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Spectral, luminescent, and lasing properties of $ZrO_2-Y_2O_3-Tm_2O_3$ crystals

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Abstract. **The absorption spectra corresponding to the transitions from the ground $^3H_6$ state to the excited multiplets $^1G_4$, $^3F_2$, $^3F_3$, $^3H_4$, $^3H_5$, $^3F_4$, as well as the luminescence spectrum of the $^3F_4 \rightarrow {}^3H_6$ laser transition of Tm^{3+} ions excited to the $^3H_4$ level in ZrO_2–12 mol% Y_2O_3–2 mol% Tm_2O_3 crystals are studied at a temperature of 300 K. The cross-relaxation ($^3H_4 \rightarrow {}^3F_4$, $^3H_6 \rightarrow {}^3F_4$) efficiency of Tm^{3+} ions estimated by the integral characteristics of decay curves of luminescence from the $^3H_4$ level exceeds 90%. The spectral dependences of the gain cross section of the $^3F_4 \rightarrow {}^3H_6$ laser transition of Tm^{3+} ions are calculated for different relative population inversions. Lasing at the $^3F_4 \rightarrow {}^3H_6$ transition of Tm^{3+} ions in diode-pumped ZrO_2–12 mol% Y_2O_3–2 mol% Tm_2O_3 crystals is obtained for the first time. The lasing wavelength is 2046 nm.**

Keywords: *absorption spectrum, luminescence spectrum, lasing, Tm^{3+} ions, ZrO_2–Y_2O_3–Tm_2O_3 crystals.*

The stabilised zirconium dioxide crystals are characterised by a disordered structure, because of which the absorption and luminescence spectra of rare-earth ions in these crystals demonstrate considerable inhomogeneous broadening. The results of investigation of the spectral and luminescent properties of stabilised zirconium dioxide crystals doped with Nd^{3+} and Yb^{3+} ions are reported in papers [1, 2].

Lasing in these crystals was obtained under diode laser pumping. Laser experiments with ZrO_2–Y_2O_3–Yb_2O_3 crystals are described in papers [3, 4]. Lasing at the $^4F_{5/2} \rightarrow {}^4F_{7/2}$ transition of Yb^{3+} ions in these crystals in the wavelength region of 1.04–1.06 μm was reported in [3]. A continuous pulse train in the same crystals was obtained in [4] under pulsed and cw pumping.

At present, of interest for medical and lidar applications are lasers emitting in the two-micron spectral region. Lasing in this region was obtained on the $^3F_4 \rightarrow {}^3H_6$ transitions of Tm^{3+} ions and $^5I_7 \rightarrow {}^5I_8$ transitions of Ho^{3+} ions in various oxide and fluoride crystals. The characteristics of two-micron lasers based on oxide and fluoride materials doped with Tm^{3+} and Ho^{3+} ions are given in review [5]. In this connection, the search for new laser materials operating in the spectral region of 1.8–2.1 μm and the study of their properties are still important.

The results of our investigation of the structure and spectral and luminescent properties of ZrO_2–Y_2O_3–Tm_2O_3 crystals are published in [6]. In the present work, we consider the spectral and luminescent characteristics of ZrO_2–12 mol% Y_2O_3–2 mol% Tm_2O_3 crystals, as well as the results of experiments on lasing in these crystals under diode laser pumping.

The zirconium dioxide crystals stabilised with yttrium oxide and doped with Tm^{3+} ions were grown using 'Kristall-407' equipment. The synthesis of crystals occurred in a cold container 130 mm in diameter with a growth rate of 10 mm h^{-1}. The grown crystals were 30–40 mm long with a cross section of 10–20 mm.

The quantitative elemental analysis of ZrO_2–12 mol% Y_2O_3–2 mol% Tm_2O_3 crystals was performed using an INCA ENERGY (Oxford Instruments) analytical attachment to a JSM-5910LV (JEOL) electron microscope. This analysis showed that the concentration of Tm^{3+} ions in theses crystals is 1.1×10^{21} cm^{-3}.

The absorption spectra of Tm^{3+} ions in the studied crystals were recorded by a Lambda 950 (Perkin-Elmer) spectrophotometer. The luminescence from the $^3F_4$ level of Tm^{3+} ions excited into the $^3H_4$ level by a laser diode with $\lambda_{rad} \sim 809$ nm was measured using an automated setup based on an MDR-23 monochromator.

