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Full Length Article

Optical spectra of $TlGaS_2$ crystals

L. Nemerenco [a], N.N. Syrbu [a,*], V. Dorogan [a], N.P. Bejan [a], V.V. Zalamai [b]

[a] Technical University of Moldova, 168 Stefan cel Mare Avenue, 2004 Chisinau, Republic of Moldova
[b] Institute of Applied Physics, Academy of Sciences of Moldova, 5 Academy Street, 2028 Chisinau, Republic of Moldova

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ABSTRACT

Wavelength modulated reflection spectra measured at temperatures 14 K and 300 K in E∥a and E∥b polarizations for $TlGaS_2$ crystals were investigated. The ground and excited states of excitons B_{2u} in E∥a polarization and B_{3u} in E∥b polarization were observed and the main parameters of exitons and bands were determined. The optical functions for wide energies (2–6 eV) were calculated by Kramers–Kronig analysis of reflection spectra. The wavelengths of isotropic points in $TlGaS_2$ crystals were defined.

1. Introduction

$TlGaS_2$ crystals belong to triple thallium chalcogenides $A^{III}B^{III}C_2^{VI}$ with well-pronounced layered structure. Due to specificity of crystal structure these crystals have a strong anisotropy of physical properties [1–8]. The effective receivers of visible and infrared emission, detectors of x-ray and gamma radiation, neutron detectors, strain gage and piezoelectric photo resistors [9,10]. The authors of Ref. [3] report about a high sensitivity of $TlGaS_2$ monocrystals in x-ray diapason at energies 25–50 keV. The dependence of the crystal conductivity on intensity of x-ray radiation dose has a power-law character.

The authors of Ref. [11] show that partial (0.1–0.5%) substitution of gallium by itterbium in layered single crystals $TlGaS_2$ leads to the shift of photocurent maximum to long-wavelentghs. This leads to the significant broadening of spectral sensitivity diapasone, to the incresing of amplitude of impurity photocurrent and to the increasing of x-ray sensitivity in three times. Discovered mechanisms create an perspective for development of photodetectors with extended in infrared spectral diapasone and sensetive x-ray detectors on the base of $TlGaS_2$:Yb single crystals. The authors of Ref. [12] show that a raplacement in small concentrations of Ga by Co in $TlGaS_2$ allow to manage its optical properties, this gives a possibility of practical application. As reported in Ref. [13] the red luminescence with complex thin structure were observed in undoped TlGaS2 crystals at 1.8 K. This low temeprature luminiscence is due to the paramagnitic centers Tl^{2+}.

Raman scattering spectra for different geometries and they temperature dependences on temperatures 77–400 K were investigated in $TlGaS_2$ crystals [14]. The vibrational reflection spectra in the region 50–4000 cm^{-1} were investigated and the main parameters of polar vibrational LO and TO modes were determined. The calculations of relative effective charges of anions and cations in E∥a and E∥b polarizations show a difference of its ionicity degree along axes *a* and *b* [14]. These materials were intensively investigated (see Ref. [14–18,20]). The birefringence effects and reflection spectra of excitons were investigated for these crystals by our research group [19]. The presence of big number of articles dedicated by layered crystal $TlGaS_2$ undoubtedly indicated about an interest to this material and a perspective of its application in optoelectronic devices.

This work is dedicated to the investigation of excitonic states and electron transitions in $TlGaS_2$ crystals. Wavelength modulated reflection spectra for energies 2–6 eV at temperatures 300 K and 14 K in E∥a and E∥b polarizations were investigated. The ground and excited states of excitons B_{2u} in E∥a and B_{3u} in E∥b polarizations were observed and the main parameters of excitons and bands in $\boldsymbol{k}=0$ were determined. Optical functions for wide energy diapason (2–6 eV) in E∥a and E∥b polarizations were calculated. The isotropic points (where crystal is isotropic) of $TlGaS_2$ crystal was identified.

* Corresponding author.
E-mail address: sirbunn@yahoo.com (N.N. Syrbu).

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2. Experimental methods

The crystals grown by Bridgmann method have 2 × 1 × 1 cm size and easy can be cleaved. The optical measurements were carried out on computerized spectrometers MDR-2, SPECORD M40 and JASCO-670. The low-temperature spectra were measured on samples mounted on cold-finger of Helium optical cryogenic system LTS-22 C 330.

3. Experimental results and discussions

3.1. Excitonic spectra in $TlGaS_2$ crystals

The structure of $TlGaS_2$ is described by C_{2h}^6 space group according crystallographic data. The unit cell has eight formula units. The main motif of structure is formed by tetrahedral polyhedrons Ga_4S_{10} consist of four tetrahedrons of GaS_4. The structure $TlGaS_2$ is pseudo-tetragonal since $a=b=10.31$ Å, $c=15.16$ Å and $\beta=99.7°$ [6]. The narrow peak at 2.605 eV due to forming of direct exciton in Brillouin zone center is observed in region of edge absorption at temperature 1.8 K in E‖c polarization [7, 8]. The value of absorption in the maximum of excitonic peak is larger than 2000 cm^{-1}. Since crystals $TlGaS_2$ are cleft perpendicular to crystallographic axis c so absorption spectra are measured for two polarizations of light waves E‖a and E‖b. The Fig. 1, A shows absorption spectra of crystals $TlGaS_2$ measured in E‖a and E‖b polarizations at temperatures 9–300 K. The excitonic peaks are observed in both polarizations and shift to higher energies. The temperature shift coefficient of exciton maxima β is equal to 2.4×10^{-4} eV/K and 3.5×10^{-4} eV/K in E‖a and E‖b polarizations, respectively. The value of absorption coefficient in excitonic peaks maxima corresponds to 4000 cm^{-1}. These results confirm the results of Ref. [8,19] that excitonic transitions are allowed for these polarizations. The Fig. 1, C shows wavelength modulated transmission spectra measured at temperature 14 K in E‖a and E‖b polarizations. The indirect transitions [5,17] considerably situated

