in the band gap as a result of the increase in Tl content in the $Tl^{1+}(Tl_xIn_{1-x})^{3+}Se_2$ compound [7]. XRD investigations of the $TlInSe_2$ compound studied under high pressure by Jabarov et al. have reported the stability of the tetragonal phase structure over the entire pressure range examined [8]. When the literature is examined, it has seen that these compounds are widely studied, and they are materials worth examining in terms of their thermoelectric properties. Besides, it is thought that they can help the emergence of new materials by doping or defects. In line with this information, $TlInSe_2$, $TlInTe_2$, $Tl_{0.75}Na_{0.25}InSe_2$ and $Tl_{0.75}Na_{0.25}InTe_2$ compounds have been investigated as theoretically in this manuscript.

2. Material and Method

The first principle investigation have been conducted by using WIEN2k code [9–11] which is based on density functional theory (DFT) [12]. Perdew-Burke-Enzerhof (PBE) generalized gradient approximation (GGA) is used as the electronic exchange-correlation potential [13]. In addition, TB-mBJ method has been carried to improve band structure and density of state calculations [14, 15]. $R_{MT}*K_{MAX}$ parameter is set to 7. Another parameter is adjusted as 12. The cut-off energy is set to -6.0 Ry. The definition of cut-off energy is energy for separating core from valence state. The 1000k point have been used for calculations. Finally, BoltzTrap code has been used to determine the thermoelectric properties.

3. Results

3.1. Structural properties

The $TlInSe_2$ and $TlInTe_2$ compounds space group are *I/4mcm* and their crystal structure is tetragonal [16]. In addition, the Bravais lattice of both compounds is the body centered tetragonal (BCT). The formation of the doped crystal structures has been provided that one Tl atoms at (0.5, 0.5, 0.25) point has been removed from the crystal structure and doped with the Na atom instead of. It is known that the ion charges of Tl, In, Se and Te are (+1), (+3), (-2) and (-2), respectively. Because of this $TlInSe_2$ and $TlInTe_2$ compounds have a zero charge. The Na atom has an ionic charge of (+1), just like the Tl atom. In this way, the replacement of the Tl atom by the Na atom does not disturb the total charge balance of compounds whose charges become zero, just like in undoped compounds. The crystal structure of $TlInSe_2$, $TlInTe_2$ $Tl_{0.75}Na_{0.25}InSe_2$ and $Tl_{0.75}Na_{0.25}InTe_2$ have been presented in Fig. 1.

The structural properties of undoped compounds at the ground state energy have been calculated and compared data with the literature [16]. In addition, structural parameters at the ground state energy are calculated using the Murnaghan equation of state (EOS) which are defined as the following equations [17];

$$P = \frac{3B(1-x)}{x^2}\exp\left[\left(\frac{3}{2}B' - 1\right)(1-x)\right] \quad (1)$$

$$P = \frac{B}{B'}\left[\left(\frac{V_0}{V}\right)^{B'} - 1\right] \quad (2)$$

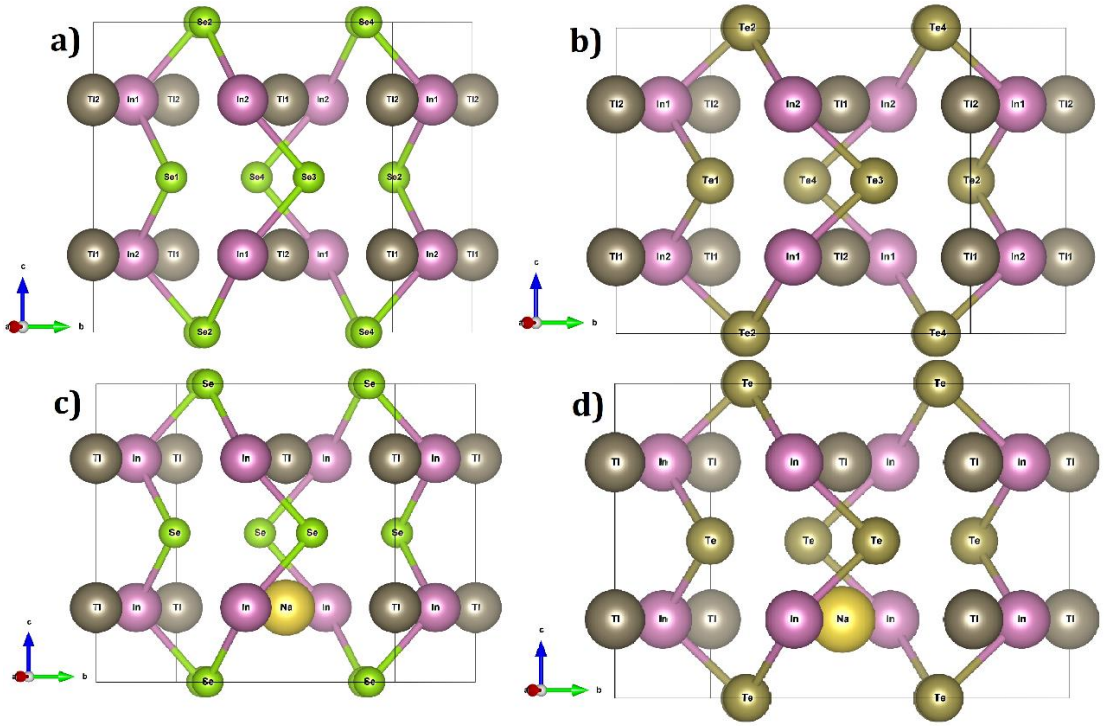

Figure 1. The crystal structure of a) $TlInSe_2$, b) $TlInTe_2$ $Tl_{0.75,}$ c) $Na_{0.25}InSe_2$ and d) $Tl_{0.75}Na_{0.25}InTe_2$

The optimization graph of all compounds is presented in Fig. 2. The results of the GGA methods are compared with the literature, given in Table 1. The GGA method is in good compromise with other studies for $TlInSe_2$ and $TlInTe_2$. Obtained lattice parameters compatible with the experimental data are important to obtain accurate results in electronic, optical, and thermoelectric calculations. Na doping to $TlInSe_2$ and $TlInTe_2$ compound caused minor changes in lattice parameters. It is observed that these small changes in lattice parameters do not cause any change in the c/a ratio.