The decay kinetics of luminescence from the $^3H_4$, $^3F_4$ levels of Tm^{3+} ions was recorded upon excitation of the $^3H_4$ level by radiation of an LX 329 pulsed tunable Ti:sapphire laser. The luminescence decay kinetics was recorded using an MDR-32 monochromator and a GDS 720C digital oscilloscope.

The lasing wavelength was measured by an MDR-23 monochromator. As a radiation detector, we used a PbS photoresistor.

The absorption spectrum related to the transition from the ground $^3H_6$ level to the $^3H_4$ level of Tm^{3+} ions in the ZrO_2–12 mol% Y_2O_3–2 mol% Tm_2O_3 crystal at the temperature $T = 300$ K is shown in Fig. 1. One can see that the spectrum consists of wide poorly structured bands. The absorption coefficient in the region of 800 nm is close to 1 cm^{-1}, which allows one to pump this crystal by available laser diode arrays. The large spectral width of the Tm^{3+} absorption line in this crystal considerably reduces the requirements to the temperature stabilisation of the pump laser diode.

A specific feature of two-micron lasing in Tm^{3+}-doped crystals is that the population of the $^3H_4$ upper laser level occurs with participation of a cross-relaxation process ($^3H_4 \rightarrow {}^3F_4$, $^3H_6 \rightarrow {}^3F_4$) upon pumping of Tm^{3+} ions to the $^3H_4$ level ($\lambda_{rad} \sim$ 800 nm). To determine the contribution made by this process to the population of the $^3F_4$ level, we studied the decay kinetics

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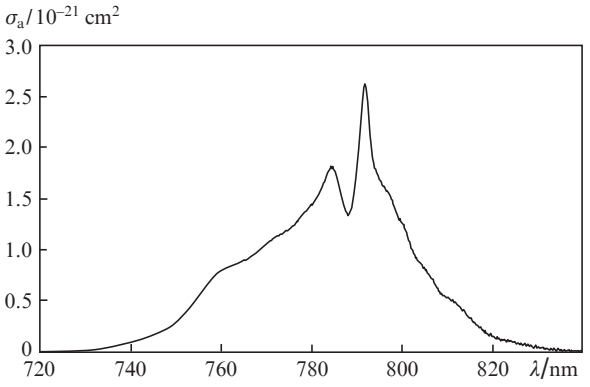

Figure 1. Absorption spectrum of the $^3H_6 \rightarrow {}^3H_4$ transition of Tm^{3+} ions in a ZrO_2–12 mol% Y_2O_3–2 mol% Tm_2O_3 crystal at $T = 300$ K.

of luminescence from the $^3H_4$ level in crystals with different concentrations of Tm^{3+} ions. Figure 2 shows the luminescence decay kinetics for ZrO_2–13.8 mol% Y_2O_3–0.2 mol% Tm_2O_3 and ZrO_2–12 mol% Y_2O_3–2 mol% Tm_2O_3 crystals recorded upon resonance excitation ($\lambda_{exc} = 770$ nm) of the $^3H_4$ level ($\lambda_{det} = 800$ nm). It should be noted that the luminescence decay kinetics for the ZrO_2–13.8 mol% Y_2O_3–0.2 mol% Tm_2O_3 crystals with the low concentration of Tm^{3+} ions is nonexponential. This is related to the existence of a variety of Tm^{3+} optical centres in zirconium dioxide crystals stabilised with yttrium. The lifetimes of the $^3H_4$ level of Tm^{3+} ions in these crystals estimated from the initial and final stages of the luminescence decay curve are 150 and 300 μs, respectively. As seen from Fig. 2, this level in the stabilised zirconium dioxide crystals with the Tm^{3+} concentration increased to 2 mol% decays much faster, which can be caused by the cross relaxation between Tm^{3+} ions ($^3H_4 \rightarrow {}^3F_4$, $^3H_6 \rightarrow {}^3F_4$). From the integral characteristics of the decay kinetics of luminescence from the $^3H_4$ level of Tm^{3+} ions, we estimated the cross-relaxation efficiency as

$$\beta_{Tm \rightarrow Tm} = \left[1 - \frac{\int (I_{Tm}/I_0)\,dt}{\int (I'_{Tm}/I'_0)\,dt}\right] 100\%, \qquad (1)$$

