OPTICAL ABSORPTION AND PHOTOCONDUCTIVITY OF $TlGaS_2$ CRYSTALS UNDER THE ACTION OF LASER RADIATION

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The optical and photoelectric properties of $TlGaS_2$ single crystals at high levels of optical excitation were experimentally studied. A pulsed Nd:YAG laser with built-in generators of the 2nd and 3rd harmonics, designed to generate radiation with wavelengths of 1064, 532 and 335 nm, was used as a radiation source. It is shown that the observed features in the absorption, photoconductivity and luminescence spectra of $TlGaS_2$ are caused by the recombination of free excitons and radiative transitions between the donor-acceptor center.

Keywords: $TlGaS_2$, optical absorption, photoluminescence.
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1. INTRODUCTION

Recently, thallium chalcogenides with a layered structure of the III-III-VI_2 family, such as $TlBX_2$ (B = Ga or In and X=S or Se), have been the subject of intensive experimental and theoretical studies [1]. These thallium chalcogenides belong to the monoclinic system and their space group is C2/c. The lattice of these crystals consists of alternating two-dimensional layers parallel to the (001) plane. Each subsequent layer is rotated by 90° relative to the previous layer. $TlGaS_2$, a member of this family of crystals, is a semiconductor with an indirect band gap of about 2.46 and 2.55 eV at 300 and 10 K, respectively [2, 3]. In view of the possibility of its application in optoelectronic devices, much attention is paid to the study of the optical and photoelectric properties of $TlGaS_2$ crystals [2, 4–8]. The direct band gap of $TlGaS_2$ crystals at T=10 K is 2.664 eV [9–12].

Of particular interest is the experimental study of the optical, photoelectric, and luminescent properties of $TlGaS_2$ crystals at high levels of optical excitation. This is due, on the one hand, to the enormous possibilities that open up the use of these materials for the purposes of nonlinear optics, and on the other hand, the possibility of realizing in them completely new phenomena of great fundamental importance, which were previously practically inaccessible for experimental studies [6–8].

This paper presents the results of a study of optical absorption, photoconductivity and luminescence of TlGaS2 crystals under the action of laser radiation.

2. EXPERIMENTAL TECHNIQUE

$TlGaS_2$ single crystals were grown by the modified Bridgman method. The samples were made by chipping off an ingot parallel to the crystalline layer perpendicular to the c axis. Chipped single-crystal layers 0.2 mm thick had plane-parallel mirror faces, which were a natural resonator. The crystals were p-type and had a resistivity of 10^{10}–10^{12} Ohm·cm, at 300 K. Ohmic contacts were obtained by applying silver paste.

The radiation source was a pulsed Nd:YAG laser with built-in generators of the 2-nd and 3-rd harmonics, designed to generate radiation with a wavelength of 1064, 532, and 335 nm. The laser pulse duration was 10 ns with a maximum power of ~12 MW/cm^2. The radiation intensity was varied using calibrated neutral light filters. Using a lens, the incident laser beam was focused onto the sample surface with a spot diameter of ~2.0 mm. The optical absorption and luminescence spectra of $TlGaS_2$ crystals were studied using an automatic M833 double dispersion monochromator (spectral resolution ~0.024 nm at a wavelength of 600 nm), computer-controlled and a detector that records radiation in the wavelength range of 350-2000 nm. Registration of photocurrent pulses was carried out according to a technique that allows one to record single nanosecond pulses on the screen of a storage oscilloscope (Le Croy 9400). The experimental procedure is similar to that described in [13].

3. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows the absorption spectra (curve 1) and photoconductivity (curve 2) of $TlGaS_2$ at 77 K. As can be seen from the figure, an absorption band with a maximum of ~2.63 eV (λ=4710 A^0) is clearly observed in the absorption spectrum. The location of this maximum in the immediate vicinity of the direct band gap (~ 0.03 eV) and stability, apparently, indicates that the absorption band with a maximum λ = 4710 A^0 is due to the presence of direct exciton transitions. A comparison of the photoconductivity and absorption spectra shows that the absorption band

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coincides with the photoconductivity maximum. Beyond the intrinsic photoconductivity edge, a broad band of the impurity level is observed.

Figure 2 shows the luminescence spectrum of $TlGaS_2$ when excited by the second harmonic of a Nd:YAG laser with a quantum energy $\hbar\omega$=2.34 eV. As can be seen from the figure, two emission bands are observed in the luminescence spectrum, with maxima λ_1=470 nm (2.63 eV) and λ_2=595 nm (2.084 eV). The observed bands have a half-width of 1.6 and 0.7 eV, respectively.

