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Optical properties of $TlGa_xIn_{1-x}S_2$ layered mixed crystals ($0 \le x \le 1$) I. Composition- and temperature-tuned energy band gap

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ABSTRACT

Optical properties of the $TlGa_xIn_{1-x}S_2$ mixed crystals ($0 \le x \le 1$) have been studied by means of 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 increasing of gallium atoms content in the $TlGa_xIn_{1-x}S_2$ 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 determined for the different compositions of mixed crystals studied.

1. Introduction

$TlInS_2$ and $TlGaS_2$ compounds belong to the group of semiconductors with layered structure [1,2]. The lattice structure of these crystals is composed of rigorously periodic two dimensional layers arranged parallel to the (0 0 1) plane and each such consecutive layer is rotated by a right angle with respect to the previous one. Tl and S atoms are bonded to form interlayer bonds whereas In(Ga) and S atoms are bonded to form intralayer bonds. The basic structural units of a layer are the $In_4(Ga_4)S_6$ adamantane-like units connected together by bridging S atoms. The Tl atoms are located in trigonal prismatic voids resulting from the combination of the $In_4(Ga_4)S_6$ polyhedra into a layer.

$TlInS_2$ and $TlGaS_2$ 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 $TlInS_2$ and $TlGaS_2$ crystals were studied in Refs. [2–11]. 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 [12].

The compounds $TlInS_2$ and $TlGaS_2$ form a series of $TlGa_xIn_{1-x}S_2$ ($0 \le x \le 1$) mixed crystals. Previously, the structural and optical properties of the $TlGa_xIn_{1-x}S_2$ mixed crystals were investigated by X-ray diffraction [13], infrared reflection [14], photoluminescence [15], Raman [14] and Brillouin [16] 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. Recently, we studied the effect of isomorphic atom substitution on the optical absorption edge of $TlGa_{1-x}In_xSe_2$ mixed crystals [17]. A structural phase transition (monoclinic to tetragonal) due to substitution of cation (indium for gallium) was revealed in the composition range of $0.50 \le x \le 0.75$. From the transmission and reflection measurements, the compositional dependence of the indirect band gap energy was established. The band gap energy was shown to drastically decrease from 1.89 ($x = 0.50$) to 0.94 eV ($x = 0.75$) in the region of the structural phase transition.

The aim of the present paper was to study the effect of the isomorphic cation substitution (indium by gallium) and the temperature on the absorption edge of $TlGa_xIn_{1-x}S_2$ 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 the $TlGa_xIn_{1-x}S_2$ ($0 \le x \le 1$) mixed crystals were grown by the Bridgman method from a stoichiometric melt of starting materials sealed in the

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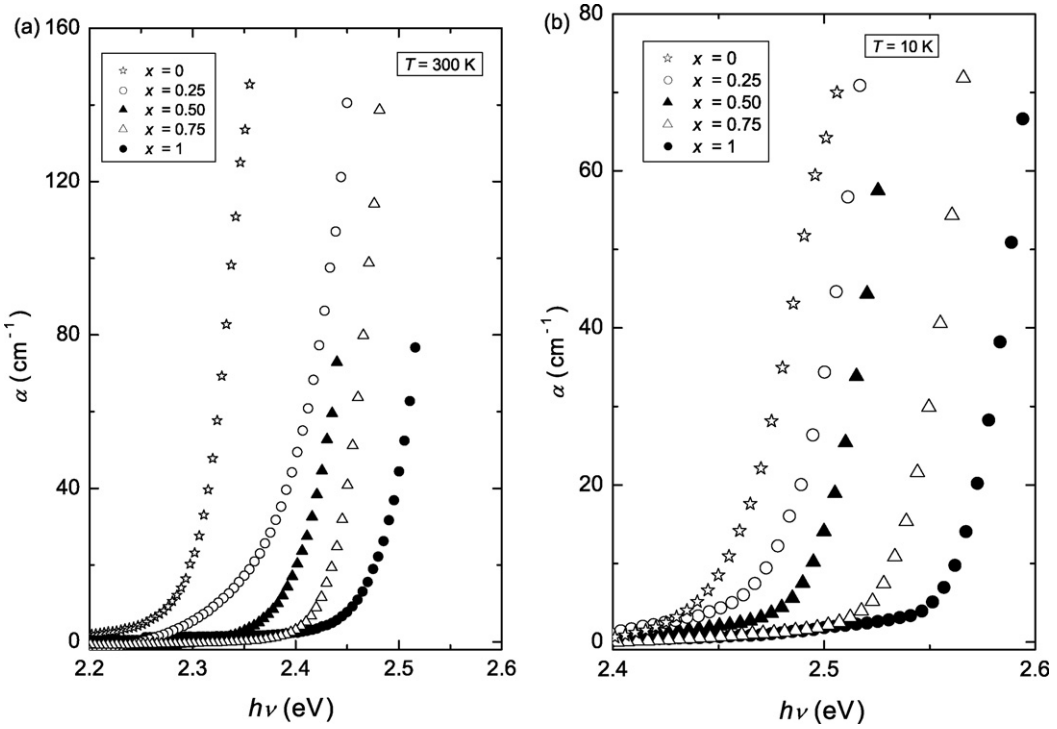

Fig. 1. Absorption coefficients vs. photon energies for $TlGa_xIn_{1-x}S_2$ mixed crystals at $T = 300$ K (a) and $T = 10$ K (b).

