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25 %Eu : $KGd(WO_4)_2$ laser crystal: spectroscopy and lasing on the $^5D_0 \rightarrow {}^7F_4$ transition

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***Abstract*. A 25 %Eu : $KGd(WO_4)_2$ crystal is grown by a modified Czochralski method and its spectral and lasing properties are studied. Generation of stimulated emission in this crystal on the $^5D_0 \rightarrow {}^7F_4$ transition of the Eu^{3+} ion is obtained, as far as we know, for the first time. The laser operates at room temperature at a wavelength of $\sim$ 703 nm under pumping into the $^7F_0 \rightarrow {}^5D_1$ absorption band of the europium ion by the second harmonic of a *Q*-switched Nd : KGW laser (λ_{pump} = 533.6 nm). With a 9.4-mm-long active element, the output energy in the free-running regime reached 244 μJ, while the optical efficiency was 1.5 %.**

Keywords: *Eu^{3+} : $KGd(WO_4)_2$ laser crystal, optical pumping into the $^7F_0 \rightarrow {}^5D_1$ band, lasing on the $^5D_0 \rightarrow {}^7F_4$ transition.*

1. Introduction

Stimulated emission of rare-earth Eu^{3+} ions as dopants was obtained for the first time in 1963 in lasers based on the Eu^{3+} : Y_2O_3 dielectric crystal [1] and on europium benzoylacetonate liquid chelate [2]. Laser radiation was achieved at low temperatures on the most intense $^5D_0 \rightarrow {}^7F_2$ transition at a wavelength near 610 nm. Then, Eu^{3+} ions were introduced in some liquid and solid dielectric [3] and semiconductor matrices [4]. Eu-doped materials were synthesised in order to create efficient laser media and phosphorescent materials for displays [5]. The absorption and emission lines of Eu^{3+} belong to the electronic transitions inside the $4f^6$ shell. Some transitions between the Eu^{3+} energy levels can be used to obtain stimulated emission in the visible spectral region, for example, the transition from the lowest excited $^5D_0$ level to the ground ^7F_j ($j = 0 - 4$). Since the $4f^6$ shell of the Eu^{3+} ion is strongly screened from external electric fields, including the crystal field, the transition wavelength only slightly differs in different matrices. The $^5D_0 \rightarrow {}^7F_2$ transition is the most intense and is traditionally used to obtain stimulated emission.

Most prominent among solid matrices known to date is the potassium – gadolinium tungstate crystal $KGd(WO_4)_2$ (KGW). The radius of the Gd^{3+} ion is close to the radii of other rare-earth ions. Therefore, KGW crystals can be doped with different lanthanide ions with high concentrations, which makes this crystal promising for creating laser elements and luminescent materials [6]. In addition, the KGW crystal clearly exhibits stimulated Raman scattering, and the laser radiation of doped KGW is linearly polarised due to its monoclinic structure [7]. These circumstances allow one to use doped KGW crystals for the development of solid-state lasers with SRS self-conversion of the initially generated radiation, i.e., of lasers emitting at a new shifted wavelength [8, 9]. To date, Eu^{3+}-doped KGW and its modification Eu^{3+} : $KGd(WO_4)_{2-y}(MO_4)_y$ are used as luminescent materials emitting in the red spectral region on the $^5D_0 \rightarrow {}^7F_2$ transition ($\sim$ 614 nm) under UV pumping [10]. Nanocrystalline Eu^{3+} : KGW has also been created and its luminescent and vibronic properties studied [11, 12].

In this paper, we report the synthesis of the 25%Eu^{3+} : KGW laser crystal. We present its luminescent properties and demonstrate (as far as we know, for the first time) the possibility of generation of stimulated emission in this crystal at room temperature on the $^5D_0 \rightarrow {}^7F_4$ transition of the Eu^{3+} ion at a wavelength of $\sim$ 703 nm.