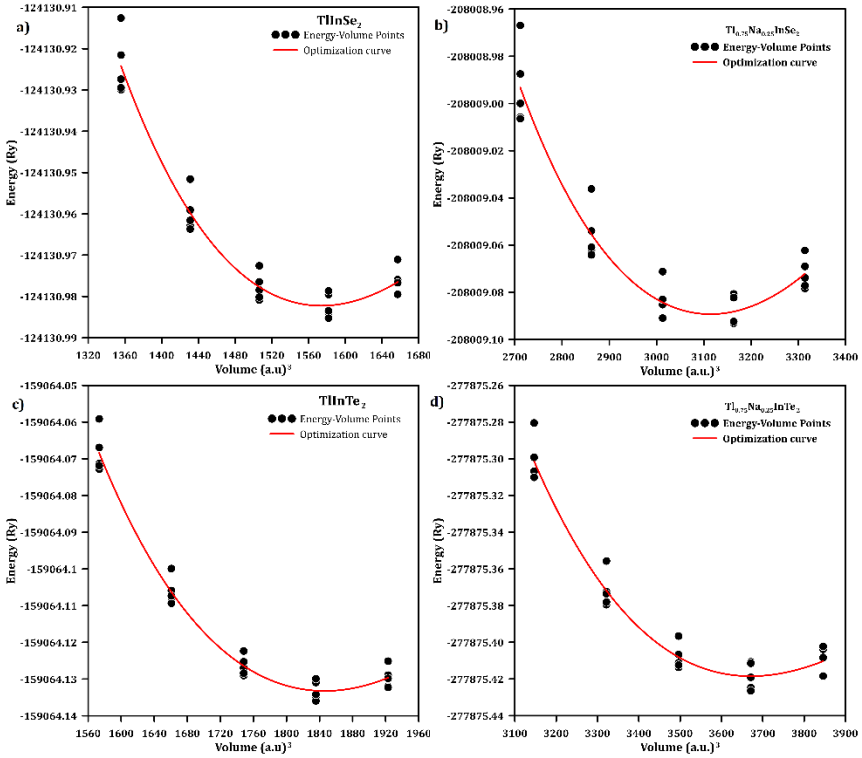

Figure 2. The optimization graph of a) $TlInSe_2$, b) $Tl_{0.75}Na_{0.25}InSe_2$, c) $TlInTe_2$ and d) $Tl_{0.75}Na_{0.25}InTe_2$

Table 1. The obtained lattice parameters, c/a ratio, bulk modulus (*B*), pressure derivatives of bulk modulus (*dB/dP*)

Compound	a (Å)	c (Å)	c/a	B (GPa)	dB/dP	References
$TlInSe_2$	8.1993	6.9403	0.84	42.5845	4.4561	This work
	8.0750 [a]	6.8470 [a]	0.84[a]	-	-	[a][16]
$TlInTe_2$	8.6651	7.2875	0.84	35.14	4.45	This work
	8.4940[b]	7.1810 [b]	0.85 [b]	-	-	[b][18]
	8.4940 [a]	7.1810 [a]	0.85 [a]	-	-	[a][16]
$Tl_{0.75}Na_{0.25}InSe_2$	8.1348	6.9545	0.85	42.7873	4.2268	This study
$Tl_{0.75}Na_{0.25}InTe_2$	8.6815	7.2544	0.84	33.0782	4.9708	This study

3.2. Electronic properties

The band structure and density of states calculations have been made to reveal electronic properties of $TlInSe_2$ and $TlInTe_2$. The band structure of $TlInSe_2$, $TlInTe_2$, $Tl_{0.75}Na_{0.25}InSe_2$ and $Tl_{0.75}Na_{0.25}InTe_2$ have been shown in Fig. 3, respectively. The maximum of valence band is at H symmetry point and minimum of conduction band is between Γ and P symmetry points. It means that, the $TlInSe_2$ has an indirect band gap energy whose energy is 1.08 eV. On the other hand, the $TlInTe_2$ has two minimum points on conduction band and one of them corresponds to H symmetry points and the other is between Γ and P symmetry points, is presented in Fig. 3(b). In addition, the maximum of valence band is at H symmetry point. It is indicated that $TlInTe_2$ has a direct and indirect band gap energy whose energy are 1.02 eV and 1.03 eV respectively. Moreover, the reported band gap values of $TlInSe_2$ are 1.02 eV [19], 1.10 eV [20], 1.35 eV and 1.07 eV [21]. The reported band gap values for $TlInTe_2$ are 1.03 eV and 0.99 eV [21], 1.13 eV and 0.97 eV [22]. The obtained results are compared with the literature; it is possible to say that the results of the theoretical study are acceptable. In addition, the mBJ method has given compatible values with the experimental results. The calculated band gap energies have shown that, these compounds are very close to the narrow band gap energy limit. Because of these, semiconductor materials with a small band gap are used as infrared detectors or thermoelectric materials. The band structure of $Tl_{0.75}Na_{0.25}InSe_2$ and $Tl_{0.75}Na_{0.25}InTe_2$ have been shown in Fig. 3(c) and Fig. 3(d), respectively. As can be clearly seen from figure 3. that, Na doping to $TlInSe_2$ and $TlInTe_2$ compound has caused an increment in band gap energies. Also, shifts are observed at high symmetry points for minimum of conduction band and maximum of valence band. Moreover, the band gap energy of Na doped $TlInSe_2$ is shifted from infrared region to visible region on the electromagnetic spectrum. The calculated band gap energy of $Tl_{0.75}Na_{0.25}InSe_2$ and $Tl_{0.75}Na_{0.25}InTe_2$ are 2.19 eV and 1.65 eV, respectively.