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 $TlGa_xIn_{1-x}S_2$ mixed crystals was determined by the energy dispersive spectroscopic analysis using JSM-6400 electron microscope. The atomic composition ratio of the studied samples was estimated as 25.6 (Tl):25.2 (In):49.2 (S) ($x = 0$); 25.8 (Tl):6.6 (Ga):19.2 (In):48.4 (S) ($x = 0.25$); 25.9 (Tl):13.0 (Ga):13.1 (In):48.0 (S) ($x = 0.50$); 26.1 (Tl):19.0 (Ga):6.1 (In):48.8 (S) ($x = 0.75$); 25.4 (Tl):25.6 (Ga):49.0 (S) ($x = 1$). The samples for the measurements were taken from the middle part of the ingots. The freshly cleaved platelets (along the layer plane (0 0 1)) were mirror-like. 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, which consisted of a 20 W halogen lamp, a holographic grating, and a silicon photodiode. The transmission measurements were done under the normal incidence of light with the polarization in the (0 0 1) 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 $TlGa_xIn_{1-x}S_2$ 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 [18]

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

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 (by repeated cleaving using the transparent adhesive tape) until it was convenient for measuring the transmission spectra in the temperature range of 10–300 K. The thick samples with $d \approx 300\,\mu$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. 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.

The dependencies of absorption coefficient α on the photon energy $h\nu$ for the $TlGa_xIn_{1-x}S_2$ mixed crystals at temperatures $T = 300$ and 10 K are shown in Fig. 1a and b, respectively. We observed the blue shift of these dependencies with decreasing temperature for all the compositions of mixed crystals studied. From the analysis of the experimental data, it was revealed that the absorption coefficient α is proportional to $(h\nu - E_g)^2$. The experimental data were fitted to a linear equation to find the energy band gaps. The linear dependencies were observed for the relations $(\alpha h\nu)^{1/2}$ versus $h\nu$. Fig. 2 presents these dependencies at different temperatures (300–10 K) for one of the representatives of mixed crystals ($TlIn_{0.5}Ga_{0.5}S_2$). This supposed the realization of the indirect allowed transitions. Using the extrapolations of the straight lines down to $(\alpha h\nu)^{1/2} = 0$, the values of the indirect band gap energies were determined for the $TlGa_xIn_{1-x}S_2$ mixed crystals. The compositional dependencies of determined energy band gaps are demonstrated in Fig. 3 for the temperatures of 10 and 300 K. As seen from this figure, the energy band gaps increase with the increase of gallium atoms content in the $TlGa_xIn_{1-x}S_2$ mixed crystals.

The obtained values of the indirect energy gaps decrease with increasing temperature from 10 to 300 K, as displayed in Fig. 4. The temperature dependence of the energy band gap can be

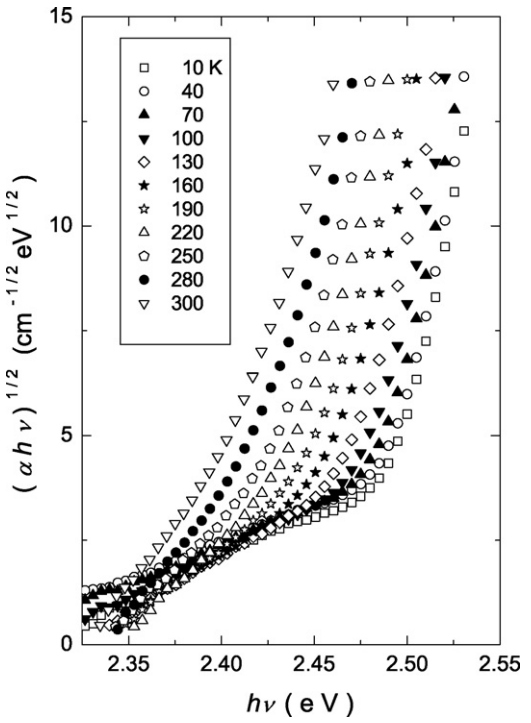

Fig. 2. The dependencies of $(\alpha h\nu)^{1/2}$ on the photon energy for $TlIn_{0.5}Ga_{0.5}S_2$ crystal at different temperatures from 10 to 300 K.

