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Composition-tuned refractive index and oscillator parameters in $TlGa_xIn_{1-x}S_2$ layered mixed crystals ($0 \leq x \leq 1$)

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ABSTRACT

The optical properties of $TlGa_xIn_{1-x}S_2$ mixed crystals have been studied through transmission and reflection measurements in the wavelength range 400–1100 nm. These measurements allowed determination of the spectral dependence of the refractive index for all compositions of the mixed crystals studied. The dispersion of the refractive index is discussed in terms of the Wemple–DiDomenico single-effective-oscillator model. The compositional dependences of the refractive index dispersion parameters (oscillator energy, dispersion energy and zero-frequency refractive index) were revealed.

1. Introduction

Information about the spectral dependence of optical parameters such as refractive index, dielectric constant, reflectivity and absorption coefficients are essential in the characterization of materials that are used in the fabrication of optoelectronic devices. The family of crystals designated with the chemical formula $TlBX_2$ (where B = In or Ga, X = S, Se or Te) is known as thallium dichalcogenides. Members of this family have both layered ($TlGaS_2$, $TlGaSe_2$, $TlInS_2$) and chain ($TlInSe_2$, $TlInTe_2$, $TlGaTe_2$) structures [1,2].

The optical and electrical properties of $TlInS_2$ and $TlGaS_2$ layered crystals have been studied in [3–7]. These crystals are useful for optoelectronic applications as they have high photosensitivity in the visible range of the spectra and a wide transparency range of 0.5–14.0 μm [8]. The layered compounds $TlInS_2$ and $TlGaS_2$ form a series of $TlGa_xIn_{1-x}S_2$ ($0 \leq x \leq 1$) isostructural mixed crystals. Previously, the structural and optical properties of these crystals have been investigated by X-ray diffraction [9], photoluminescence [10], infrared reflection and Raman spectroscopy [11].

Recently, we studied the effect of isomorphic atom substitution on the lattice structure and optical absorption edge of $TlGa_{1-x}In_xSe_2$ [9,12] and $TlInS_{2x}Se_{2(1-x)}$ mixed crystals [9,13]. For $TlGa_{1-x}In_xSe_2$ mixed crystals, a structural phase transition (monoclinic to tetragonal) due to substitution of the cation (indium for gallium) was revealed in the composition range $0.50 \leq x \leq 0.75$. 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 $TlInS_{2x}Se_{2(1-x)}$ mixed crystals, a structural phase transition (monoclinic to tetragonal) due to substitution of the anion (selenium for sulfur) was observed in the composition range $x < 0.25$. 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.

Previously, we have reported the effect of isomorphic cation substitution and temperature on the absorption edge of $TlGa_xIn_{1-x}S_2$ isostructural mixed crystals ($0 \leq x \leq 1$) [14]. It was found that the energy band gaps increase with the increase of gallium atom content in the mixed crystals studied. From the transmission measurements carried out in the temperature range 10–300 K, the rates of change of the indirect band gaps with temperature were determined.

The aim of the present investigation was to study the effect of isomorphic cation substitution (indium by gallium) on the dispersion parameters of $TlGa_xIn_{1-x}S_2$ mixed crystals through transmission and reflection measurements in the wavelength range 400–1100 nm. The refractive index dispersion data were analyzed using the Wemple–DiDomenico single-effective-oscillator model. The refractive index, the oscillator energy, the dispersion energy and the zero-frequency refractive index were determined for different compositions of the mixed crystals studied.

2. Experimental details

Single crystals of $TlGa_xIn_{1-x}S_2$ ($0 \leq x \leq 1$) were grown by the Bridgman method from a stoichiometric melt of starting

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materials sealed in evacuated and carbon-coated silica tubes in our crystal growth laboratory. The resulting ingots had no cracks or voids on the surface. The chemical composition of the $TlGa_xIn_{1-x}S_2$ mixed crystals was determined by energy dispersive spectroscopic analysis using a JSM-6400 electron microscope. The atomic composition ratios of the studied samples were estimated as 25.6 (Tl): 25.2 (In): 49.2 (S) ($x = 04$); 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 (001)) 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. The transmission measurements were done under the normal incidence of light with polarization in the (001) plane, which is perpendicular to the **c**-axis of the crystal. For the reflection experiments, a specular reflectance measurement attachment with 5° incident angle was used. The resolution of the spectrophotometer was 5 nm.

3. Results and discussion

The transmittance (T) and reflectivity (R) spectra for $TlGa_xIn_{1-x}S_2$ mixed crystals were obtained in the wavelength (λ) range 400–1100 nm (Fig. 1). The observed oscillations of transmittance at longer wavelengths are due to interference fringes. The absorption coefficient α and refractive index n were obtained from the following relations [15].