The total density of states (TDOS) and partial density of states (PDOS) calculations have been made to explain the valence and conduction band formations. The density of states versus energy graphs have been presented for $TlInSe_2$ and $Tl_{0.75}Na_{0.25}InSe_2$ in Fig. 4. TDOS calculations have shown that these materials are semiconductors, like band structure calculations. The valence band have occurred between -5.74 eV and Fermi Level for $TlInSe_2$. The density of states has approached almost zero at about the -3.17eV level, it has divided the valence band almost in two. The weak effect of Tl and In atoms has prevented this splitting into two. Moreover, the s-states of Tl atoms are dominant between -5.74 eV and -3.17 eV. The d-states of Tl atoms and p-states of Se atoms have a weak effect on their formation. After 3.17 eV, the s-states of Se atoms are more effective in the formation of the valence band between -3.17 eV and the Fermi Level. The s-, p-, and d-states of other atoms are seen in this energy range, but they are rather weak. In addition,

the s-states of In and the p-states of Se atoms are effectively dominant in the formation of the conduction band between 1.07 eV and 2.08 eV. After this energy value, all other states are seen in the formation of the conduction band in dominant and weak ratios. Although the Na contribution does not cause a great change in the valence band, it causes an increase in the band gap energy by shifting the conduction band. With this increase, the band gap energy is transferred from the infrared region to the visible region.

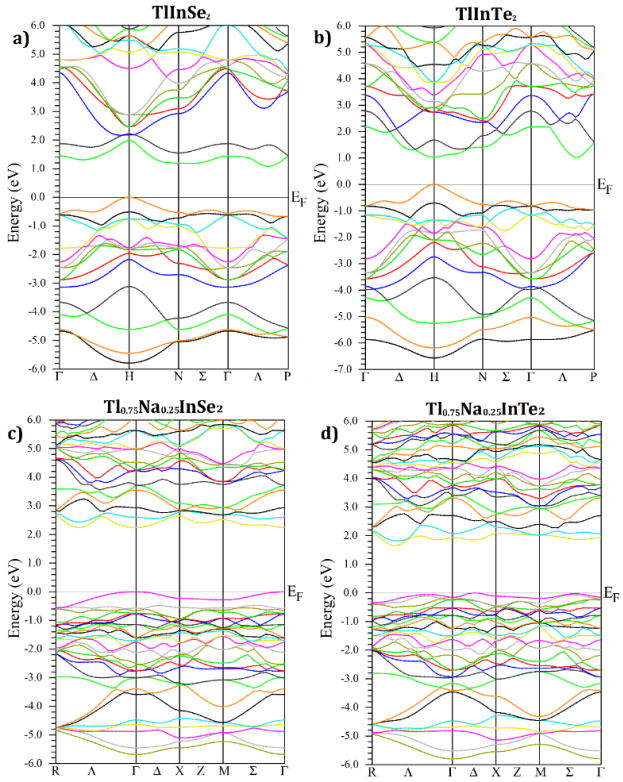

Figure 3. The calculated band structure graph of all compounds

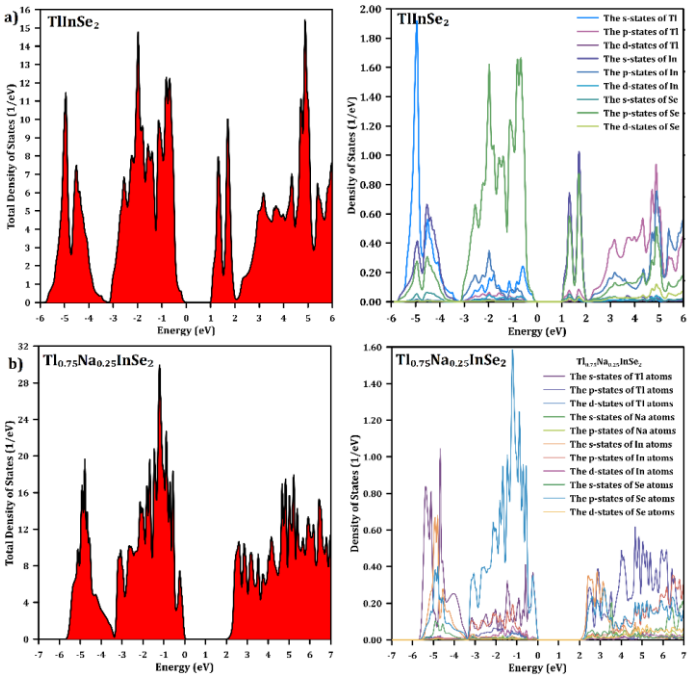

Figure 4. The TDOS and PDOS graphs of a) $TlInSe_2$ and b) $Tl_{0.75}Na_{0.25}InSe_2$

The density of states versus energy graphs have been presented for $TlInTe_2$ and $Tl_{0.75}Na_{0.25}InTe_2$ in Fig. 5. The valence band of $TlInTe_2$ is formed between -6.92 eV and Fermi Level. It has almost divided the valence band into two, around -3.93 eV. However,

the weak effects of the p- and d-states of In atoms have prevented the division of the valence band. The p-states of Te atoms are dominant in the valence band between -3.93 eV and Fermi level. The p-states of Tl, the s- and p-states of In and p-states of Te atoms are dominant in the conduction band. The states of other atoms are seen in this conduction band, but they are rather weak. Na doping has caused a narrowing in the valence band energy range on the $TlInTe_2$ compound but also has caused an increment in the band gap energy. However, the band gap energy corresponds to the infrared region, like the band gap energy of an undoped $TlInTe_2$ compound.