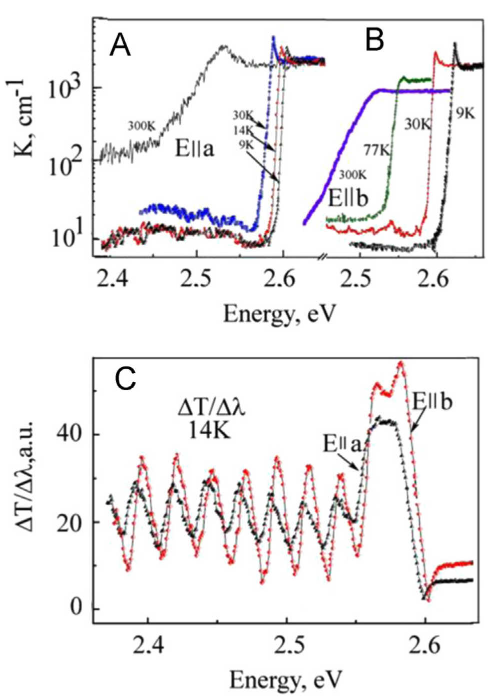

Fig. 1. A, B-Absorption spectra of $TlGaS_2$ crystals of 17.5 μm thickness in polarizations E‖a (A) and E‖b (B) measured at different temperatures. C-Wavelength modulated transmission spectra measured at temperature 14 K.

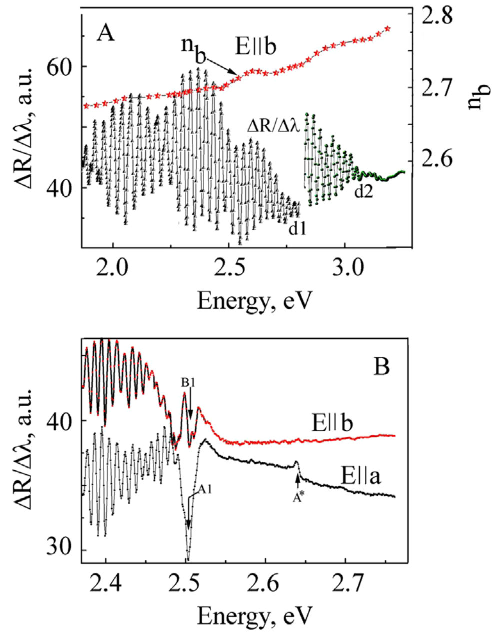

Fig. 2. Wavelength modulated reflection spectra in excitonic region in polarizations E‖a and E‖b of $TlGaS_2$ crystals with thicknesses d1 = 350 μm and d2 = 7.5 μm (A) and $d=950$ nm (B) and refractive indices n_a(E‖a) and n_b(E‖b) measured at temperature 300 K.

at energies 2.3–2.5 eV are not observed by us in both absorption spectra and wavelength modulated transmission spectra. The interference was observed in wavelength modulated transmission spectra measured at temperature 14 K at energies $E < 2.55$ eV.

The well-pronounced interference right up to 3 eV was discovered in wavelength modulated reflection spectra of 7.5 μm thickness crystals in E‖a and E‖b polarizations (see Fig. 2). The Fig. 2, A shows the wavelength modulated reflection spectra only for one polarization inasmuch as for another polarization the spectrum has a similar shape. The refractive indices for corresponding polarizations were calculated from interference spectra. The spectral dependences of refractive indices (n_a(E‖a) and n_b(E‖b)) at temperature 300 K intersect at energies 2.505 eV (495 nm) and 3.01 eV (412 nm). The interference spectra of thick crystals ($d \approx 970$ μm) were observed at energies $E < 2.5$ eV (see Fig. 2, B).

The optical absorption spectra of these crystals at temperature 1.8 eV were considered and the symmetry of excitonic bands was calculated and oscillator strengths of transitions in excitonic band were calculated in Ref. [8]. The authors of Ref. [8] note that exciton–phonon interaction is less than exciton–photon at 1.8 K and so the line shapes of excitonic absorption have small distortions. According the data of Ref. [8] the shape of excitonic absorption curve in $TlGaS_2$ crystals is described by the antiresonance Fano contour. The experimentally observed excitonic peak corresponds to the modified state, which appears as a result of the configuration interaction of discrete state (exciton) with the quasi-infinite continuum of conduction band states. One can conclude that the exctionic transitions allowed according the calculations of oscillator strength ($F_n = 1.22 \times 10^{-2}$) for transition into the discrete ("pure") excitonic state. These conclusions were confirmed by the results of this work and data of Ref. [19].

The maxima at energies 2.643 eV ($n^B=1$), 2.685 eV ($n^B=2$), 2.81 eV (b1), 2.929 eV (b2) and 3.016 eV (b3) were observed in reflection spectra of E‖b polarizations (see Ref. [14]). The maximum of reflection at 2.604 eV ($n^A=1$) and weak feature at 2.620 eV were discovered in E‖a polarization at long-wavelengths. The ascertained maxima (2.604 eV ($n^A=1$), 2.643 eV ($n^B=1$) and 2.691 eV ($n^B=2$)) are due to the ground and excited states of