

Tuning Optical Absorption Edge by Composition and Temperature in $\text{TlGaS}_{2x}\text{Se}_{2(1-x)}$ Layered Mixed Crystals ($0 \leq x \leq 1$)

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Optical properties of $\text{TlGaS}_{2x}\text{Se}_{2(1-x)}$ mixed crystals ($0 \leq x \leq 1$) have been studied using the transmission and reflection measurements in the wavelength range of 400–1100 nm. The optical indirect band gap energies were determined through the analysis of the absorption data. It was found that the energy band gaps increase with increase of sulfur atoms content in $\text{TlGaS}_{2x}\text{Se}_{2(1-x)}$ mixed crystals. From the transmission measurements carried out in the temperature range of 10–300 K, the rates of change of the indirect band gaps with temperature were established for the different compositions of mixed crystals studied.

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1. Introduction

TlGaS_2 and TlGaSe_2 compounds belong to the group of semiconductors with layered structure [1, 2]. These crystals have received a great deal of attention due to their optical and electrical properties in view of the possible optoelectronic device application. Optical and photoelectrical properties of TlGaS_2 and TlGaSe_2 crystals were reported in Refs. [3–10]. A high photosensitivity in the visible range of spectra, high birefringence in conjunction with a wide transparency range of 0.5–14 μm make this crystal useful for optoelectronic applications [10].

The compounds TlGaS_2 and TlGaSe_2 form a series of $\text{TlGaS}_{2x}\text{Se}_{2(1-x)}$ ($0 \leq x \leq 1$) isostructural mixed crystals. Previously, the structural and optical properties of the $\text{TlGaS}_{2x}\text{Se}_{2(1-x)}$ mixed crystals were investigated by X-ray diffraction [11], infrared reflection [12, 13] and the Raman [13, 14] spectroscopy. It was established that the phonon spectra of the mixed crystals exhibit the typical features of vibrational spectra of molecular crystals, namely the presence of low-frequency translational modes and high-frequency “intramolecular” modes.

The results of systematic investigations of electrical conductivity and photoconductivity on $\text{TlGaS}_{2x}\text{Se}_{2(1-x)}$ mixed crystals were reported in Ref. [15]. Bakhyshov et al. [16] carried out the measurements of the transmission spectra on $\text{TlGaS}_{2x}\text{Se}_{2(1-x)}$ crystals in the temperature range of 77–300 K. Recently, we studied the effect of isomorphic atom substitution on the lattice structure and optical absorption edge of $\text{TlGa}_{1-x}\text{In}_x\text{Se}_2$ [11, 17] and $\text{TlInS}_{2x}\text{Se}_{2(1-x)}$ [11, 18] mixed crystals. For the $\text{TlGa}_{1-x}\text{In}_x\text{Se}_2$ crystals, a structural phase transition (monoclinic to tetragonal) due to substitution of cation (indium for gallium) was revealed in the composition range of $0.50 \leq x \leq 0.75$. The band gap energy was

shown to drastically decrease from 1.89 eV ($x = 0.50$) to 0.94 eV ($x = 0.75$) in the region of the structural phase transition. For the $\text{TlInS}_{2x}\text{Se}_{2(1-x)}$ mixed crystals, a structural phase transition (monoclinic to tetragonal) due to substitution of anion (selenium for sulfur) was observed in the composition range of $x < 0.25$. It was revealed that the energy band gaps decrease with the increase of selenium atoms content in these mixed crystals. In the range $x < 0.25$, the band gap energy decreases sharply from 1.96 to 1.07 eV.

The aim of the present paper was to study the effect of the isomorphic anion substitution (sulfur by selenium) and the temperature on the absorption edge of $\text{TlGaS}_{2x}\text{Se}_{2(1-x)}$ mixed crystals through the transmission and reflection measurements in the wavelength range of 400–1100 nm and in the temperature range of 10–300 K.