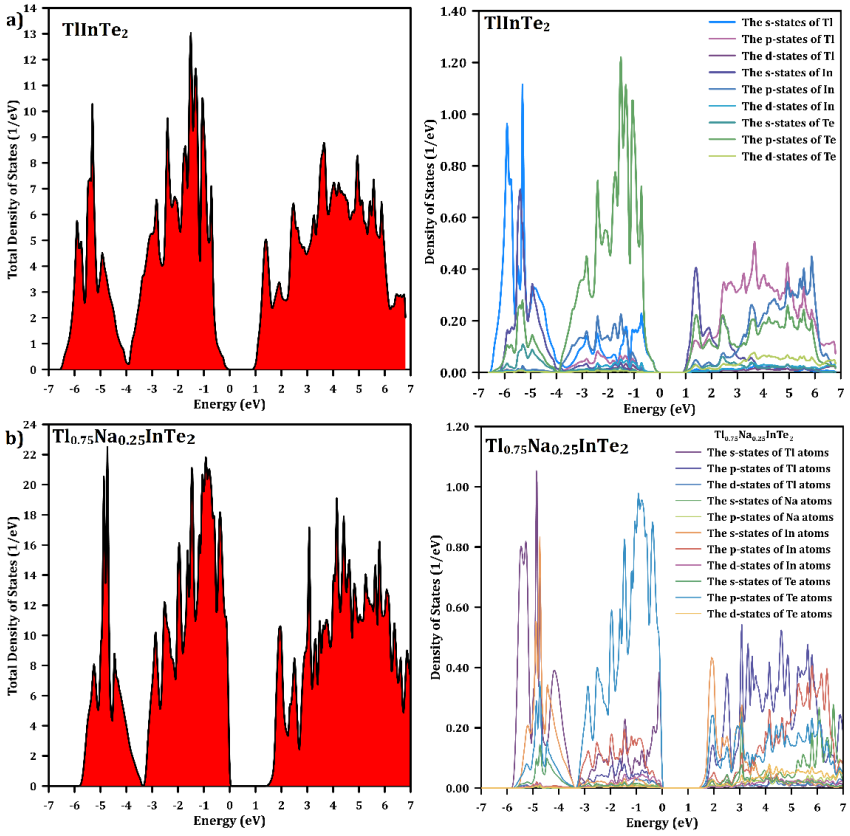

Figure 5. The calculated TDOS and PDOS a) $TlInTe_2$ and b) $Tl_{0.75}Na_{0.25}InTe_2$

3.3. Optic properties

The optical properties of a material are explained by its dielectric function. The dielectric function consists of two parts which are real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ parts. The general expression of the dielectric function is as follows $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ can be obtained from the following equation [23, 24];

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi}\mathbf{p}\int_0^{\infty}\frac{\omega'\varepsilon_2(\omega')d\omega'}{\omega'^2 - \omega^2} \tag{3}$$

$$\varepsilon_2(\omega) = \frac{V^2e^2}{2\pi m^2\omega^2}x\int d^3k\sum_{nn'}|kn|p|kn'|^2f(kn)x[1-f(kn')]\partial(E_{kn} - E_{kn'} - \omega) \tag{4}$$

The behavior of the material in the electromagnetic field is due to two types of electron transition. The first is the intra-band transitions that occur in each individual band that crosses the Fermi Level. Such a transition is more likely at low energy. The other type of transition is the transition between bands that occurs from one band to another. When the energy required to excite an electron is sufficient, the electron can jump to the other band,

and the transition between bands occurs when the electron jumps to the upper band. Optical properties like the absorption coefficient $\alpha(\omega)$, the refraction index, $n(\omega)$, reflectivity, $R(\omega)$, and optical conductivity have differed in such band transitions which are calculated using the dielectric function [25].

$$n(\omega) = 2^{-1/2}(\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} + \varepsilon_1^2(\omega))^{1/2} \quad (5)$$

$$\alpha(\omega) = \frac{2^{1/2}\omega}{c}(\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1^2(\omega))^{1/2} \quad (6)$$

$$R(\omega) = \left|\frac{\sqrt{\varepsilon(\omega)} - 1}{\sqrt{\varepsilon(\omega)} + 1}\right|^2 \quad (7)$$

Fig. 6 (a) shows plots of the real parts of the dielectric function as a function of photon energy. The dielectric constant at zero energy have differed according to the direction. Because of this, these materials could be candidates for nonlinear optical applications. The static dielectric constants $\varepsilon_{xx}(0)$ and $\varepsilon_{zz}(0)$ are equal to 7.55 and 9.13 for the $TlInSe_2$, respectively. Similarly, the static dielectric constants $\varepsilon_{xx}(0)$ and $\varepsilon_{zz}(0)$ are calculated 10.12 and 11.16 for $TlInTe_2$, respectively. The calculated $\varepsilon_{xx}(\omega)$, $\varepsilon_{zz}(\omega)$ for Na-doped $TlInSe_2$ and $TlInTe_2$ are 6.89, 7.63 and 9.48,10.59, respectively. In addition, the $\varepsilon_{xx}(\omega)$ and $\varepsilon_{zz}(\omega)$ values have negative values in some energy ranges. It means that this compound has metallic characteristic in this range. $\varepsilon_{xx}(\omega)$ and $\varepsilon_{zz}(\omega)$ have reached its maximum values at 11.89 and 19.99 for $TlInSe_2$, respectively. The energies corresponding to these values are 1.70 eV and 2.84 eV, respectively. While $\varepsilon_{xx}(\omega)$ reaches a maximum at the infrared visible region boundary, $\varepsilon_{zz}(\omega)$ reaches a maximum within the visible region for $TlInSe_2$. On the other hand, for $TlInTe_2$, the maximum values are 16.22 and 21.21 for $\varepsilon_{xx}(\omega)$ and $\varepsilon_{zz}(\omega)$, respectively. Their corresponding energy values are 2.44 eV and 2.54 eV, respectively, it reaches its maximum in the visible region in both directions. The plots of the imaginary parts of the dielectric function as a function of photon energy is presented in Fig. 6 (b). The imaginary part of dielectric function $\varepsilon_{xx}(\omega)$ for $TlInSe_2$ have four peak whose values are 6.19, 5.60, 7.68 and 8.10, respectively. Their corresponding energy values are 1.86 eV, 2.35 eV, 3.66 eV and 5.56 eV, respectively. In line with this information, we can say that, the first two peaks have occurred in the visible region, whereas the other two peaks are formed ultraviolet region. When we look for the $TlInSe_2$ in the $\varepsilon_{zz}(\omega)$ direction, two peaks are seen whose values are 20.80 and 13.45, respectively. These peaks are formed 3.36 eV and 4.26 eV, respectively. It means that they have reached to maximum in ultraviolet region. When it has been examined for the other compound, $TlInTe_2$, it has been calculated those three peaks occurred in the $\varepsilon_{xx}(\omega)$ direction, while it has been found that there is only one peak in the $\varepsilon_{zz}(\omega)$ direction. Moreover, all peaks have been formed in the ultraviolet region. In addition, these peaks have explained which energies the intraband transitions will consist of. Although the doping of the Na atom on $TlInSe_2$ and $TlInTe_2$ has caused small energy changes at the maximum peaks, the corresponding region in the electromagnetic spectrum has remained constant.

