

Optical and Photoelectric Properties of TlInS₂ Layered Single Crystals

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Single crystals of the layered compound TlInS₂ were grown by direct synthesis of their constituents. The spectral and optical parameters have been determined using spectrophotometric measurements of transmittance and reflectance in the wavelength range 200-2500 nm. Absorption spectra of thin layers of TlInS₂ crystals are used to study the energy gap and the interband transitions of the compound in the energy region 2 – 2.4 eV. The direct band gap were determined to be 2.34 eV. The dispersion curve of the refractive index shows an anomalous dispersion in the absorption region and a normal one in the transmitted region. Photoconductivity measurements at room temperature show that both dark and photocurrent increase linearly with the applied voltage. The average energy gap obtained from the spectral dependence of the photocurrent determined to be 2.32 eV.

1. Introduction:

TlInS₂ belongs to the interesting group A^{III}B^{III}C₂^{VI} of chalcogenide semiconductors and considered one of the highly anisotropic crystals whose properties have recently become the subject of extensive research [1-3]. Members of this group of crystals, designated with the chemical formula TlBX₂ (where B = In or Ga, X = S, Se or Te) are known as thallium dichalcogenide. They have both layered (TlGaS₂, TlGaSe₂, TlInS₂) and chain (TlInSe₂, TlInTe₂, TlGaTe₂) structures. Among many TlBX₂ - type compounds, TlInS₂ has been studied rather well. This compound has attracted widespread attention for its structural, electrical and optical properties [4].

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At room temperature, TlInS₂ belongs to the monoclinic system with space group C_{2/c} and is arranged in the form of layered structure with a 1:1 ratio of InS:TlS. The lattice of TlInS₂ consists of alternating two-dimensional layers parallel to the (001) plane with each successive layer turned through a right angle with respect to the preceding layer [5]. The fundamental structural unit of a layer is the In₄S₁₀ polyhedron representing a combination of four elementary In S₄ tetrahedra linked together by bridging S atoms. The combination of the In₄S₁₀ polyhedra into a layer results in trigonal prismatic voids where Tl atoms are located [6, 7].

This paper reports the results on the optical properties of TlInS₂ layered single crystal in the wavelength range 200 -2500 nm. Furthermore, the photoelectric properties at room temperature are studied. As a result of this study we calculated all the optical parameters and energy gap of TlInS₂ layered single crystal. To the best of our knowledge the data presented in this work have not been reported before.

2. Experimental procedure:

2.1. Materials and sample preparation

TlInS₂ poly crystals were synthesized by fusing the high purity elements (99.999%) in stoichiometric proportions into evacuated silica ampoules with a tip at the bottom. To prevent the ampoule from exploding, it was heated in a temperature gradient furnace, so that the sulphur condensed at the cold end and slowly reacted with the heated elements at the hot end. After complete reaction, the ampoule was kept at 1173 K for 10 hours to ensure homogenization. Using the Bridgman-Stock Bauer technique [8], single crystals of TlInS₂ were grown by lowering the ampoule from the hot side of zone furnace at 1323 K to the cold side at 673 K at a speed of 0.3 mm/h. In the cold zone, the crystal cooled down slowly within a couple of days. The obtained crystals have a layered structure with glossy orange color and were easily split along the cleavage planes with a smooth-mirror surface. EDAX patterns for the TlInS₂ layered single crystal are shown in Figs. (1).

2.2. Optical properties measurements

The transmittance $T(\lambda)$ and the reflectance $R(\lambda)$ of the TlInS₂ layered single crystals of thickness 0.35 mm were measured at normal incidence in the spectral range 200-2500 nm using a double beam spectrophotometer (JASCO model V- 570 UV-VIS-NIR). These measurements were performed at room temperature. The relative uncertainty for the transmittance and reflectance are given by manufactures as 1 %. The thickness was measured by means of highly precision traveling microscope, Man Company (Burlington).