It has been established that the emission line with a maximum at 2.63 eV agrees satisfactorily with the maxima observed in the absorption and photoconductivity spectrum of $TlGaS_2$. Therefore, it can be argued that the observed radiation is due to the recombination of free excitons at the edge of the intrinsic absorption band. The long-wavelength maximum λ_2=595 nm (2.084 eV) is apparently due to the presence of impurity centers located inside the band gap. This is evidenced by the presence of donor and acceptor centers in $TlGaS_2$ with activation energies ΔE_D=0.035 eV and ΔE_A=0.005 eV [3]. The presence of these centers in $TlGaS_2$ allows us to assert that the radiation we observe is due to a radiative transition from a deep donor level of 0.035 eV to a shallow acceptor level of 0.005 eV above the valence band.

Of particular interest are studies of the photoluminescence spectra of $TlGaS_2$ crystals at various excitation intensities (Fig. 3a). As can be seen from the figure, an increase in the pump power from 2 MVt/cm^2 to 12 MVt/cm^2 leads to a significant increase in the photoluminescence intensity. Figure 3b shows the dependence of the photoluminescence intensity ($I_{lum.}$) of $TlGaS_2$ at the wavelength maximum (λ=470 nm) on the laser radiation intensity I_{las}. It can be seen that this dependence is sublinear, $I_{\text{lum}} \sim I_{\text{las}}^4$. This indicates that light amplification occurs in thin $TlGaS_2$ films at high levels of optical excitation.

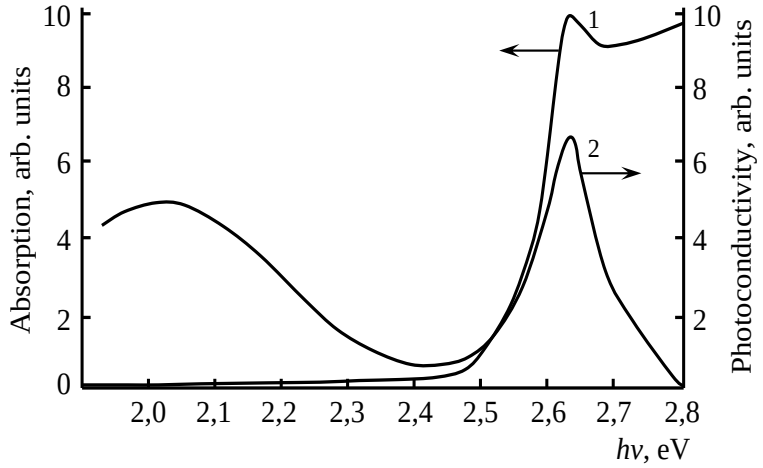

Fig.1. Spectral distribution of the absorption coefficient (curve 1) and photoconductivity (curve 2) of $TlGaS_2$ single crystals at 77 K.

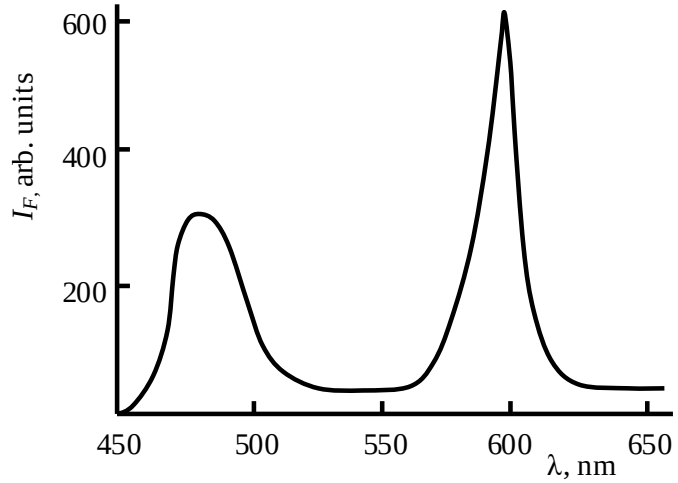

Fig.2. Luminescence spectrum of $TlGaS_2$ upon excitation by the second harmonic of a Nd:YAG laser, with quantum energy $\hbar\omega$=2.34 eV.