2. Experimental details

Single crystals of $\text{TlGaS}_{2x}\text{Se}_{2(1-x)}$ ($0 \leq x \leq 1$) mixed crystals were grown by the Bridgman method from a stoichiometric melt of starting materials sealed in the evacuated (10^{-5} Torr) and carbon coated silica tubes (10 mm in diameter and about 25 cm in length) with a tip at the bottom in our crystal growth laboratory. The resulting ingots had no cracks and voids on the surface. The chemical composition of the $\text{TlGaS}_{2x}\text{Se}_{2(1-x)}$ mixed crystals were determined by the energy dispersive spectroscopic analysis using JSM-6400 electron microscope. The atomic composition ratio of the studied samples were estimated as 25.4 : 25.6 : 49.0 ($x = 1$, TlGaS_2), 26.0 : 25.8 : 35.9 : 12.3 ($x = 0.75$, $\text{TlGaS}_{1.5}\text{Se}_{0.5}$), 25.7 : 25.9 : 24.1 : 24.3 ($x = 0.50$, TlGaSSe), 25.8 : 26.0 : 12.2 : 36.0 ($x = 0.25$, $\text{TlGaS}_{0.5}\text{Se}_{1.5}$) and 25.4 : 25.2 : 49.4 ($x = 0$, TlGaSe_2). The samples for the measurements were taken from the middle part of the ingots. The freshly cleaned platelets (along the layer plane (001)) were mirror-like.

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That is why no further polishing and cleaning treatments were required.

The transmission and reflection measurements were carried out in the 400–1100 nm wavelength region with a “Shimadzu” UV-1201 model spectrophotometer. The transmission measurements were done under the normal incidence of light with the polarization in the (001) plane, which is perpendicular to the c -axis of the crystal. For the room temperature reflection experiments, the specular reflectance measurement attachment with 5° incident angle was used. The resolution of the spectrophotometer was 5 nm. An “Advanced Research Systems, Model CSW-202” closed-cycle helium cryostat was utilized to cool the sample from room temperature down to 10 K.

3. Results and discussion

The transmittance (T) and the reflectivity (R) spectra of the $\text{TlGaS}_{2x}\text{Se}_{2(1-x)}$ mixed crystals were registered in the wavelength range from 400 to 1100 nm in the temperature range 10–300 K. The absorption coefficient α was calculated using the following relation [19]:

$$\alpha = \frac{1}{d} \ln \left(\frac{(1-R)^2 + [(1-R)^4 + 4R^2T^2]^{1/2}}{2T} \right), \quad (1)$$

where d is the sample thickness.

The reflection measurements were carried out using the specimens with natural cleavage planes and the thickness such that $\alpha d \gg 1$. The sample thickness was then reduced until it was convenient for measuring the transmission spectra in the temperature range of 10–300 K. The thick samples with $d \approx 300 \mu\text{m}$ were used in the experiments since the thin layered samples broke into the pieces at low temperatures due to their high fragility. Therefore, we were only able to analyze the temperature dependence of the indirect band gap energy (E_{gi}). Technical reasons did not allow us a direct measurement of the reflectivity spectra at low temperatures. The point is that we utilized the specular reflectance attachment for “Shimadzu” UV-1201 model spectrophotometer, which is not adapted for the low-temperature reflection measurements by using closed-cycle helium cryostat. Therefore, we were able to register the reflectivity spectra of studied samples only at room temperature (Fig. 1). In order to calculate the absorption coefficient α at low temperatures, the spectral dependence of the room temperature reflectivity was uniformly shifted in the energy according to the blue shift of measured low-temperature transmission spectra.