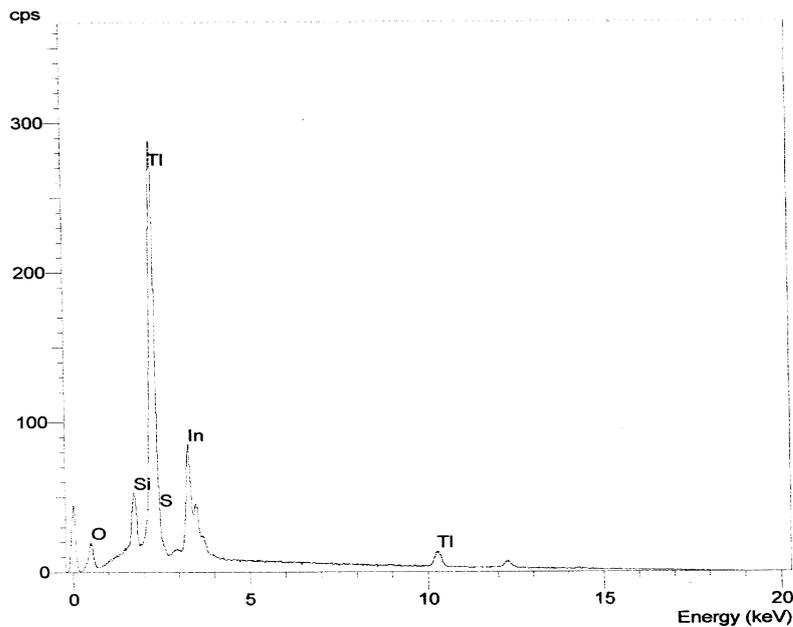


Fig. (1): EDAX patterns for TlInS₂ layered single crystal.

2.3. Photoelectric properties measurements

Photoconductivity measurements were performed with a Zeiss double prism monochromator (SMP2), in the energy region 1.9 – 3.1 eV. All samples used in photoconductivity experiments were cleaved from the same crystal used for the optical experiments. Two indium parallel contacts were evaporated in vacuum and were found to be ohmic and of low resistance. The distance between the electrodes was much greater than the thickness of the samples, thus providing homogeneous distribution of the applied voltage. Care was taken to achieve uniform illumination of the surface area between the two contacts. The uniform excitation over the whole volume of the crystals was provided by choosing the appropriate thickness d , so that the condition $\alpha d \approx 1$, where α is the absorption coefficient, held all over the spectral region. All measurements were performed with an applied voltage, in the ohmic region of the corresponding current-voltage characteristics. The photocurrent was measured with a Keithly electrometer (610C). The samples were mounted on the copper cold-finger of a cryostat that enabled the measurements to be carried out at a constant room temperature of 300K and under a vacuum of 10^{-5} Torr. All samples used in the present study were found to have p -type conductivity, as proved by thermal EMF. In all cases non-polarized light incident normal to the layer planes was used.

3. Results and Discussion:

3.1. Optical properties

Transmission measurements were used to determine the absorption coefficient of this compound. Averaging over multiple reflection effects, the values of transmittance (T) are given by [9],

$$T = (1 - R)^2 \exp(-\alpha d) \quad (1)$$

where $\alpha = \text{Log}[\frac{(1-R)^2}{2T} + \frac{(1-R)^4}{(4T^2 + R^2)}]^{1/2}$ (2)

where R and α are the reflectivity, (R is 0.2605 [10]) and the optical absorption coefficient, respectively, and d is the thickness of the sample. The refractive index (n) is given by [9]:

$$n = [(1+R)/(1-R) + 4R/((1-R)^2 - k^2)]^{1/2} \quad (3)$$

where k is the absorption index, $k = \alpha\lambda/4\pi$ and λ is the wavelength of the incident light on the sample. The optical absorption coefficient was determined using the values of R at room temperature [11]. To avoid multiple reflections and interference fringes the samples were put with a small angle with respect to the incident beam.

The spectral dependence (in the wavelength range of 200 – 2500 nm) of transmittance, T, and reflectance, R, for TlInS₂ layered single crystal are given in Fig. (2). It is quite clear that at a larger wavelength ($\lambda > 540$ nm), the TlInS₂ layered single crystal becomes transparent and no light is absorbed, i.e. non-absorbing region (T+R =1). The inequality R+T<1 at a shorter wavelength ($\lambda < 540$ nm) implies the existence of absorption i.e. absorbing region. The accuracy of the calculated values of the refractive index (n) and the absorption index (k) is mainly limited by the error of measurement of the wavelength (λ). In this work the accuracy of $n \pm 0.3$ and for $k \pm 0.2$.

The single oscillator model is applied in the region of normal dispersion $\lambda > 540$ nm and the data are used to obtain the oscillator parameters. Fig. (3) shows the dependence of refractive index (n) on the wavelength (λ).