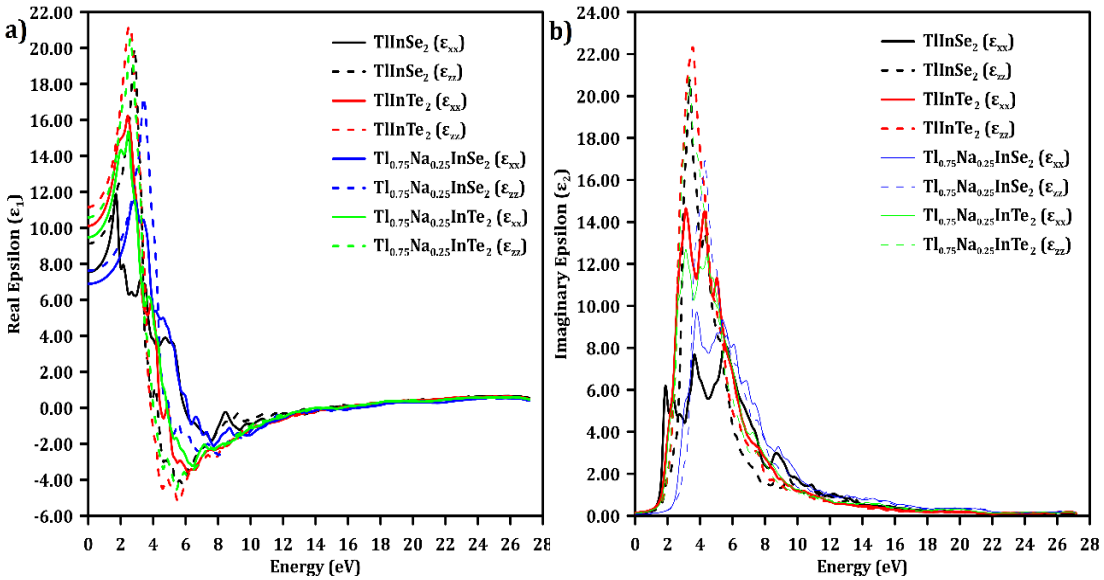

Figure 6. The calculated dielectric function for all compounds a) Real epsilon and b) Imaginary epsilon

Refraction index and reflectivity can be calculated by the real part of the dielectric function. The refraction index graph depending on energy has presented in Fig 7. (a). The refraction index values for $TlInSe_2$ at zero energy are 2.75 and 3.02 for $\varepsilon_{xx}(\omega)$ and $\varepsilon_{zz}(\omega)$, respectively. These values are 2.63 and 2.76 for $Tl_{0.75}Na_{0.25}InSe_2$, respectively. The calculated refraction index values for $\varepsilon_{xx}(\omega)$ and $\varepsilon_{zz}(\omega)$ at zero energy are 3.18 and 3.34 for $TlInTe_2$, respectively. These values are 3.08 and 3.25 for $Tl_{0.75}Na_{0.25}InTe_2$, respectively. The refraction index for $TlInSe_2$ depending on $\varepsilon_{xx}(\omega)$ has reached maximum in infrared region about 1.72 eV. On the other hand, the maximum value of refraction index for $TlInSe_2$ depending on $\varepsilon_{zz}(\omega)$ have occurred in the visible region about 2.88 eV. For the $TlInTe_2$, the refraction index has reached maximum in visible region about 2.49 eV and 2.67 eV for $\varepsilon_{xx}(\omega)$ and $\varepsilon_{zz}(\omega)$, respectively. The energy-dependent percentage reflectivity graphs have been shown in Fig. 7(b). The reflectivity calculations are one of the important parameters that give information about the transmittance of the material. For this reason, reflectivity is inversely proportional to transmission. The percentage reflectivity for $TlInSe_2$ at zero energy are 22% and 25% for $\varepsilon_{xx}(\omega)$ and $\varepsilon_{zz}(\omega)$, respectively. These values are 27% and 29% for $TlInTe_2$, respectively. In addition, the percentage reflectivity is maximum in the ultraviolet region for both compound and directions. According to these results, we can say that, depending on the direction, the refraction indices and percentage reflectivity have differed depending on direction. According to these results, all compounds can be used for non-linear optic applications.

The absorption coefficient and optical conductivity are directly related to the imaginary part of the dielectric function. In particular, the absorption coefficient is one of the parameters that determine whether a material can be used as a solar cell. The absorption coefficient and optical conductivity versus energy graph is presented in Fig. 8. As can be clearly from figure that, there is an absorption limit for both compounds and direction. In addition, their maximum values have corresponded to ultraviolet region. The region where absorption and optical conductivity begin corresponds to the infrared region, which agrees with the band gap energy calculations.

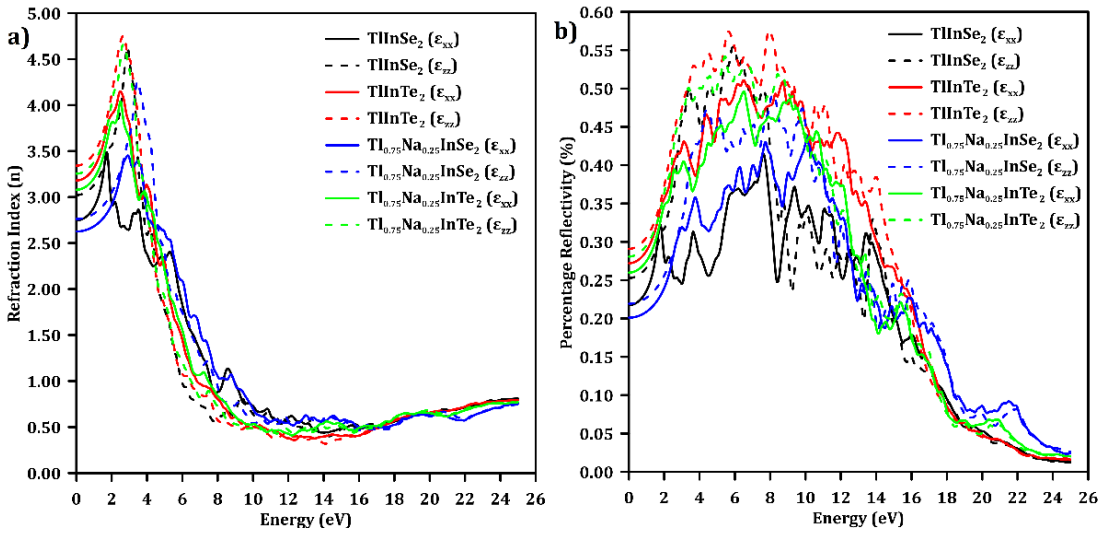

Figure 7. The calculated (a) refraction index and (b) percentage reflectivity for all compounds