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

$$n = \frac{1+R}{1-R}+\left[\frac{4R}{(1-R)^2}-\left(\frac{\alpha\lambda}{4\pi}\right)^2\right]^{1/2}, \tag{2}$$

where d is the sample thickness.

The reflectivity was measured using specimens with natural cleavage planes and a thickness such that $\alpha d \gg 1$. But for the transmission measurements, the thickness of the sample was reduced by using transparent adhesive tape. The thicknesses of the thin samples were determined using transmission interference fringes at a wavelength slightly longer than the intrinsic absorption edge, i.e., in a region with relatively high transmission (Fig. 1). In most cases, the thickness of the sample was about 10 μm for transmission measurements.

The refractive index n was calculated using Eqs. (1) and (2) as a function of wavelength, and is shown in Fig. 2. The refractive index in the energy region $h\nu < E_g$ gradually decreases with increasing wavelength. The dispersive refractive index data in this region were analyzed by means of the single-effective-oscillator model which was proposed by Wemple and DiDomenico [16,17]. The refractive index can be expressed in terms of photon energy $h\nu$, the single-oscillator energy E_{so} and the dispersion energy E_d, which is a measure of the strength of interband optical transitions, by the relation

$$n^2(h\nu) = 1+\frac{E_{so}E_d}{E_{so}^2-(h\nu)^2}. \tag{3}$$

Plotting $(n^2-1)^{-1}$ versus $(h\nu)^2$ allows the determination of the oscillator parameters by fitting a linear function to the lower-energy data range. The fittings of the above-reported function are presented in the insets of Fig. 2 for different compositions of the

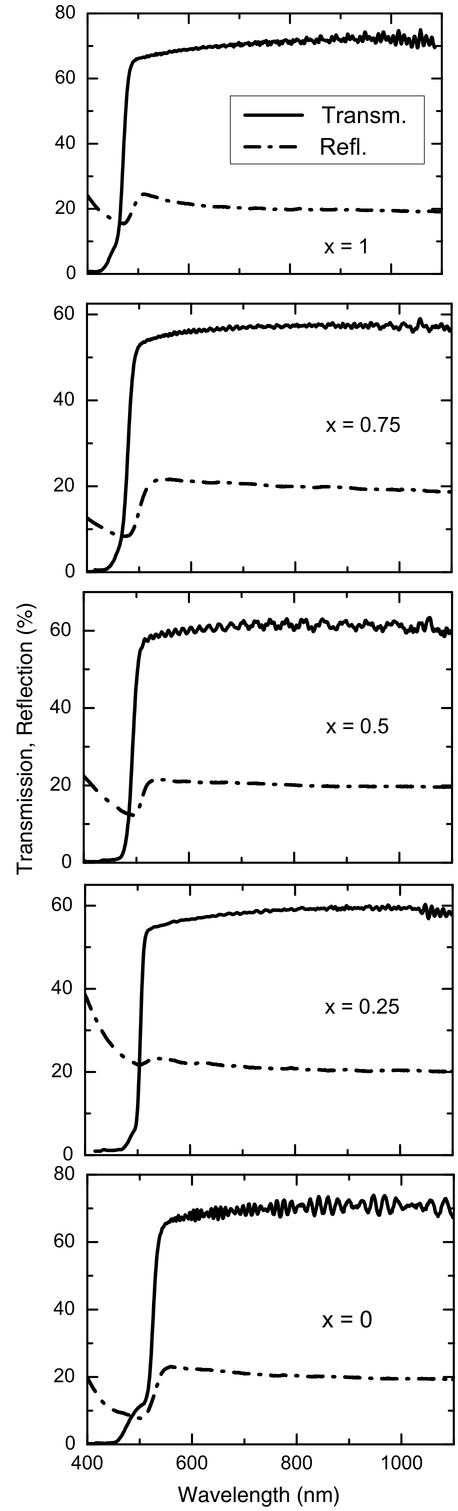

Fig. 1. The spectral dependences of the transmittance and the reflectivity for different compositions of $TlGa_xIn_{1-x}S_2$ mixed crystals.

mixed crystals studied. The zero-frequency refractive index n_0 is obtained using Eq. (3), i.e., based on the expression $n_0^2 = 1+E_d/E_{so}$.

The values of the parameters E_{so} and E_d were calculated from the slopes and the intersections with y-axis of the straight lines (insets of Fig. 2). The dependences of the parameters E_{so} and E_d as functions of composition of the mixed crystals studied are shown in the inset of Fig. 3. As seen from this figure, the values of E_{so} and E_d decrease monotonically with increase of the gallium content.