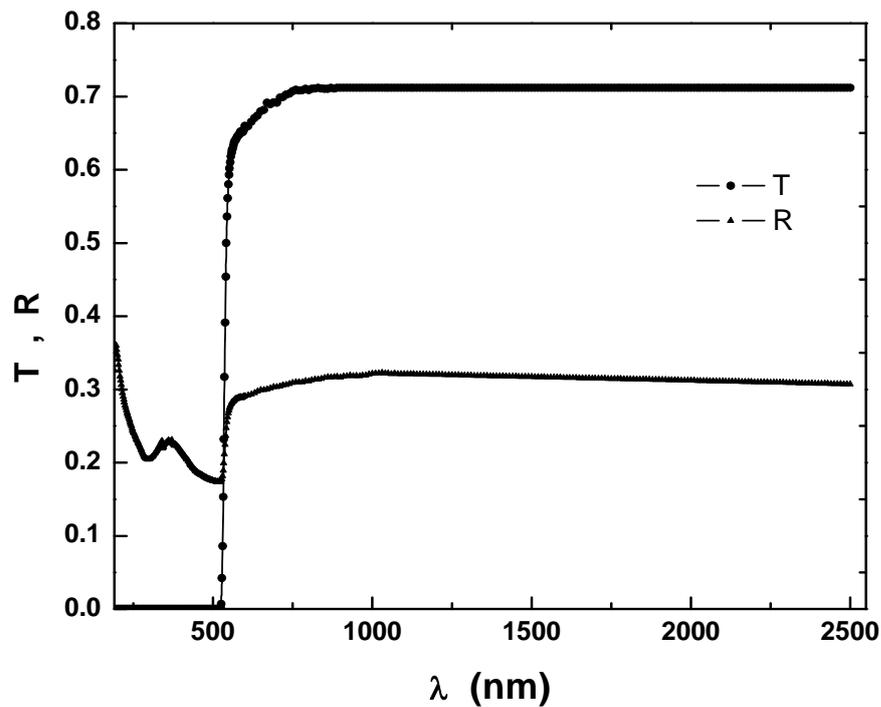


Fig. (2): The spectral distribution of transmittance (T) and reflectance (R) for TIInS₂ layered single crystal in the spectral range 200-2500 nm.

The dielectric constant is partially due to free electrons and partially due to bound electrons as represented by [12]:

$$n^2 = \varepsilon_L - \left[\frac{e^2}{\pi c^2} \right] (N / m^*) \lambda^2 \quad (4)$$

where e is the electron charge, c is the light speed, λ is the light wavelength, ε_L is the lattice dielectric constant and N / m^* is the ratio of carrier concentration to its effective mass. Fig. (4) represents the dependence of n^2 as a function of λ^2 for TIInS₂ layered single crystal is linear at longer wavelength. Extrapolating the linear part towards short wavelengths, the points of interception with the ordinate, at $\lambda^2 = 0$, yield the value of ε_L , which has the value 13.26. The value (N / m^*) is determined from the slope of the linear part of the graph as is obtained $0.24 \times 10^{48} \text{ gm}^{-1} \text{ cm}^{-3}$.

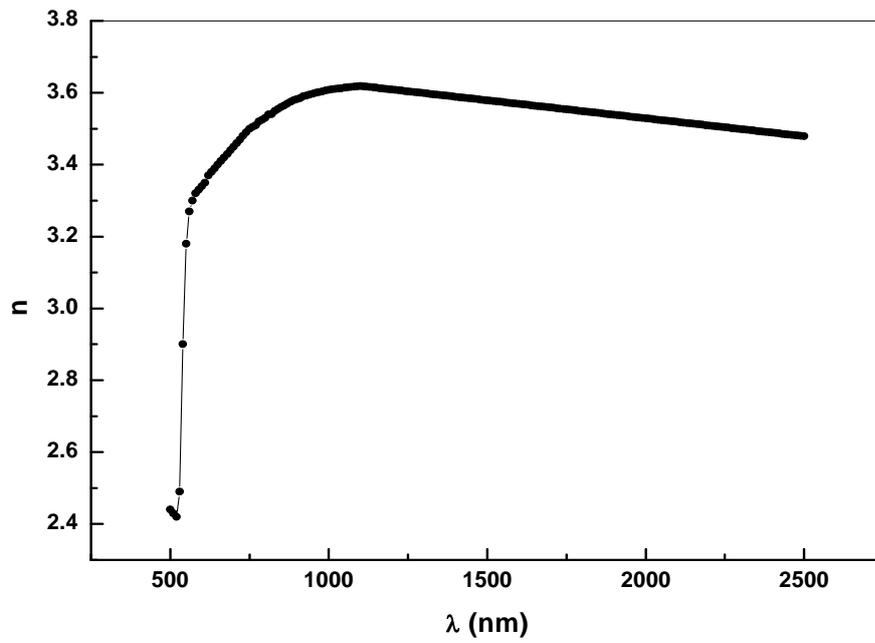


Fig. (3): The dependence of refractive index (n) on the wavelength (λ) for TlInS₂ layered single crystal.