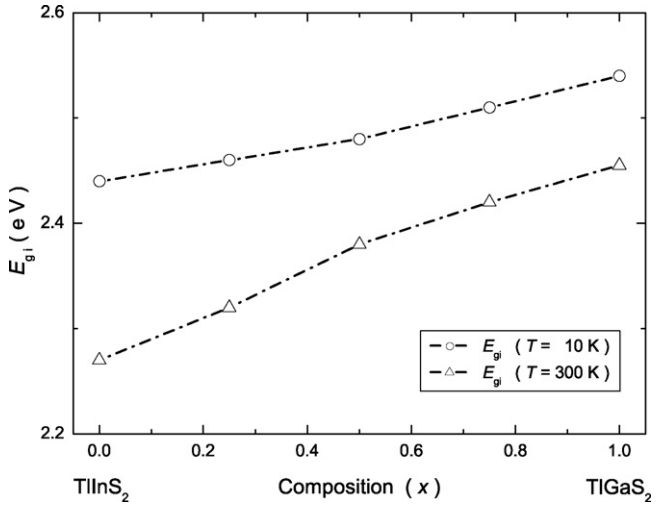

Fig. 3. Compositional dependencies of the indirect band gaps of $TlGa_xIn_{1-x}S_2$ mixed crystals at $T = 10$ and 300 K. The dashed-dotted lines are only the guides for the eyes.

represented by the relation [18]

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

where $E_{gi}(0)$ is the absolute zero value of the band gap, $\gamma = dE_{gi}/dT$ is the rate of change of the band gap with temperature, and β is approximately the Debye temperature. The experimental data for the dependencies of E_{gi} on the temperature (10–300 K) in $TlGa_xIn_{1-x}S_2$ mixed crystals were fitted using Eq. (2) as shown in Fig. 4 (the solid lines correspond to the theoretical fits). The fitting parameters were found to be $E_{gi}(0) = 2.44$, 2.46, 2.48, 2.51 and 2.54 eV, $\gamma = -9.2 \times 10^{-4}$, -6.0×10^{-4}, -4.7×10^{-4}, -6.0×10^{-4} and -5.4×10^{-4} eV/K, and $\beta = 160$, 180, 169 190 and 203 K for the values of $x = 0$, 0.25, 0.50, 0.75 and 1, respectively. It should be

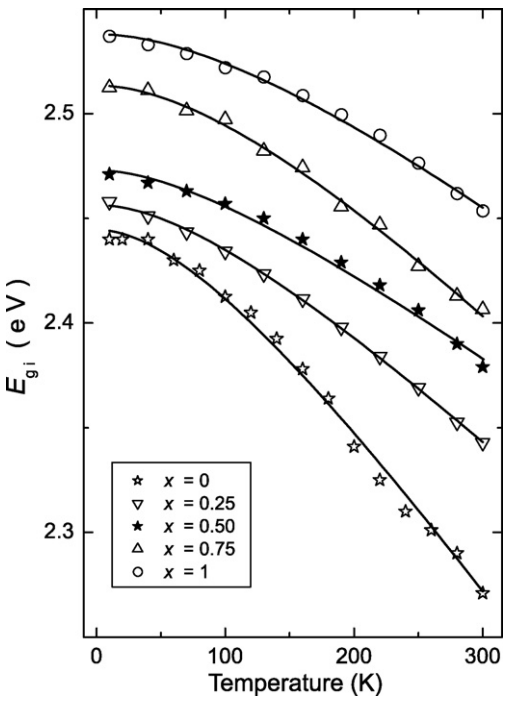

Fig. 4. The indirect band gap energies as a function of temperature for $TlGa_xIn_{1-x}S_2$ mixed crystals. The solid lines represent the fits using Eq. (2).

noted, that the Debye temperatures, evaluated by Lindemann's melting rule [19] by using the X-ray results [20,21] and the melting temperatures, were found to be $\beta = 155$, 173, 173, 183 and 195 K, respectively.

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

$$\frac{dE_g}{dT} = \left(\frac{dE_g}{dT}\right)_{l.\exp.} + \left(\frac{dE_g}{dT}\right)_{e-ph}. \tag{3}$$

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 [3]. 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 $TlGa_xIn_{1-x}S_2$ 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 dependencies of the indirect band gaps of $TlGa_xIn_{1-x}S_2$ mixed crystals were established. It was revealed that the energy band gaps increase with the increase of gallium atoms content in these mixed crystals. Moreover, the transmission measurements in $TlGa_xIn_{1-x}S_2$ 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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