

OPTICAL ABSORPTION AND PHOTOCONDUCTIVITY OF TlGaS₂ CRYSTALS
UNDER THE ACTION OF LASER RADIATIONV.M. SALMANOV¹, A.G. GUSEINOV¹, G.B. IBRAGIMOV^{1,2},
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The optical and photoelectric properties of TlGaS₂ 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 TlGaS₂ are caused by the recombination of free excitons and radiative transitions between the donor-acceptor center.

Keywords: TlGaS₂, optical absorption, photoluminescence.**PACS:** 78.20.-e; 78.40.-q

1. INTRODUCTION

Recently, thallium chalcogenides with a layered structure of the III-III-VI₂ family, such as TlBX₂ (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. TlGaS₂, 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 TlGaS₂ crystals [2, 4–8]. The direct band gap of TlGaS₂ 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 TlGaS₂ 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

TlGaS₂ 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 10¹⁰–10¹² 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/cm². 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 TlGaS₂ 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 TlGaS₂ at 77 K. As can be seen from the figure, an absorption band with a maximum of ~2.63 eV ($\lambda=4710 \text{ \AA}$) 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 $\lambda = 4710 \text{ \AA}$ is due to the presence of direct exciton transitions. A comparison of the photoconductivity and absorption spectra shows that the absorption band

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 TlGaS₂ 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 $\lambda_1=470$ nm (2.63 eV) and $\lambda_2=595$ 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 TlGaS₂. 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 $\lambda_2=595$ 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 TlGaS₂ with activation energies $\Delta E_D=0.035$ eV and $\Delta E_A=0.005$ eV [3]. The presence of these centers in TlGaS₂ 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 TlGaS₂ crystals at various excitation intensities (Fig. 3a). As can be seen from the figure, an increase in the pump power from 2 MVt/cm² to 12 MVt/cm² leads to a significant increase in the photoluminescence intensity. Figure 3b shows the dependence of the photoluminescence intensity ($I_{lum.}$) of TlGaS₂ at the wavelength maximum ($\lambda=470$ nm) on the laser radiation intensity I_{las} . It can be seen that this dependence is sublinear, $I_{lum.} \sim I_{las}^4$. This indicates that light amplification occurs in thin TlGaS₂ films at high levels of optical excitation.

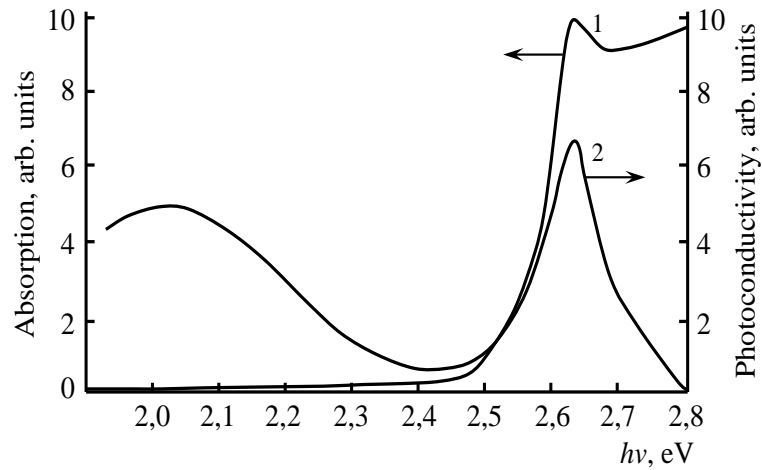


Fig.1. Spectral distribution of the absorption coefficient (curve 1) and photoconductivity (curve 2) of TlGaS₂ single crystals at 77 K.