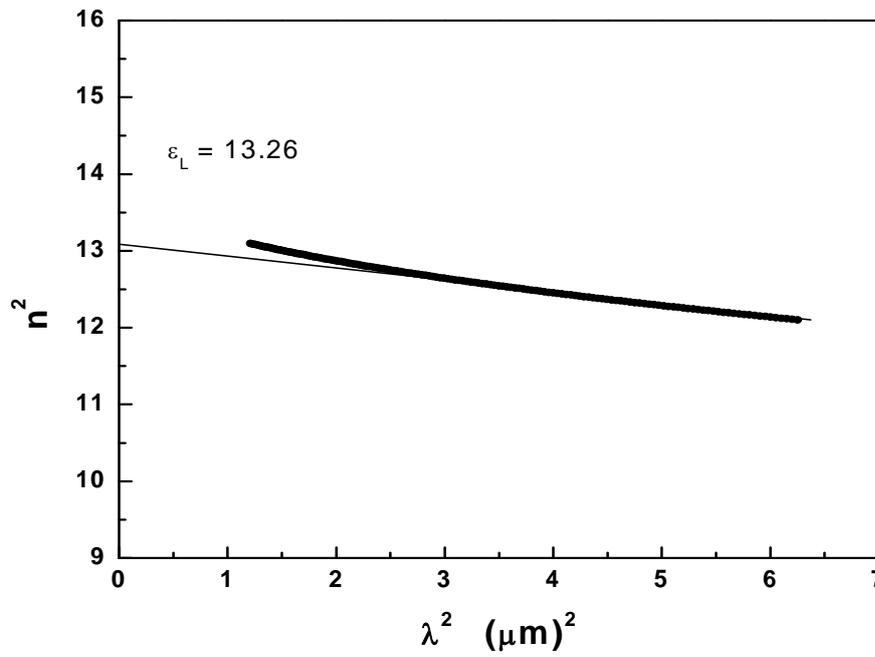


Fig. (4): The dependence of n^2 on λ^2 for TlInS₂ layered single crystal.

It is known that in the range of transparency, where the electron damping parameter $\gamma \ll \omega$,

$$n^2 = \epsilon_\infty - \omega_p^2 / \omega^2 \tag{5}$$

where, ω_p is the plasma frequency ($\omega_p^2 = e^2 N / \epsilon_0 m^*$), ϵ_0 is the vacuum dielectric function and ω is the incident light frequency. From the approximation of the linear part of the dependences $n^2(\lambda^2)$ of the TlGaSe₂ layered single crystal to $\lambda=0$ and $n=0$ the values of (ϵ_∞) and (ω_p) were found [13,14].

The energy dependence of the refractive index for TlInS₂ layered single crystal can be fitted by using the single oscillator model in the normal dispersion region developed by Wemple and DiDomenico[15] as:

$$1 / (n^2 - 1) = (E_o / E_d) - (1 / E_o E_d) (hv)^2 \tag{6}$$

where E_o is the energy of the effective dispersion oscillator and E_d is the dispersion energy or oscillator strength. Fig. (5) illustrates $(n^2 - 1)^{-1}$ as a function of $(hv)^2$, for the investigated sample. Extrapolating the linear part towards long wavelengths, the point of interception with the ordinate at $(hv)^2 = 0$ yield the value of the dielectric constant at higher wavelength (ϵ_∞), the obtained value is 12.51. The values of E_o and E_d obtained from the intercept and the slope of the curve are 5.025 eV and 57.85 eV, respectively. There is an important parameter called the oscillator strength (f) as reported in [16]:

$$f = E_o E_d \text{ (eV)}^2 \tag{7}$$

for the investigated sample, the oscillator strength is equal to 290.7 (eV)².