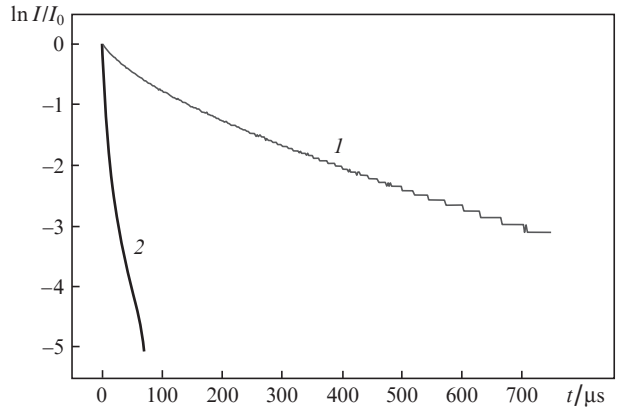

Figure 2. Decay kinetics of luminescence from the $^3H_4$ level of Tm^{3+} ions in ZrO_2–13.8 mol% Y_2O_3–0.2 mol% Tm_2O_3 (*1*) and ZrO_2–12 mol% Y_2O_3–2 mol% Tm_2O_3 (*2*) crystals measured at $\lambda_{exc} = 770$ nm, $\lambda_{det} = 800$ nm, and $T = 300$ K.

where I_{Tm} is the intensity of luminescence from the $^3H_4$ level of Tm^{3+} ions for the ZrO_2–12 mol% Y_2O_3–2 mol% Tm_2O_3 crystal, I'_{Tm} is the same intensity for the ZrO_2–13.8 mol% Y_2O_3–0.2 mol% Tm_2O_3 crystal, I_0 and I'_0 are the corresponding luminescence intensities at $t = 0$. The efficiency of cross relaxation between Tm^{3+} ions ($^3H_4 \rightarrow {}^3F_4$, $^3H_6 \leftrightarrow {}^3F_4$) estimated by formula (1) exceeds 90%.

To obtain and experimentally study lasing in crystals, it is important to know the spectral dependence of the gain cross section for the laser transition. This helps to choose the laser cavity mirrors with the optimal reflection coefficients in the spectral region of interest.

The spectral dependence of the luminescence cross section of the $^3F_4 \rightarrow {}^3H_6$ laser transition of Tm^{3+} ions for the ZrO_2–12 mol% Y_2O_3–2 mol% Tm_2O_3 crystals was determined by the Füchtbauer–Ladenburg formula

$$\sigma_e(\lambda) = \frac{\lambda^5}{8\pi c n_\lambda^2} \frac{1}{\tau_{rad}} \frac{I(\lambda)}{\int \lambda I(\lambda)\,d\lambda}, \qquad (2)$$

where τ_{rad} is the radiative lifetime of the $^3F_4$ level of Tm^{3+} ions, n_λ is the refractive index of the material, λ is the wavelength, and I is the luminescence intensity in relative units. Assuming that the probability of nonradiative relaxation from the $^3F_4$ level is small, we substituted $\tau_{rad} = A^{-1} = 6.7$ ms into formula (2). Here, A is the probability of the radiative transition from the $^3F_4$ level, which was estimated by the formula

$$A = \frac{8\pi n_\lambda^2 c}{N\lambda^4} \frac{2J^1 + 1}{2J + 1} \int k(\lambda)\,d\lambda, \qquad (3)$$

where $k(\lambda)$ is the absorption coefficient, J^1 and J are the total angular momenta of 4f electrons in the ground and excited states of the transition, and N is the concentration of Tm^{3+} ions.

Figure 3 shows the absorption and luminescence spectra for the $^3H_6 \rightarrow {}^3F_4$ transitions of Tm^{3+} ions in the ZrO_2–12 mol% Y_2O_3–2 mol% Tm_2O_3 crystal at $T = 300$ K.