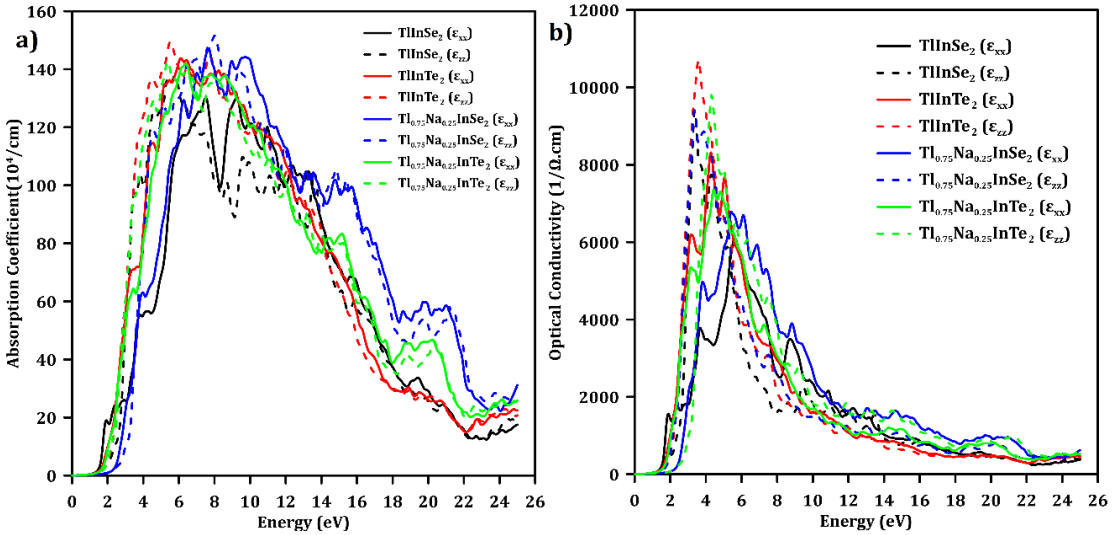

Figure 8. The calculated (a) absorption coefficient and (b) optical conductivity for all compounds

3.4. Thermoelectric properties

Boltztrap code is one of the program used to analyze thermoelectric properties like electrical conductivity and the Seebeck coefficient [26]. Their formula is given following. The equations are dependent on chemical potential (μ) and temperature (K).

$$\sigma_{\alpha\beta}(T,\mu) = \frac{1}{\Omega}\int \sigma_{\alpha\beta}\left[-\frac{\partial f_0(T,\varepsilon,\mu)}{\partial\varepsilon}\right]d\varepsilon \tag{6}$$

$$S_{\alpha\beta}(T,\mu) = \frac{1}{eT\Omega\sigma_{\alpha\beta}(T,\mu)}\int \sigma_{\alpha\beta}(\varepsilon)(\varepsilon - \mu)\left[-\frac{\partial f_0(T,\varepsilon,\mu)}{\partial\varepsilon}\right]d\varepsilon \tag{7}$$

$$\sigma_{\alpha\beta}(\varepsilon) = \frac{1}{N}\sum_{i,k}\sigma_{\alpha\beta}(i,k)\frac{\delta(\varepsilon-\varepsilon_{i,k})}{\delta(\varepsilon)} \tag{8}$$

$$\sigma_{\alpha\beta}(i,\vec{k}) = e^2\tau_{i,k}v_\alpha(i,\vec{k})v_\beta(i,\vec{k}) \tag{9}$$

The electrical conductivity curves depending on temperature is presented in Fig 9. (a). It is seen that the electrical conductivity has linearly increased with increasing temperature

owing to the transition of excited electrons from valence band to conduction band. At room temperature (300K) value of electrical conductivity is $0.41x10^{18}$ $(\Omega.m.s)^{-1}$, $0.37x10^{18}$ $(\Omega.m.s)^{-1}$, $0.94\ x10^{18}$ $(\Omega.m.s)^{-1}$ and $5.02\ x10^{18}$ $(\Omega.m.s)^{-1}$ for $TlInSe_2$, $TlInTe_2$, $Tl_{0.75}Na_{0.25}InSe_2$ and $Tl_{0.75}Na_{0.25}InTe_2$ respectively. At 800 K, these values are $1.70\ x10^{18}$ $(\Omega.m.s)^{-1}$, $1.59\ x10^{18}$ $(\Omega.m.s)^{-1}$, $4.01x10^{18}$ $(\Omega.m.s)^{-1}$ and $9.69x10^{18}$ $(\Omega.m.s)^{-1}$ respectively. The second thermoelectric parameter examined in this study is thermal conductivity. The capacity of a material to conduct heat is called thermal conductivity. It is directly related to lattice vibrations and electron mobility. Therefore, it should be optimized and minimized in order to be used in thermoelectric device. In this study, the thermal conductivity is plotted against the temperature, is presented in Fig. 9. (b), indicates that, it is not high in the low temperature region for both compounds. On the other hand, the thermal conductivity rapidly increases in the high temperature region, whose values at 800K are $1.28x10^{14}$ (W/m.K.s), $1.17\ x10^{14}$ (W/m.K.s), $1.79\ x10^{14}$ (W/m.K.s) and $3.76\ x10^{14}$ (W/m.K.s) for $TlInSe_2$, $TlInTe_2$, $Tl_{0.75}Na_{0.25}InSe_2$ and $Tl_{0.75}Na_{0.25}InTe_2$, respectively. In addition, the temperature region 300K- 800K, this increment occurs linearly. Another thermoelectric parameter is Seebeck coefficient. The Seebeck coefficient versus temperature graph for $TlInSe_2$ and $TlInTe_2$ is presented in Fig. 9 (c) which shows that, it is decreased from 50 K to 150 K, whereas it changes nonlinearly between 150 K and 800 K. The maximum value of the Seebeck coefficient is $4.11x10^{-4}$ (V/K) and $6.15x10^{-4}$ (V/K) for $TlInSe_2$ and $TlInTe_2$, respectively. In addition, it is almost equal to each other at 300 K whose values are $2.3215x10^{-4}$ (V/K) and $2.3115x10^{-4}$ (V/K), respectively. On the other hand, Na-doped compounds have differed. While the Seebeck coefficient of Na doped $Tl_{0.75}Na_{0.25}InSe_2$ has shown a rapid decrease between 50K and 200K, the decrease has occurred very slowly between 200K and 800K. In the $Tl_{0.75}Na_{0.25}InTe_2$ compound, on the other hand, the Seebeck coefficient has shown a linear increase from 50 K to 150 K, while after this point it has shown a nearly constant state. Between 500K and 800K, the Seebeck coefficient is calculated to vary between $1.80\ x10^{-4}$ (V/K) and $1.85\ x10^{-4}$ (V/K). The final thermoelectric parameter calculated in this study is power factor which parameter used to indicate the efficiency of the material. The power factor increases linearly with the increasing temperature, is presented in Fig. 9 (d). The room temperature values of $TlInSe_2$, $TlInTe_2$, $Tl_{0.75}Na_{0.25}InSe_2$ and $Tl_{0.75}Na_{0.25}InTe_2$, respectively are $0.22x10^{11}$, $0.19x10^{11}$,$0.83x10^{11}$ and $1.17x10^{11}$ respectively. At 800 K, the power factor reaches maximum and the power factor values corresponding to 800 K are $1.04x10^{11}$, $0.74x10^{11}$, $1.83x10^{11}$ and $3.33x10^{11}$for $TlInSe_2$, $TlInTe_2$, $Tl_{0.75}Na_{0.25}InSe_2$ and $Tl_{0.75}Na_{0.25}InTe_2$, respectively.