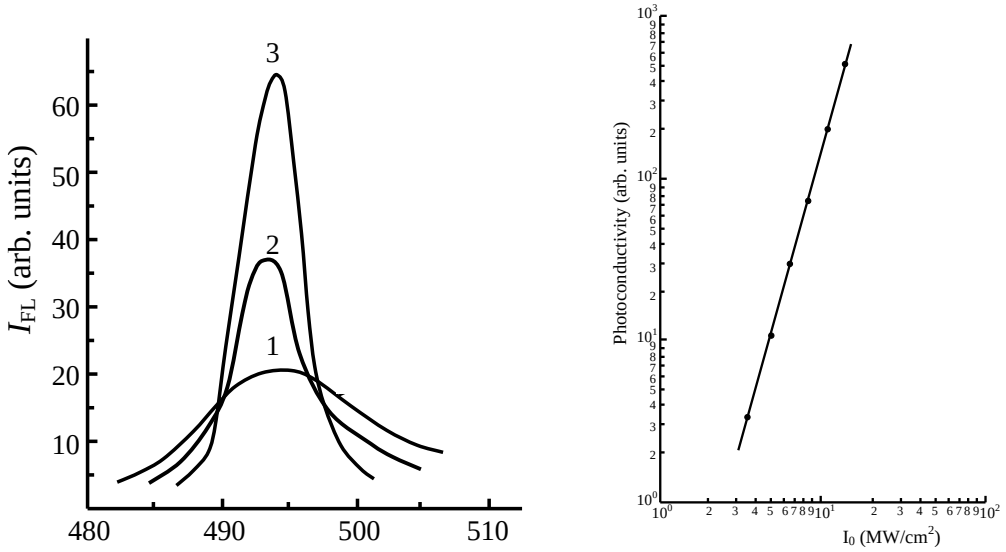

Fig. 3. a - Photoluminescence spectra of $TlGaS_2$ crystals at three intensities of exciting laser radiation, I_{las} (MVt/cm2): 1-2; 2-6; 3-12. b - Dependence of the intensity of photoluminescence (I_{lum}) $TlGaS_2$ at the maximum wavelength (λ=470 nm), on the intensity of laser radiation I_{las}.

The presence of recombination centers associated with the donor-acceptor level, along with luminescence with a maximum of λ_2=595 nm, is also evidenced by the photocurrent relaxation kinetics shown in Figure 4. As can be seen from the figure, two recombination channels are observed: fast with τ=12 ns and slow with τ=200 ns. The fast recombination channel is apparently associated with the recombination of free excitons, while the slow section is probably due to an impurity center. It is known that in layered semiconductors, the lifetime of free excitons is ~ 10–20 nsec [14].

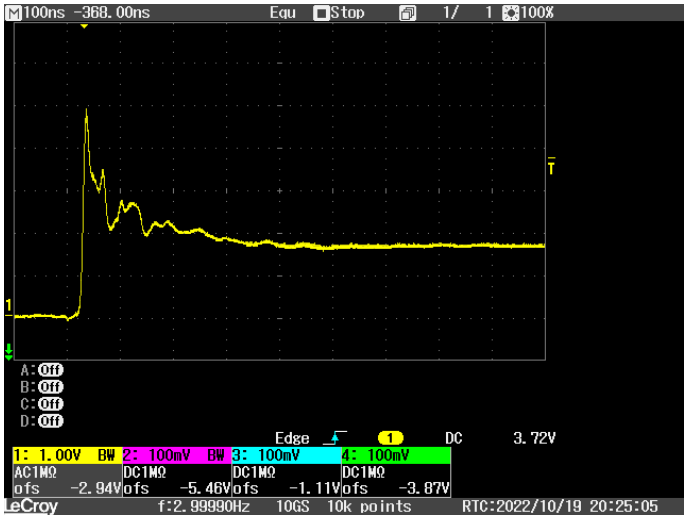

Fig. 4. Photocurrent relaxation curve in $TlGaS_2$ crystals excited by the second harmonic of a Nd:YAG laser.

4. CONCLUSION

The absorption, photoconductivity, and luminescence spectra and photocurrent relaxation curves under laser excitation in layered $TlGaS_2$ ternary compounds grown by the modified Bridgman method were studied experimentally. The absorption band centered at 470 nm is associated with the recombination of free excitons near the edge of the $TlGaS_2$ absorption band. An analysis of the luminescence spectra with a maximum at 595 nm allows us to propose a possible model for the recombination of donor-acceptor levels located in the band gap of the $TlGaS_2$ crystal. The fast and slow components of the relaxation curves are related to the recombination of free excitons and impurity centers.

The observed superlinear dependence ($I_{lum.} \sim I_{las.}^4$) in the lux-ampere characteristic of $TlGaS_2$ indicates the presence of stimulated emission at high excitation levels.

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