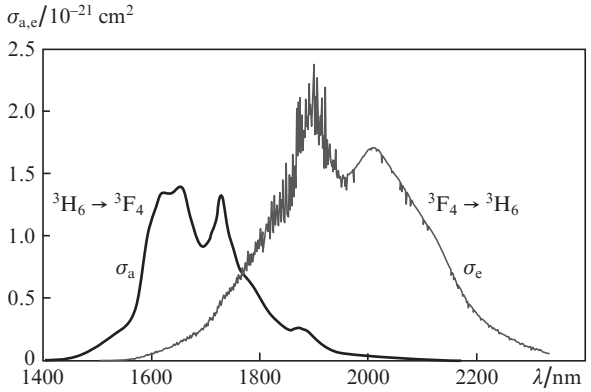

Figure 3. Absorption and luminescence spectra for the $^3H_6 \leftrightarrow {}^3F_4$ transitions of Tm^{3+} ions in a ZrO_2–12 mol% Y_2O_3–2 mol% Tm_2O3 crystal at $T = 300$ K.

The spectral dependence of the gain cross section of the laser transition was calculated as

$$\sigma_g = P\sigma_e - (1 - P)\sigma_a, \qquad (4)$$

where σ_e is the luminescence cross section at the chosen wavelength, σ_a is the absorption cross section at the same wavelength,

$P = N_e/(N_e + N_f)$ is the relative population inversion, N_e is the population of the $^3F_4$ upper laser level, and N_f is the population of the $^3H_6$ lower laser level. The dependences calculated by formula (4) for the $^3F_4 \rightarrow {}^3H_6$ transition of Tm^{3+} ions in the ZrO_2–12 mol% Y_2O_3–2 mol% Tm_2O_3 crystal are given in Fig. 4.

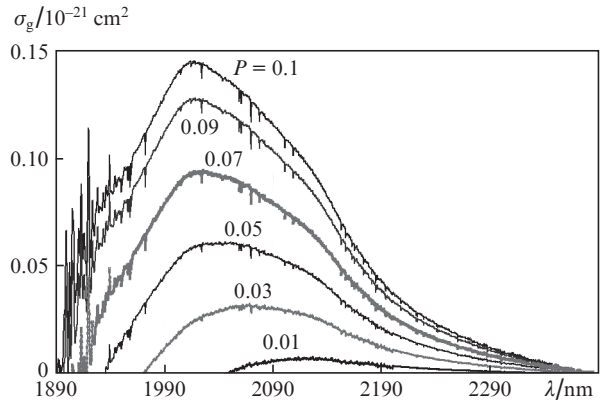

Figure 4. Spectral dependences of the gain cross section $\sigma_g(\lambda)$ for the $^3F_4 \rightarrow {}^3H_6$ laser transition of Tm^{3+} ions in ZrO_2–12 mol% Y_2O_3–2 mol% Tm_2O_3 crystals at different values of the relative population inversion P.

The optical scheme of the laser used to obtain and study lasing at the $^3F_4 \rightarrow {}^3H_6$ transition of Tm^{3+} ions in ZrO_2–12 mol% Y_2O_3–2 mol% Tm_2O_3 crystals is shown in Fig. 5. The initially unstable 15-mm cavity becomes stable due to the appearance of a positive induced thermal lens in the active element in the process of laser pumping.

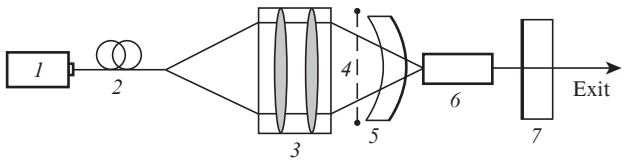

Figure 5. Optical scheme of a laser based on the ZrO_2–12 mol% Y_2O_3–2 mol% Tm_2O_3 crystal: (*1*) laser diode array; (*2*) optical fibre; (*3*) objective; (*4*) chopper; (*5*) input mirror; (*6*) active element; (*7*) output mirror.