Figure 2 shows the transmission spectra of the $\text{TlGaS}_{2x}\text{Se}_{2(1-x)}$ mixed crystals registered in the temperature range of 10–300 K. The dependences of absorption coefficient α on the photon energy $h\nu$ for the $\text{TlGaS}_{2x}\text{Se}_{2(1-x)}$ mixed crystals at temperatures $T = 300$ and 10 K are shown in Fig. 3a and b, respectively. Figure 4 presents the dependences of absorption coefficient on photon energy at different temperatures (10–300 K) for one of the representatives of mixed crystals

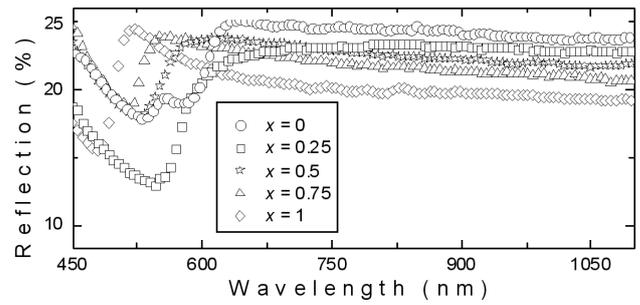


Fig. 1. The spectral dependences of reflection for $\text{TlGaS}_{2x}\text{Se}_{2(1-x)}$ mixed crystals at room temperature.

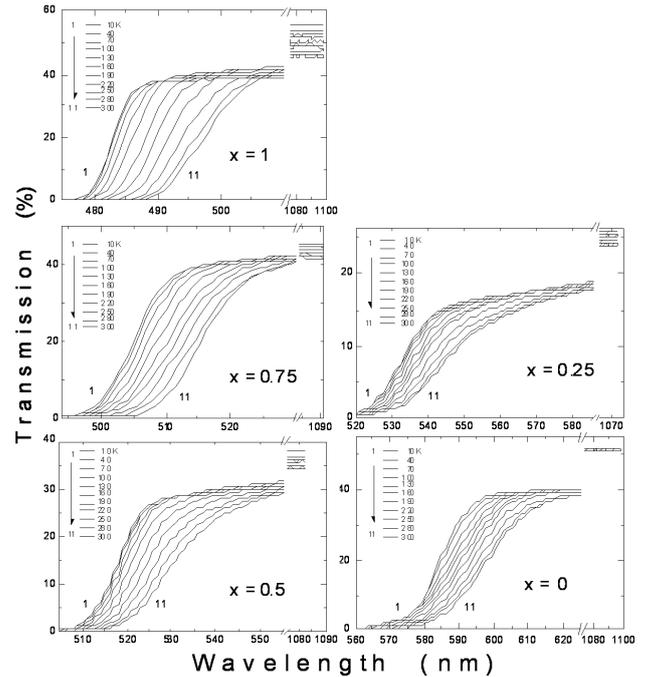


Fig. 2. The spectral dependences of transmission for $\text{TlGaS}_{2x}\text{Se}_{2(1-x)}$ mixed crystals in the temperature range of 10–300 K.

(TlGaSeS). We observed the blue shift of these dependences with decreasing temperature for all the compositions of mixed crystals studied.

The relation between absorption coefficient α and photon energy $h\nu$ is given by [19]:

$$(\alpha h\nu) = A(h\nu - E_g)^p, \quad (2)$$

where A is a constant, which depends on the transition probability and p is an index, which is theoretically equal to 2 or 1/2 for indirect and direct allowed transitions, respectively. Equation (2) can be also written as [20]:

$$\frac{d[\ln(\alpha h\nu)]}{d(h\nu)} = \frac{p}{h\nu - E_g}. \quad (3)$$

The type of optical transition can be determined by finding the value of p . In order to obtain the preliminary value of E_g , $d\{\ln(\alpha h\nu)\}/d(h\nu)$ versus $h\nu$ was plotted.

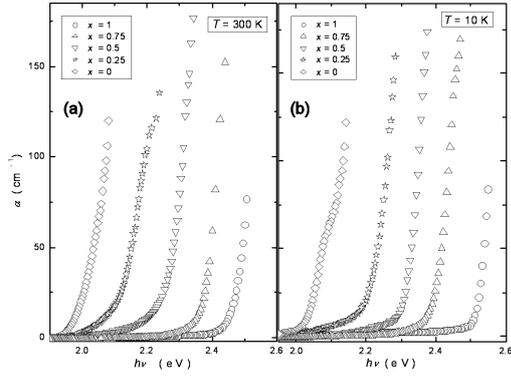


Fig. 3. Absorption coefficients vs. photon energies for $\text{TiGaS}_{2x}\text{Se}_{2(1-x)}$ mixed crystals at $T = 300\text{ K}$ (a) and $T = 10\text{ K}$ (b).