The oscillator energy, E_o is an “average” energy gap and, in close approximation, it scales with the optical band gap, $E_g^d : E_o \approx 2 E_g^d$, as was found by Tanaka [17]. The ratio E_o / E_g^d for TlInS₂ layered single crystal is calculated as 2.17, which shows good agreement with this relation. The values of the lattice dielectric constant (ϵ_L), dielectric constant at high frequencies (ϵ_∞), oscillator energy (E_o), dispersion energy (E_d), plasma wavelength (λ_p) and plasma frequency (ω_p) are listed in Table (1).

Table (1): The dispersion parameters of TlInS₂ layered single crystal.

Parameter	ϵ_∞	ϵ_L	E_o (eV)	E_d (eV)	λ_p (μm)	ω_p (Hz)	E_o / E_g^d
Value	$12.51 \pm 8.7 \times 10^{-5}$	13.26 ± 0.0065	$5.025 \pm 7.1 \times 10^{-5}$	$57.85 \pm 6.7 \times 10^{-5}$	2.264 ± 0.04	$8.33 \times 10^{14} \pm 3.2 \times 10^{-5}$	2.17

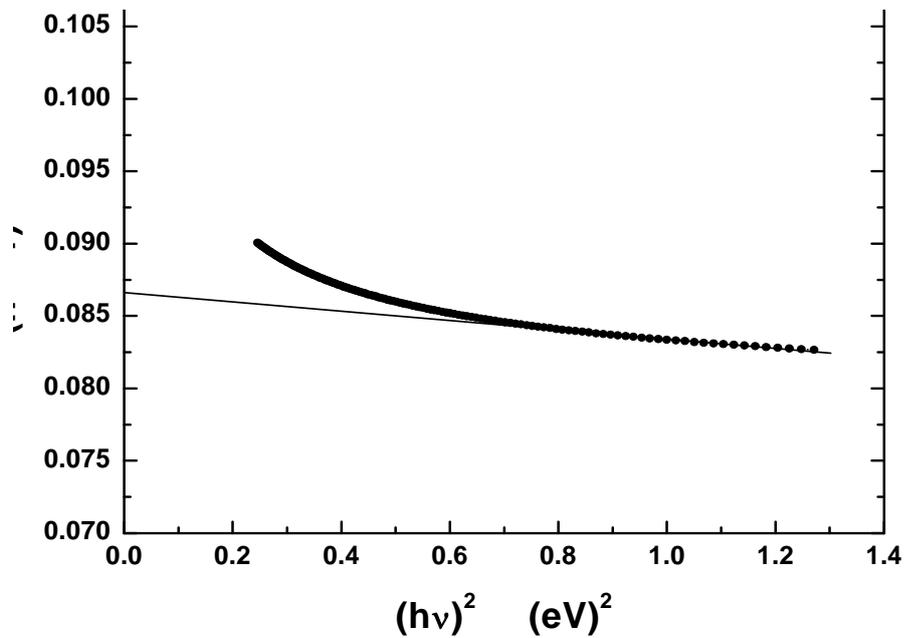


Fig. (5): The dependence of $(n^2-1)^{-1}$ on $(h\nu)^2$ for TlInS₂ layered single crystal.

As suggested in Ref. [16], the dispersion energy (E_d) obeys a simple empirical relationship in more than 100 widely different ionic and covalent crystalline solids, viz.,

$$E_d = \beta N_c Z_a N_e \text{ eV} \quad (8)$$

where $\beta = 0.37 \pm 0.04$ eV in covalent materials, and $\beta = 0.26 \pm 0.03$ eV in the more ionic materials. Z_a is the anion valency, N_c is the coordination number of the nearest-neighbour cation, and N_e is the effective number of valence electrons per anion. For the investigated sample $Z_a = 4$, $N_e = 10$ and $N_c = 4$ this yields to $\beta = 0.36$ eV which shows covalent crystal.

The absorption index k for TlInS₂ layered single crystal was determined from the absolute values of the measured transmittance and reflectance at normal light incidence, after correcting for the absorbency and reflectance of the substrate [18]. The result for the spectral dependence of k for TlInS₂ layered single crystal was illustrated in Fig. (6).

