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Low-temperature absorption edge and photoluminescence in layered structured $Tl_2Ga_2S_3Se$ single crystals

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ABSTRACT

The absorption edge of undoped $Tl_2Ga_2S_3Se$ crystals have been studied through transmission and reflection measurements in the wavelength range 440–1100 nm and in the temperature range 10–300 K. The absorption edge was observed to shift toward lower energy values with increasing temperature. As a result, the rate of the indirect band gap variation with temperature $\gamma = -2.6 \times 10^{-4}$ eV/K and the absolute zero value of the band gap energy $E_{gi}(0) = 2.42$ eV were obtained.

The emission band spectra of $Tl_2Ga_2S_3Se$ crystals have been studied in the temperature range 10–60 K and in the wavelength region 505–605 nm. A broad photoluminescence (PL) band centered at 550 nm (2.25 eV) was observed at $T = 10$ K. Variation of emission band has been studied as a function of excitation laser intensity in the 0.3–41.5 mW cm^{-2} range. Radiative transitions from the shallow donor level $E_d = 0.01$ eV to the moderately deep acceptor level $E_a = 0.16$ eV were suggested to be responsible for the observed PL band.

1. Introduction

Ternary and quaternary layered-structured semiconductors show many peculiar properties. There are large number of applications as memory switching elements, emission modulators and nonlinear optical transducers in nonlinear optics and photoelectronics [1,2]. The quaternary compound $Tl_2Ga_2S_3Se$ is a structural analog of $TlGaS_2$ [3] in which one quarter of sulfur atoms are replaced by selenium atoms. The lattice structure of this crystal is composed of rigorously periodic two dimensional layers arranged parallel to the (0 0 1) plane and each such consecutive layer is rotated by 90° with respect to the previous one.

The optical and electrical properties of $TlGaS_2$, $TlGaSe_2$, TlGaSeS and $Tl_2Ga_2Se_3S$ crystals were studied in Refs. [4–12]. These crystals are useful for optoelectronic applications as they have high photosensitivity in the visible range of the spectra and wide transparency range 0.5–14.0 μm [10]. In our previous study, the optical properties of $Tl_2Ga_2S_3Se$ crystals were investigated from transmission and reflection (1.1–3.1 eV) and ellipsometric (1.2–4.7 eV) measurements at room temperature [13]. The analysis of absorption data revealed the presence of both optical indirect and direct transitions with band gap energies of 2.38 and 2.62 eV, respectively. The real and imaginary parts of the dielectric function as well as refractive and absorption indices were found as a result of analysis of ellipsometric data. Moreover, we have studied thermally stimulated currents (TSC) in $Tl_2Ga_2S_3Se$ crystals in the temperature ranges 10–60 K [14] and 200–320 K [15]. Experimental evidences were obtained for trapping centers with activation energies of 11 meV [14] and 498 meV [15].

The influence of defects on the performance of optoelectronic devices is a well-known subject. In optoelectronic devices such as LEDs or lasers, defects may introduce non-radiative recombination centers to lower the internal quantum efficiency or even render light generation impossible, depending on defect density. In the case of electronic devices, defects introduce scattering centers lowering carrier mobility, hence hindering high-frequency operation. Thus, it is very useful to get detailed information on energetic parameters of defect centers in semiconductors in order to obtain high-quality devices.

Photoluminescence (PL) spectroscopy is a very suitable and widely used non-destructive technique to study the defect structures of semiconductors. Recently, we have measured the low temperature PL spectra of $TlGaS_2$ [16], TlGaSeS [17] and $TlGaSe_2$ [18] crystals and observed two, two and one broad emission bands, respectively, which have been attributed to donor–acceptor pair recombinations. The activation energies of revealed levels were found to be 5 and 85 meV ($TlGaS_2$), 8 and 11 meV (TlGaSeS) and 12 meV ($TlGaSe_2$). However, no PL study of $Tl_2Ga_2S_3Se$ crystals has been reported so far.

The aim of the present work was to study the optical properties of the $Tl_2Ga_2S_3Se$ crystal in the wavelength range 440–1100 nm and in the temperature range 10–300 K by means of transmission

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and reflection measurements. Analysis of temperature dependence of calculated absorption coefficients in the 10–300 K range allowed evaluating the rate of the variation of the indirect band gap with temperature. We also report the intensity variations of photoluminescence emission band with temperature (10–60 K) and excitation laser intensity (0.3–41.5 mW cm^{-2}). Analysis of the data suggests that the radiative transitions originate from recombination of charge carriers from donor to acceptor states. Furthermore, from X-ray analysis in the 10–70° diffraction angle (2θ) range the lattice parameters of $Tl_2Ga_2S_3Se$ crystals were determined.

2. Experimental details

$Tl_2Ga_2S_3Se$ semiconductor polycrystals were synthesized using high-purity elements (at least 99.999%) taken in stoichiometric proportions. The single crystals were grown by the Bridgman method in evacuated (10^{-5} Torr) silica tubes with a tip at the bottom. The resulting ingots (yellow–green in color) showed good optical quality and the freshly cleaved surfaces were mirror-like. The atomic composition of $Tl_2Ga_2S_3Se$ samples (Tl: Ga: S: Se), determined by energy dispersive spectroscopic analysis (EDSA), was found to be 26.0: 25.8: 35.9: 12.3, respectively [13]. Moreover, EDSA indicated that silicon impurities were present in $Tl_2Ga_2S_3Se$ crystals. A "Rigaku Miniflex" diffractometer with Cu$K\alpha$ radiation ($\lambda=0.154049$ nm) was used at a scanning speed of 0.02°/sec for the X-ray powder diffraction experiments.