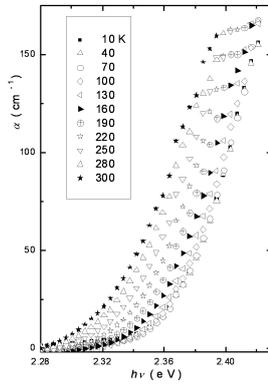


Fig. 4. Absorption coefficients vs. photon energies for $\text{TiGaS}_{2x}\text{Se}_{2(1-x)}$ mixed crystals at different temperatures from 10 to 300 K.

This plot comprises a peak and the position of peak maximum gives approximately the optical band gap. Then, the $\ln(\alpha h\nu)$ versus $\ln(h\nu - E_g)$ was plotted to determine p value, which was found to be about 2 from the slope of this dependence. Thus, in order to calculate the more precise value of the optical band gap, $(\alpha h\nu)^{1/2}$ was plotted as a function of photon energy, and this plot gives the straight line. The linear dependence of $(\alpha h\nu)^{1/2}$ on photon energy $h\nu$ suggest that the fundamental absorption edge in studied crystal is formed by the indirect allowed transitions. Using the extrapolations of the straight line down to $(\alpha h\nu)^{1/2} = 0$, the value of the indirect band gap energy (E_{gi}) was determined for the $\text{TiGaS}_{2x}\text{Se}_{2(1-x)}$ mixed crystals. The compositional dependences of determined energy band gaps for the temperatures of 10 and 300 K are demonstrated in Fig. 5. As seen from this figure, the energy band gaps increase with the increase of sulfur atoms content in the $\text{TiGaS}_{2x}\text{Se}_{2(1-x)}$ mixed crystals.

The determined values of the indirect energy gaps decrease with increasing temperature from 10 to 300 K, as shown in Fig. 6. The temperature dependence of the en-

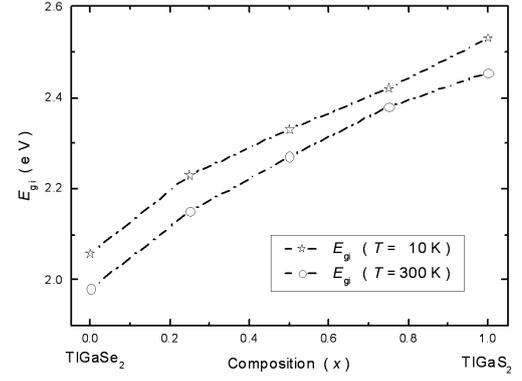


Fig. 5. Compositional dependences of the indirect band gaps of $\text{TiGaS}_{2x}\text{Se}_{2(1-x)}$ mixed crystals at $T = 10$ and 300 K. The dashed-dotted lines are only the guides for the eye.

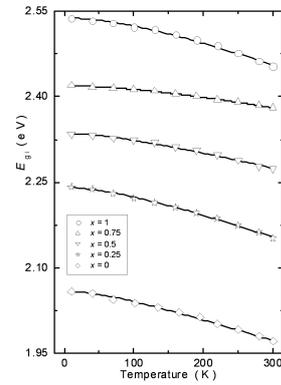


Fig. 6. The indirect band gap energies as a function of temperature for $\text{TiGaS}_{2x}\text{Se}_{2(1-x)}$ mixed crystals. The solid lines represent the fits using Eq. (4).