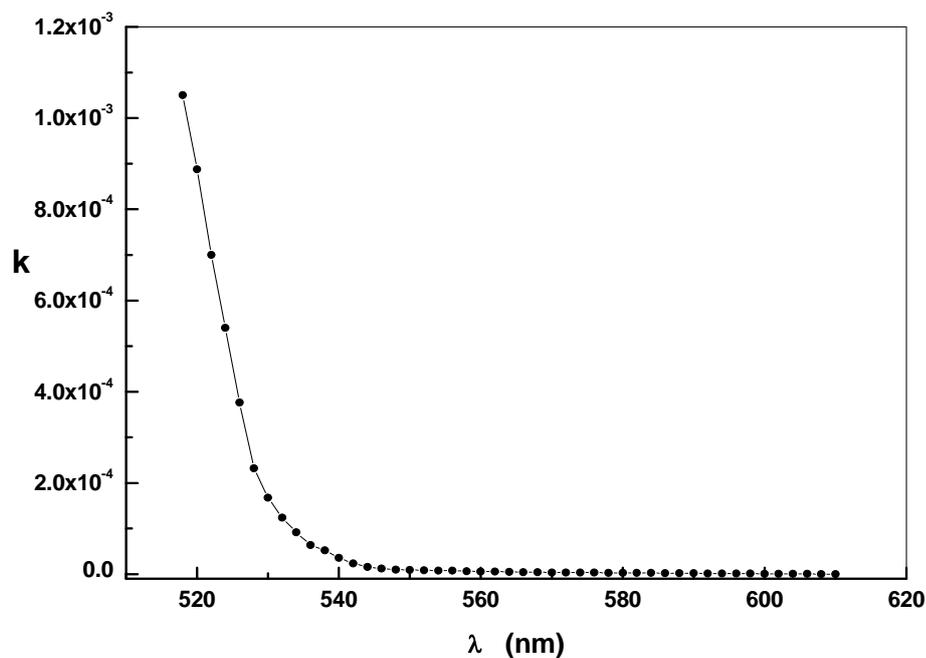


Fig. (6): The dependence of absorption index (k) on the wavelength (λ) for TlInS₂ layered single crystal.

The variation in absorption coefficient, α , is related to the photon energy $h\nu$ for the inter-band transition by the relation [19-21] :

$$(\alpha h\nu)^x = A (h\nu - E_g) \quad (9)$$

where, $x = 2$ and $1/2$ in the case of allowed direct and indirect optical transitions, respectively while, $x = 2/3$ and $1/3$ in the case of forbidden direct and indirect optical transitions. Therefore, the dependence of $(\alpha h\nu)^x$ on photon energy ($h\nu$) was plotted of $x = 2$ for direct transitions Fig (7). Extrapolating the linear part of the figure towards lower photon energies, the point of interception with the $h\nu$ axis exists at $(\alpha h\nu)^2 = 0$ giving the corresponding direct energy band gap. The obtained value of the direct energy gap E_g^d is 2.34 eV for TlInS₂ layered single crystal as shown in Fig. (7). This result agrees with the investigation by Allakhverdiev[22].

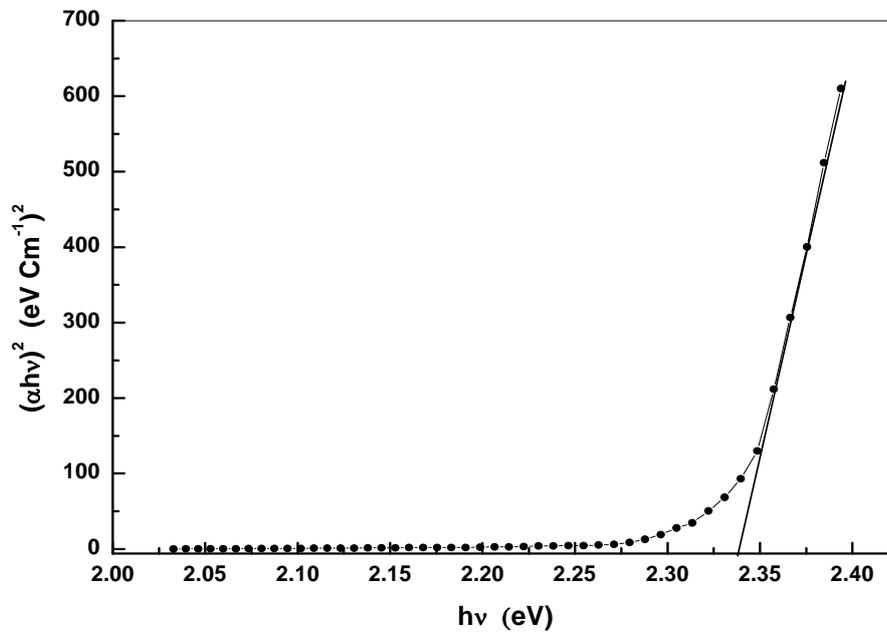


Fig. (7): Dependence of $(\alpha hv)^2$ on the photon energy (hv) for TlInS₂ layered single crystal..