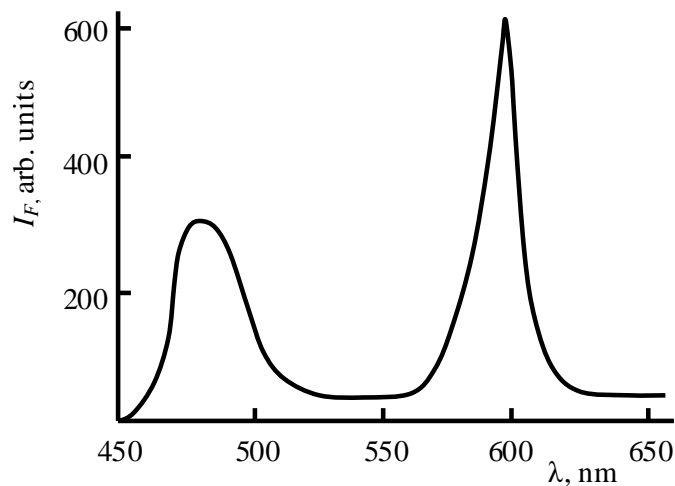


Fig.2. Luminescence spectrum of TlGaS₂ upon excitation by the second harmonic of a Nd:YAG laser, with quantum energy $\hbar\omega=2.34$ eV.

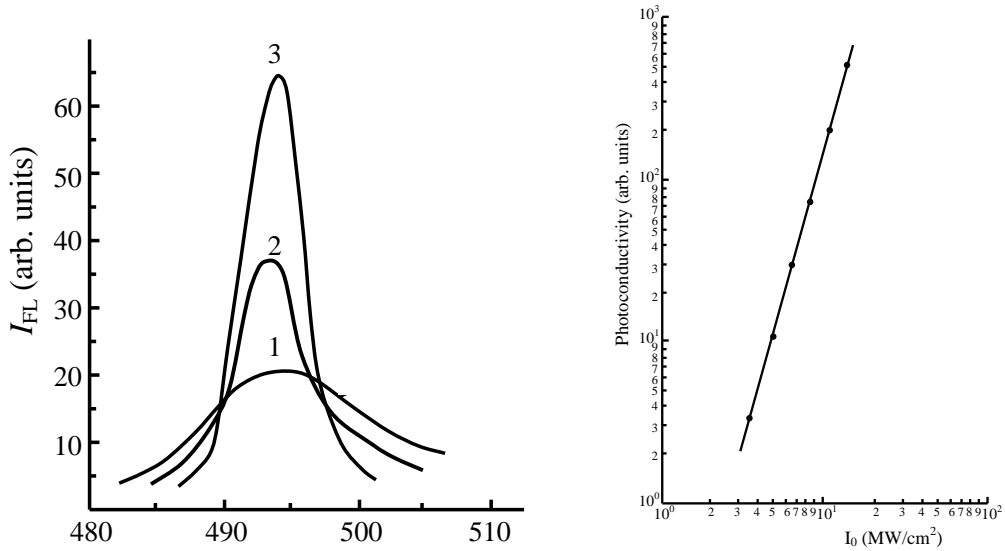


Fig. 3. a - Photoluminescence spectra of TlGaS₂ crystals at three intensities of exciting laser radiation, I_{las} (MW/cm²): 1-2; 2-6; 3-12. b - Dependence of the intensity of photoluminescence (I_{lum}) TlGaS₂ at the maximum wavelength ($\lambda=470$ nm), on the intensity of laser radiation I_{las} .

The presence of recombination centers associated with the donor-acceptor level, along with luminescence with a maximum of $\lambda_2=595$ 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

$\tau=12$ ns and slow with $\tau=200$ 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 $\sim 10-20$ nsec [14].

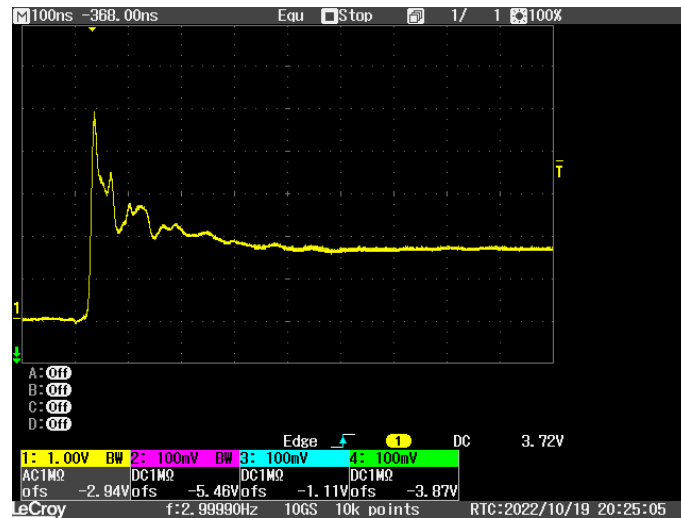


Fig. 4. Photocurrent relaxation curve in TlGaS₂ crystals excited by the second harmonic of a Nd:YAG laser.