4. Conclusion and Comment

This theoretical study on Na doped $TlInSe_2$ and $TlInTe_2$ compounds is done with the WIEN2k program. It has been determined that the GGA method used lattice parameter calculations is compatible with the experimental results for $TlInSe_2$ and $TlInTe_2$ compounds. In addition, the lattice parameter "a" has decreased while lattice parameter "c" has increased for $Tl_{0.75}Na_{0.25}InSe_2$. On the other hand, lattice parameters "a and c" have increased together for $Tl_{0.75}Na_{0.25}InTe_2$ compound. Despite this change in lattice parameters, there is almost no change in the c/a ratio. As a result of this, Na adding to the compounds does not change the tetragonality. The mBJ method have been used for electronic and optic properties. The calculations for $TlInSe_2$ and $TlInTe_2$ have been shown that, it is suitable thanks to giving data consistent with experimental results. Na doping to $TlInSe_2$ and $TlInTe_2$ compounds has caused an increment in band gap energies. Moreover, the band gap energy of Na-doped $TlInSe_2$ is shifted from the infrared region to the visible region. One of the relevant features of optical materials is non-linear optical applications. It has been determined that the optical parameters of the pure doped materials change depending on the direction. These materials can be used for non-linear optic applications.

Especially, $Tl_{0.75}Na_{0.25}InTe_2$ compound can be one of the compounds that can be used in infrared technology. In addition, this compound has a high electrical conductivity, thermal conductivity, and power factor compared to other compounds.

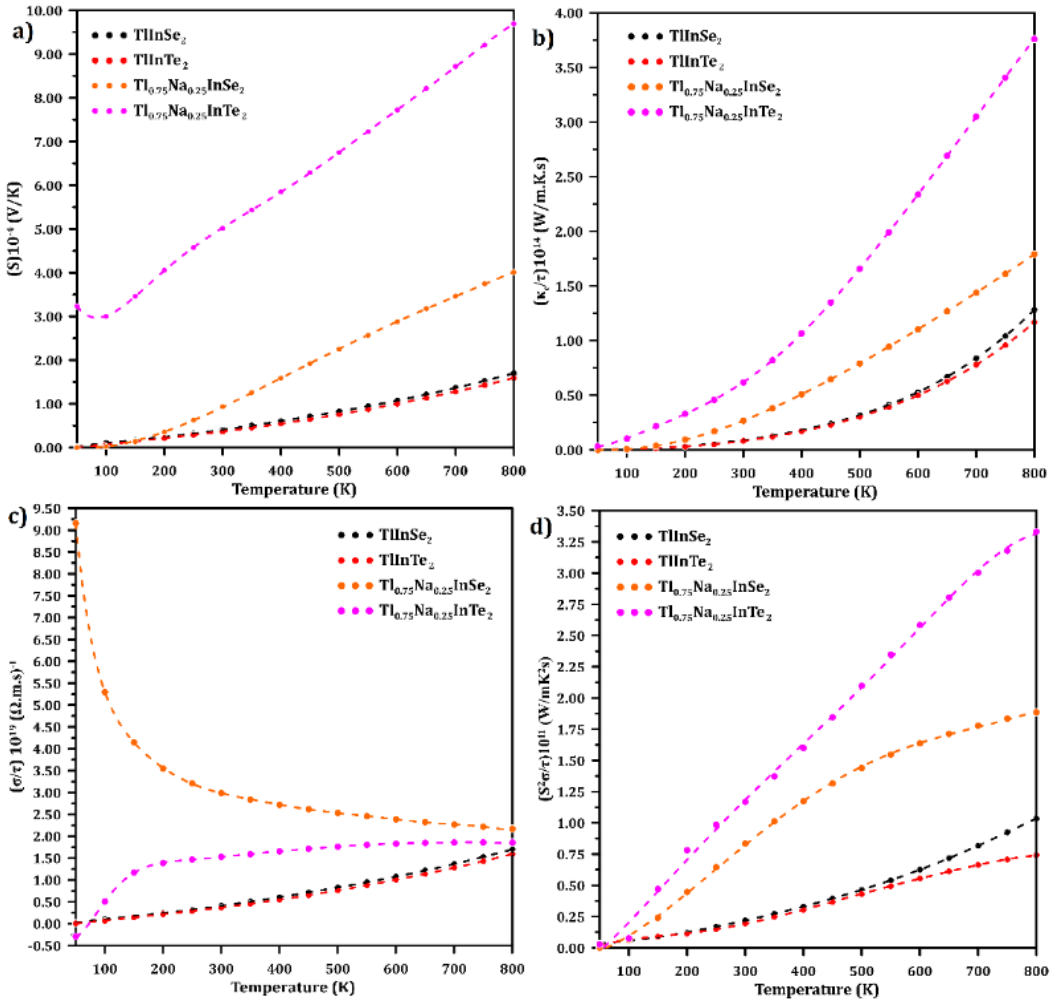

Figure 9. The obtained thermoelectric parameters for $TlInSe_2$ and $TlInTe_2$ (a) Electrical conductivity, (b) Thermal conductivity (c) Seebeck coefficient and (d) Power factor

Acknowledgment

The numerical calculations reported in this paper were fully performed in Physics Department at Suleyman Demirel University. Thanks to Prof. Dr. Seyfettin Çakmak, faculty member of the Physics department at Suleyman Demirel University.