The tails associated to the onset edge is attributed to the phonons assisted indirect electronic transitions. It is analyzed by using Urbach's empirical relation [23].

$$\ln(\alpha) = \ln(\alpha_0) - [1/E_c] hv \quad (10)$$

where E_c the width of the tail and α_0 is a constant. Fig. (8) shows the linear dependence of the natural logarithm of absorption coefficient on the photon energy. The reciprocal of the slope yields the magnitude of the width of the tail (E_c) the obtained value are 108 meV which is confirmed with data in [3].

The direct energy gap and the width of the tail of TlInS₂ layered single crystal are listed in Table (2). These results are in agreement with literature reports [6, 22, 24].

Table (2): The values of the energy gap of TlInS₂ layered single crystal .

Parameter	E_g^d (eV)	E_c (meV)
Value	2.34	108

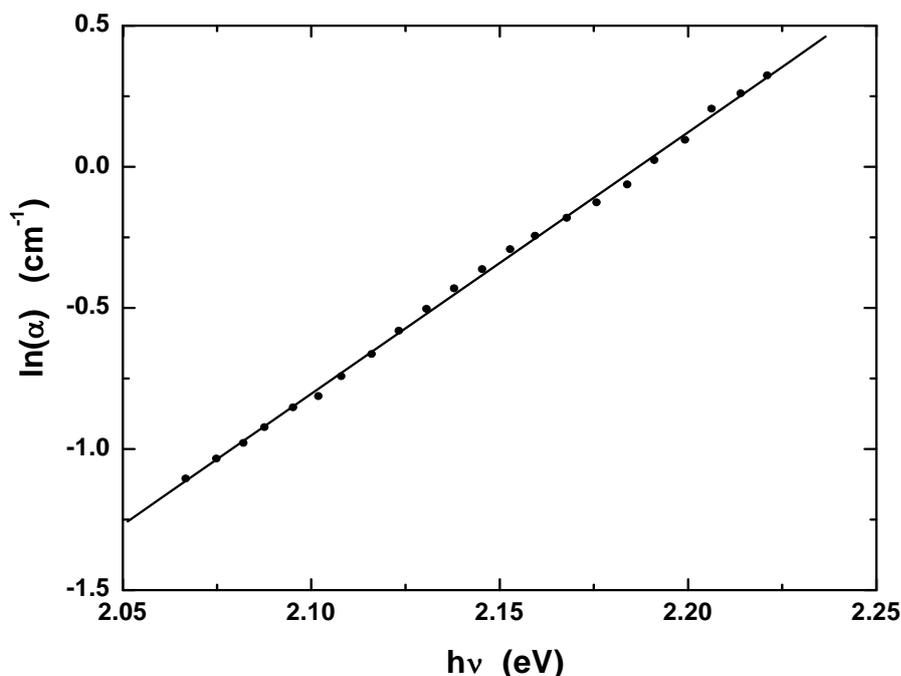


Fig. (8): Plotting of $\ln(\alpha)$ as a function of photon energy ($h\nu$) for TlInS₂ layered single crystal.

3.2. The Photoelectric property

In the following, the results of the photoconductivity measurements are presented. The applied voltage dependence of dark and photocurrent of TlInS₂ layered single crystal is shown in Fig. (9). It is observed that both dark and photocurrent increase linearly with the applied voltage. The photocurrent is more than the dark current, which termed as positive photoconductivity. This may attributed to the generation of mobile charge carriers caused by absorption of photons [25]. Fig. (10) depicts the photocurrent spectral distribution of p-type TlInS₂ layered single crystal in the wavelength range (400-650nm) at room temperature. This study was done without a change of the incident light intensity. The shape of the spectral distribution was practically independent of the applied bias voltage. An upward shift towards higher values of the photocurrent with the increasing of the applied bias voltage is observed. The photocurrent rises continuously with photon energy, and reaches a certain maximum value at 530 nm, then a steep fall is found at a high photon energy. The spectral dependence of the photocurrent agreed with previous measurements of the photocurrent of similar compound [26]. By applying the half maximum value [27] for the observed peak, we could evaluate the average energy gap as 2.32 eV.