4. CONCLUSION

The absorption, photoconductivity, and luminescence spectra and photocurrent relaxation curves under laser excitation in layered TlGaS₂ 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 TlGaS₂ 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 TlGaS₂ 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 TlGaS₂ indicates the presence of stimulated emission at high excitation levels.

- [1] *K.A. Yee and A. Albright.* Bonding and structure of gallium thallium selenide (GaTlSe₂). *J. Am. Chem. Soc.* 113, 1991, 6474-6478.
- [2] *M.P. Haniyas, A.N. Anagnostopoulos, K. Kambas, and J. Spyridelis.* Electrical and optical properties of as-grown TlInS₂, TlGaSe₂ and TlGaS₂ single crystals. *Mat. Res. Bull.* 27, 1992, 25-38.
- [3] *N. S. Yuksek, N. M. Gasanly, I.A. Aydin, H. Ozkan, and M. Acikgoz.* Infrared photoluminescence from TlGaS₂ layered single crystals. *Cryst. Res. Technol.* 39, №9, 2004, 800-806.
- [4] *N. Kalkan, J.A. Kalomiros, M. Haniyas, and A. N. Anagnostopoulos.* Optical and photoelectrical properties of the TlGaS₂ ternary compound. *Solid State Commun.* 99, 1996, 375-379.
- [5] *B. Abay, H. S. Guder, H. Efeoglu, and Y.K. Yogurtcu.* Urbach-Martienssen Tails in the Absorption Spectra of Layered Ternary Semiconductor TlGaS₂. *Phys. Stat. Sol. (b)* 227, 2001, 469-476.
- [6] *K. Allakhverdiev, T. G. Mammadov, R. Suleymanov, and N. Gasanov.* Deformation effects in electronic spectra of the layered semiconductors TlGaS₂, TlGaSe₂ and TlInS₂. *J. Phys.: Condens. Matter* 15, 2003, 1291-1299.
- [7] *H.J. Song, S.H. Yun, and W.T. Kim.* Deep levels in TlGaS₂ single crystal. *Solid State Commun.* 94, 1995, 225-229.
- [8] *A. Kato, M. Nishigaki, N. Mammadov, M. Yamazaki, H. Uchiki, and S. Iida.* Optical properties and photo-induced memory effect related with structural phase transition in TlGaS₂. *J. Phys. Chem. Solids* 64, 2003, 1713-1716.
- [9] *J. Krustok, J. H. Schon, H. Collan, M. Yakushev, J. Mudasson, and E. Bucher.* Origin of the deep center photoluminescence in CuGaSe₂ and CuInS₂ crystals. *J. Appl. Phys.* 86, 1999, 364-369.
- [10] *C.J. Hwang.* Evidence for Luminescence Involving Arsenic Vacancy-Acceptor Centers in p-Type GaAs. *Phys. Rev.* 180, 1969, 827.
- [11] *S. Shigetomi, T. Ikari, and H. Nakashima.* Optical and electrical properties of layer semiconductor p-GaSe doped with Zn. *J. Appl. Phys.* 74, 1993, 4125-4129.
- [12] *N.M. Gasanly.* Optical properties of TlGa(SxSe1-x)₂ layered mixed crystals (0 ≤ x ≤ 1): Absorption edge and photoluminescence study at T = 10 K. *Indian Academy of Sciences, Pramana – J. Phys.* 2018, 91:30
- [13] *V.M. Salmanov, A.G. Guseinov, M.A. Джафаров, P.M. Мамедов, Т.А. Мамедова.* Особенности фотопроводимости и люминесценции тонких пленок CdS и твердых растворов Cd_{1-x}Zn_xS при лазерном возбуждении. *Optics and Spectroscopy.* 130, 10, 2022, 1567-1570.
- [14] *T. Kushida, F. Minami, Y. Oka, Y. Nakazaki, Y. Tanaka.* Population dynamics and spin relaxations of excitons in GaSe. *Nuovo Cimento B* 39, 1977, 650-654.