Transmission and reflection measurements were carried out in the 440–1100 nm wavelength region with a "Shimadzu" UV-1201 model spectrophotometer. The transmission spectra were registered under normal incidence of light with polarization direction along the (0 0 1) plane, which is parallel to the layers of the crystal. For room temperature reflection experiments we utilized the specular reflectance measurement attachment with 5° incident angle. The sample was cooled from room temperature down to 10 K by using an "Advanced Research Systems, Model CSW-202" closed-cycle helium cryostat. The temperature was controlled within an accuracy of ± 0.5 K.

Crystals suitable for PL measurements had typical sample dimensions of $6\times4\times1$ mm^3. The electrical conductivity of the studied samples was n-type as determined by the hot probe method. A 325 nm line of He–Cd laser was used as the excitation light source. PL experiments were carried out by collecting the light from the laser-illuminated face of the sample in a direction close to the normal of the layer. The PL spectra of the sample in the region 505–605 nm were analyzed using a "Oriel MS-257" grating monochromator and "Hamamatsu S7010-1008" FFT-CCD Image Sensor with single stage electric cooler. The registered PL spectra have been corrected for the spectral response of the optical apparatus.

3. Results and discussion

Fig. 1 shows the X-ray diffractogram of $Tl_2Ga_2S_3Se$ crystal. The Miller indices ($h\,k\,l$), the observed and calculated interplanar spacings (d), and the relative intensities (I/I_0) of the diffraction lines are listed in Table 1. The lattice parameters of the monoclinic unit cell, $a=0.46219$, $b=0.75498$, $c=0.78408$ nm, and $\beta=101.66°$, were calculated by using a least-squares computer program "DICVOL 04".

3.1. Absorption edge analysis

Fig. 2 shows the temperature dependence of the transmission spectra of the $Tl_2Ga_2S_3Se$ single crystals in the wavelength range 400–1100 nm and in temperature range 10–300 K. The room temperature reflection measurements were accomplished using the samples with natural cleavage planes and the thickness such that $\alpha d >> 1$ (inset of Fig. 2). The absorption coefficient (α) was

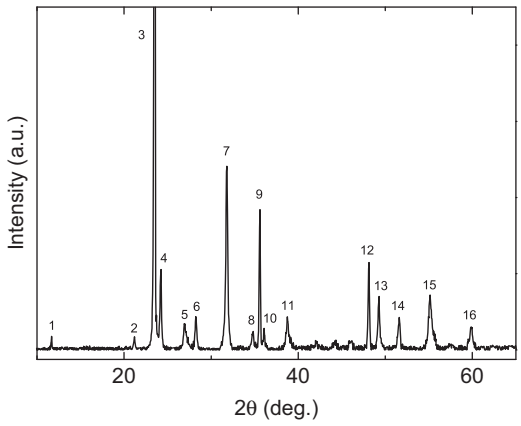

Fig. 1. X-ray diffraction pattern of $Tl_2Ga_2S_3Se$ powder sample.

Table 1
X-ray powder diffraction data for $Tl_2Ga_2S_3Se$ crystals.

No.	*hkl*	d_{obs} (nm)	d_{calc} (nm)	I/I_0
1	020	0.757044	0.756649	1.6
2	10−1	0.418751	0.419083	1.5
3	021	0.379224	0.379245	100
4	12−1	0.366752	0.366464	9.5
5	031	0.330818	0.330704	3.1
6	21−1	0.315647	0.316010	3.9
7	150	0.281077	0.281264	21.7
8	141	0.257303	0.257281	2.2
9	060	0.251898	0.251838	16.5
10	051	0.248740	0.248789	2.5
11	32−1	0.232057	0.231862	3.9
12	080	0.188879	0.188841	10.3
13	31−2	0.184701	0.184694	6.3
14	142	0.176929	0.176938	3.8
15	181	0.166323	0.166320	6.5
16	51−1	0.154276	0.154291	2.7

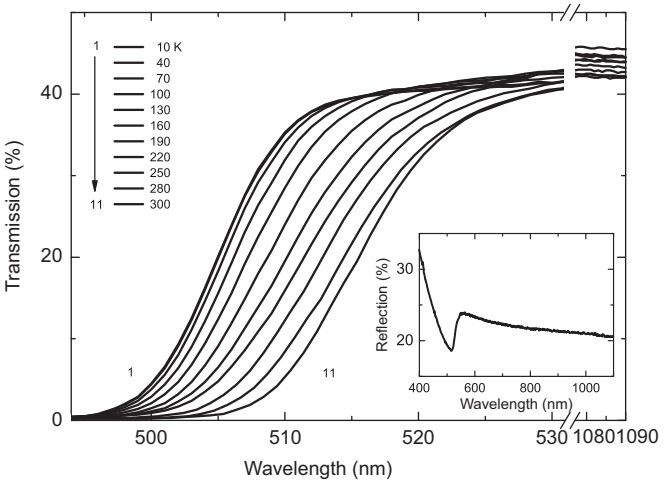

Fig. 2. Spectral dependence of transmission for $Tl_2Ga_2S_3Se$ crystal in the temperature range 10–300 K. Inset: The spectral dependence of reflection at room temperature.