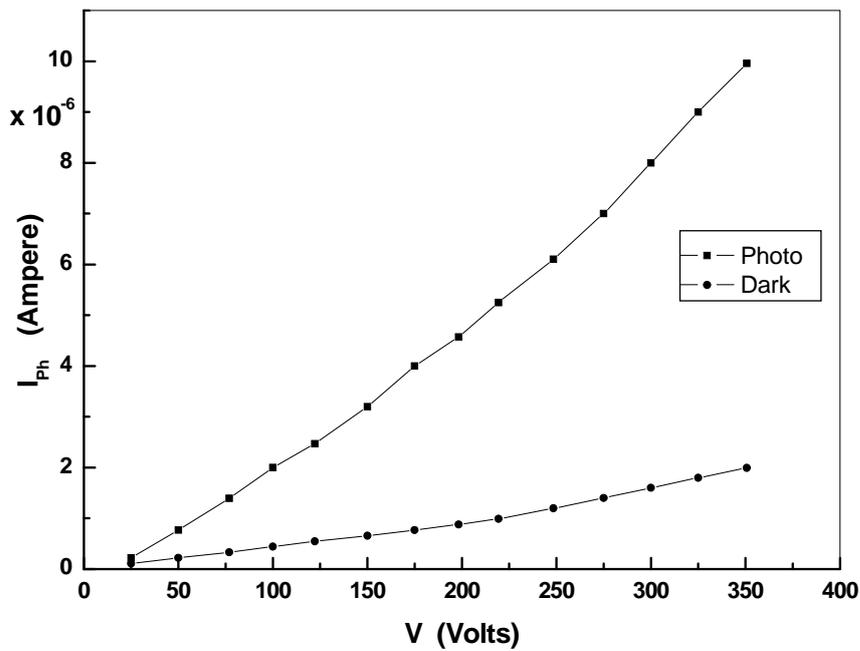


Fig. (9): Plotting of the photocurrent (I_{ph}) as a function of the applied voltage (V) for TlInS₂ layered single crystal.

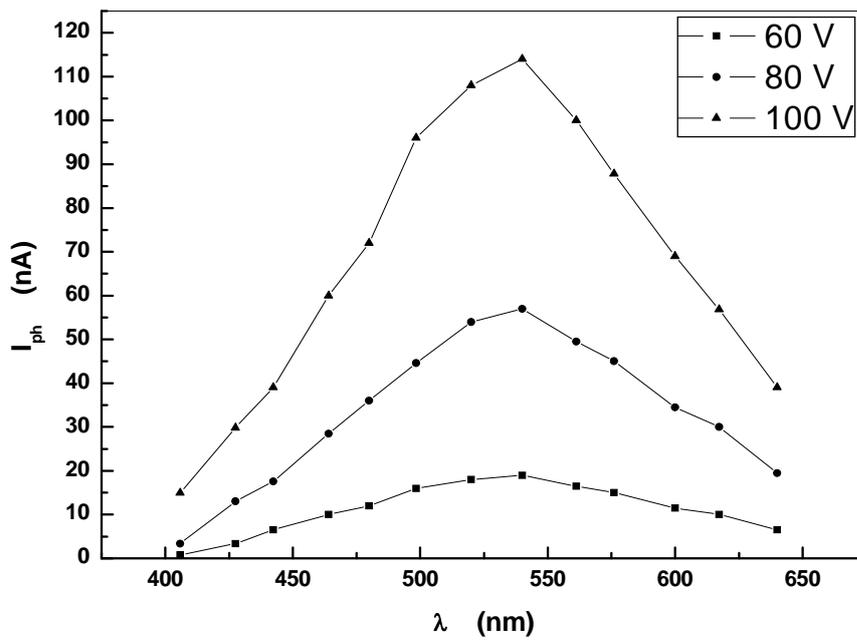


Fig. (10): Plotting of the photocurrent (I_{ph}) as a function of the wavelength (λ) for TlInS₂ layered single crystal.

4. Conclusion:

Optical and photoelectric properties of TlInS₂ layered single crystal were studied. In the optical studies, the direct (E_g^d) energy gap was determined to be 2.34 eV and in the photocurrent studies to be 2.32 eV and the width of the tail (E_c) to be 108 meV. The refractive index showed an anomalous dispersion in the absorption region as well as normal one in the transparent region. From the analysis of dispersion curves the single oscillator energy (E_o), the dispersion energy (E_d), and the plasma frequency (ω_p) were determined to be 5.025 eV, 57.85 eV and 8.33×10^{14} Hz, respectively.

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