The active element was pumped into the $^3H_4$ level of Tm^{3+} ions by a laser diode array (*1*) with a radiation wavelength of 798 nm. To decrease the thermal load to the active element, we used a chopper (*4*), which formed pump pulses with a duration of 10 ms and a repetition rate of ~3 Hz. The radiation of the laser diode array coupled to a fibre (*2*) (fibre diameter 400 μm) was projected into the sample by an objective (*3*) without magnification. An active element (*6*) 3×3×5 mm in size was made of a ZrO_2–12 mol% Y_2O_3–2 mol% Tm_2O_3 crystal. The 3×3-mm faces of the active element were antireflection coated for the laser wavelength ($\lambda_{gen} \sim 2$ μm). The cavity used in the experiments was formed by a spherical mirror (*5*) (curvature radius 600 mm, transmittance at the pump wavelength no less than 90%, reflectivity at the laser wavelength higher than 99%) and a plane output mirror (*7*) with a transmittance at the laser wavelength below 1%. The copper holder of the active element was kept at a temperature of ~18 °C by a temperature stabilisation system.

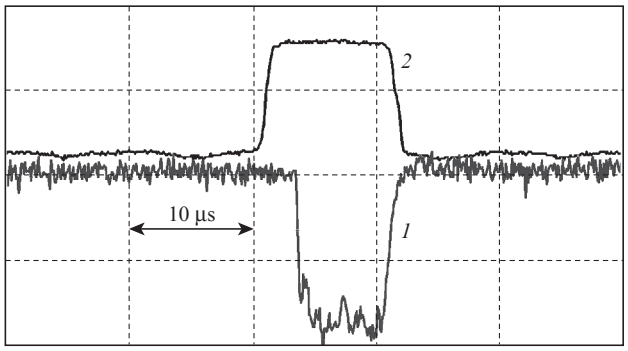

Figure 6. Oscillograms of a laser pulse of a ZrO_2–12 mol% Y_2O_3–2 mol% Tm_2O_3 crystal (*1*) and of an excitation pulse (*2*).

The oscillograms of a laser pulse of the ZrO_2–12 mol% Y_2O_3–2 mol% Tm_2O_3 crystal and of a pump pulse recorded on the GDS 720C digital oscilloscope are shown in Fig. 6.

Lasing at the $^3F_4 \rightarrow {}^3H_6$ transition of Tm^{3+} ions in the ZrO_2–12 mol% Y_2O_3–2 mol% Tm_2O_3 crystal was obtained at the wavelength $\lambda_{gen} = 2046$ nm. The lasing threshold was 5 W of absorbed pump power.

In this work, we studied the spectral and luminescent properties of ZrO_2–12 mol% Y_2O_3–2 mol% Tm_2O_3 crystals. The efficiency of cross relaxation between Tm^{3+} ions in these crystals estimated from the decay curves of luminescence from the $^3H_4$ level of Tm^{3+} ions in ZrO_2–13.8 mol% Y_2O_3–0.2 mol% Tm_2O_3 and ZrO_2–12 mol% Y_2O_3–2 mol% Tm_2O_3 exceeded 90%.

Lasing at the wavelength $\lambda_{gen} = 2046$ nm ($^3F_4 \rightarrow {}^3H_6$ transition of Tm^{3+} ions) in ZrO_2–12 mol% Y_2O_3–2 mol% Tm_2O_3 crystals under diode laser pumping was obtained for the first time. Note that this wavelength lies between the longest-wavelength line of the $Tm:Y_3Al_5O_{12}$ laser ($\lambda_{gen} = 2013$ nm) and the $Tm:Lu_2O_3$ laser line ($\lambda_{gen} = 2070$ nm) [5].

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References

1. Voron'ko Yu.K., Lomonova E.E., Vishnyakova M.A., Popov A.V., Sobol A.A., Shukshin V.E. *Neorg. Mater.*, **40** (5), 585 (2004).
2. Voron'ko Yu.K., Lomonova E.E., Popov A.V., Sobol A.A., Ushakov S.N. *Neorg. Mater.*, **41** (8), 955 (2005).
3. Shukshin V.E. *Trudy IOFRAN*, **64**, 3 (2008).
4. Khromov M.N. *Extended Abstract of Cand. Sci. Dissertation* (Moscow: IOFRAN, 2009).
5. Scholle K., Lamrini S., Koopmann P., Fuhberg P., in *Frontiers in Guided Wave Optics and Optoelectronics* (Croatia, InTech, 2010).
6. Ryabochkina P.A., Borik M.A., Kulebyakin A.V., Lomonova E.E., Malov A.V., Somov N.V., Ushakov S.N., Chabushkin A.N., Chuprunov E.V. *Opt. Spektrosk.*, **112** (3), 513 (2012).