Author Statement

İsmail Yücel: Theoretical Calculations, Original Draft Writing, Visualization.

Conflict of Interest

As the authors of this study, we declare that we do not have any conflict-of-interest statement.

Ethics Committee Approval and Informed Consent

As the authors of this study, we declare that we do not have any ethics committee approval and/or informed consent statement.

References

[1] F. J. Disalvo, "Thermoelectric cooling and power generation," *Science*, 285 (5428), 703–706, 1999.
[2] L. E. Bell, "Cooling, heating, generating power, and recovering waste heat with thermoelectric systems," *Science*, 321 (5895), 1457–1461, 2008.
[3] S. Raoux, W. Wełnic, and D. Lelmini, "Phase change materials and their application to nonvolatile memories," *Chem. Rev.*, 110 (1), 240–267, 2010.

[4] N. P. Padture, M. Gell, and E. H. Jordan, "Thermal barrier coatings for gas-turbine engine applications," *Science*, 296 (5566), 280–284, 2002.
[5] G. Ding, J. He, Z. Cheng, X. Wang, and S. Li, "Low lattice thermal conductivity and promising thermoelectric figure of merit of Zintl type TlInTe2," *J. Mater. Chem. C*, 6 (48), 13269–13274, 2018.
[6] N. Mamedov, K. Wakita, A. Ashida, T. Matsui, and K. Morii, "Super thermoelectric power of one-dimensional TlInSe2," *Thin Solid Films*, 499 (1–2), 275–278, 2006.
[7] M. Isik and N. M. Gasanly, "Effect of thallium (Tl) substitution for indium (In) on ellipsometric characteristics of TlInSe2 single crystals," *Mater. Sci. Semicond. Process.*, 134 (June), 106005, 2021.
[8] S. H. Jabarov *et al.*, "Structural and elastic properties of TlInSe2 at high pressure," *Solid State Sci.*, 111 (June), 106343, 2021.
[9] K. Schwarz, P. Blaha, and S. B. Trickey, "Electronic structure of solids with WIEN2k," *Mol. Phys.*, 108 (21–23), 3147–3166, 2010.
[10] K. Schwarz and P. Blaha, "Solid state calculations using WIEN2k," *Comput. Mater. Sci.*, 28 (2), 259–273, 2003.
[11] K. Schwarz, P. Blaha, and G. K. H. Madsen, "Electronic structure calculations of solids using the WIEN2k package for material sciences," *Comput. Phys. Commun.*, 147 (1–2), 71–76, 2002.
[12] K. Schwarz, "DFT calculations of solids with LAPW and WIEN2k," *J. Solid State Chem.*, 176 (2), 319–328, 2003.
[13] J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," *Phys. Rev. Lett.*, 77 (18), 3865–3868, 1996.
[14] F. Tran and P. Blaha, "Accurate band gaps of semiconductors and insulators with a semilocal exchange-correlation potential," *Phys. Rev. Lett.*, 102 (22), 5–8, 2009.
[15] D. Koller, F. Tran, and P. Blaha, "Improving the modified Becke-Johnson exchange potential," *Phys. Rev. B - Condens. Matter Mater. Phys.*, 85 (15), 1–8, 2012.
[16] J. Banys, F. R. Wondre, and G. Guseinov, "Powder diffraction study of TlGaTe2, TlInTe2 and TlInSe2," *Mater. Lett.*, 9 (7–8), 269–274, 1990.
[17] F. D. Murnaghan, "The compressibility of media under extreme pressures," *Proc. Natl. Acad. Sci. U. S. A.*, 30 (9), pp. 244–247, 1944.
[18] A. M. Panich, "Electronic properties and phase transitions in low-dimensional semiconductors," *J. Phys. Condens. Matter*, 20 (29), 293202, 2008.
[19] G. S. Orudzhev, N. A. Ismayilova, and V. N. Jafarova, "Electronic structure and effective masses of TlInSe2 under pressure," *Mater. Sci. Pol.*, 35 (4), 857–860, 2017.
[20] G. D. Guseinov, A. M. Ramazanzade, E. M. Kerimova, and M. Z. Ismailov, "About a group of three-component compounds being analogous to binary semiconductors of the AIII BVI type," *Phys. Status Solidi*, 22 (2), K117–K122, 1967.
[21] M. Hanias, A. Anagnostopoulos, K. Kambas, and J. Spyridelis, "On the non-linear properties of TlInX2 (X = S, Se, Te) ternary compounds," *Phys. B Condens. Matter*, 160 (2), 154–160, 1989.
[22] K. R. Allakhverdiev, T. G. Niamedov, V. E. Shteinshreiber, and I. K. Efendieva, "Fundamental Absorption Edge of TlSe and TlInTe2 Crystals," 127 (1), K55-K60, 1985.
[23] M. A. Khan, A. Kashyap, A. K. Solanki, T. Nautiyal, and S. Auluck, "Interband optical properties of Ni3Al," *Phys. Rev. B*, 48 (23), 16974–16978, 1993.
[24] F. Wooten, *Optical Properties of Solids*, Academic Press, 1972, pp. 1-260.
[25] C. Ambrosch-Draxl and J. O. Sofo, "Linear optical properties of solids within the full-potential linearized augmented planewave method," *Comput. Phys. Commun.*, 175 (1), 1–14, 2006.
[26] G. K. H. Madsen and D. J. Singh, "BoltzTraP. A code for calculating band-structure dependent quantities," *Comput. Phys. Commun.*, 175 (1), 67–71, 2006.