ergy band gap can be represented by the relation [19]:

$$E_{gi}(T) = E_{gi}(0) + \frac{\gamma T^2}{T + \beta}, \quad (4)$$

where $E_{gi}(0)$ is the absolute zero value of the band gap, $\gamma = dE_{gi}/dT$ is the rate of the band gap variation with temperature, and β is approximately the Debye temperature. The experimental data for the dependences of E_{gi} on the temperature (10–300 K) in $\text{TiGaS}_{2x}\text{Se}_{2(1-x)}$ mixed crystals were fitted using Eq. (4) as shown in Fig. 6 (the solid lines correspond to the theoretical fits). The fitting parameters were found to be $E_{gi}(0) = 2.06, 2.24, 2.34, 2.42,$ and 2.54 eV , $\gamma = -4.2 \times 10^{-4}, -4.6 \times 10^{-4}, -3.2 \times 10^{-4}, -2.6 \times 10^{-4},$ and $-5.3 \times 10^{-4}\text{ eV/K}$, and $\beta = 164, 174, 165, 170,$ and 203 K for the values of $x = 0, 0.25, 0.50, 0.75,$ and 1 , respectively. It should be noted that the Debye temperatures, evaluated by Lindemann's melting rule [21] by using the X-ray results [11] and the melting temperatures, were found to be $\beta = 155, 162, 157, 188,$ and 195 K , respectively.

At this point, it is worthwhile to compare present results concerning $E_{gi}(T = 300\text{ K})$ and $\gamma = dE_{gi}/dT$ with

those obtained by Bakhyshev et al. [16]. Since the authors studied $\text{TlGaS}_{2x}\text{Se}_{2(1-x)}$ mixed crystals with compositions $x = 0, 0.1, 0.3, 0.5, 0.7, 0.9,$ and 1 , we are able to compare only results obtained for the common compositions $x = 0, 0.5,$ and 1 . Our results on E_{gi} ($T = 300$ K) and $\gamma = dE_{\text{gi}}/dT$ equal 1.98 eV and -4.2×10^{-4} eV/K ($x = 0$); 2.27 eV and -3.2×10^{-4} eV/K ($x = 0.5$); 2.45 eV and -5.3×10^{-4} eV/K ($x = 1$). The corresponding results, reported in Ref. [16], were equal to 2.03 eV and -1.8×10^{-4} eV/K; 2.29 eV and -3.2×10^{-4} eV/K; 2.46 eV and -3.5×10^{-4} eV/K. Let us note that the latter parameters were determined from only transmission measurements in the temperature range of 77 – 300 K. Since the authors did not utilize the fitting procedure for the temperature dependence of energy band gap, they could not evaluate $E_{\text{gi}}(0)$ and the Debye temperatures for crystals studied.

It is well known that the temperature dependence of the band gap energy for a semiconductor can be expressed in two main parts as [19]:

$$\frac{dE_g}{dT} = \left(\frac{dE_g}{dT} \right)_{\text{l.exp.}} + \left(\frac{dE_g}{dT} \right)_{\text{e-ph}}. \quad (5)$$

The first term results from the variation of the band gap due to the thermal expansion of the crystal. It may be either positive or negative in sign depending on the specific properties of the electron states of the band extrema and the relative ordering of levels [22]. The second term represents the change in the energy band gap arising from electron–phonon interaction and is always negative in sign for all semiconductors. Therefore, overall dependence of the band gap of the material on temperature may be either negative or positive depending on the term that contributes more. The temperature coefficients of indirect band gaps of $\text{TlGaS}_{2x}\text{Se}_{2(1-x)}$ mixed crystals were found to have negative signs which suggest that the electron–phonon interaction term is larger than the lattice expansion contribution.

4. Conclusions

From the transmission and reflection measurements in the wavelength range of 400 – 1100 nm, the compositional dependences of the indirect band gaps of $\text{TlGaS}_{2x}\text{Se}_{2(1-x)}$ mixed crystals were established. It was revealed that the energy band gaps increase with the increase of sulfur atoms content in these mixed crystals. Moreover, the transmission measurements in $\text{TlGaS}_{2x}\text{Se}_{2(1-x)}$ mixed crystals were carried out in the temperature range of 10 – 300 K. The absorption edge was observed to shift toward lower energy values as temperature increases from 10 to 300 K. The data were used to calculate the indirect energy band gaps of the crystals as a function of temperature. As a result, the rates of the change of the indirect band gap with temperature were

determined for different compositions of mixed crystals studied.

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