2. Experimental

The 25%Eu^{3+} : KGW crystal was grown by a modified Czochralski method from $K_2W_2O_7$ melt under conditions of a low temperature gradient ($\sim$ 1 K cm^{-1}) [13]. The crystal (orientation [010]) was grown using a cylindrical platinum crucible 70 mm in diameter and 120 mm in height; the growth rate was 0.1 – 0.2 mm h^{-1}. A photograph of the grown boule is given in Fig. 1. From this boule, we cut two plates 1.9 and 9.4 mm thick for spectroscopic and laser experiments, respectively. The normal to the polished faces of the plates corresponds to the [010] direction (*b*-cut). The polished faces of the 9.4-mm plate were coated with dielectric materials. One of the coatings was a mirror with a high reflectance ($R > 99.8$ %) in the region of 650 – 750 nm and a high transmittance

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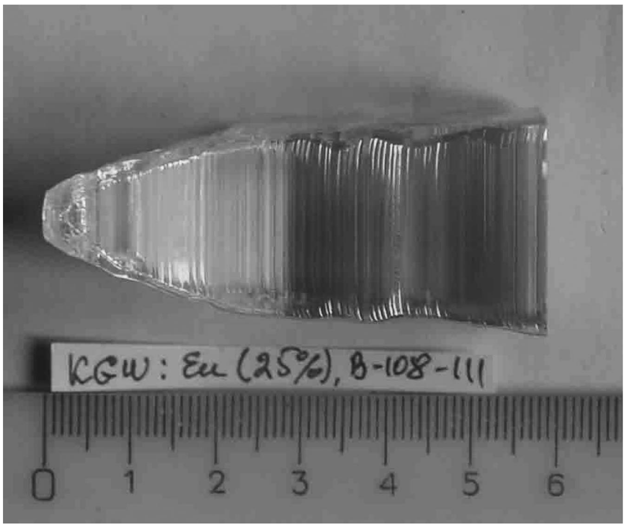

Figure 1. 25 %Eu^{3+} : KGW crystal boule.

($T > 95$ %) at the pump wavelength. The other face was antireflection coated for a wide wavelength range including the spectral band of the $^5D_0 \rightarrow {}^7F_4$ transition ($R < 0.2$ % for $\lambda = 700$ nm).

The polarised absorption spectra in the visible and near IR regions were measured with a UV 3101 PC (Shimadzu) spectrophotometer using a Glan–Thompson prism, which was placed in one of the shoulders of the optical scheme. The luminescence and laser spectra were recorded in the standard geometry using a SL40-2-3648USB (SOLAR TII, Belarus) computerised spectrometer. The luminescence kinetics for the $^5D_0 \rightarrow {}^7F_4$ transition was studied using a fast germanium pin-photodiode and a Tektronix 3052B oscilloscope. We recorded radiation passed through a corresponding interference filter ($\lambda_{max} = 706.5$ nm, $\Delta\lambda_{0.5} = 28$ nm, and $\Delta\lambda_{0.1} = 62.5$ nm). In the spectroscopic and laser experiments, the 25 %Eu^{3+} : KGW crystal was excited by the second harmonic of a *Q*-switched Nd : KGW laser. The pump pulse parameters were as follows: wavelength $\lambda_{pump} = 533.6$ nm, duration $\Delta t \approx 10$ ns, and energy $E_{pump} = 1 - 16.3$ mJ (measured by an Ophir PE50-BB pyroelectric meter). The output radiation energy of the 25 %Eu^{3+} : KGW laser was measured by a PE9-SH detector.

3. Results and discussion

Figure 2 shows a fragment of the general transmission spectrum of the 25 %Eu^{3+} : KGW crystal. The radiation incident on the plate is linearly polarised along the N_m axis of the optical indicatrix of the crystal (below, we will show that this polarisation corresponds to the maximum absorption of the sample). One can see that this spectrum contains some comparatively narrow absorption bands in the visible spectral region. A rather intense band belongs to the $^7F_0 \rightarrow {}^5D_1$ transition. The wavelength dependence of the absorption cross section of this transition is shown in the inset in Fig. 2. The absorption maximum lies at $\lambda = 534.2$ nm; the width of the most intense line of the transition is ~ 1.5 nm. One can see that the crystal can be rather efficiently pumped by the radiation of the second harmonic of a Nd^{3+} : KGW laser at a wavelength of 533.6 nm (dash-and-dot line).

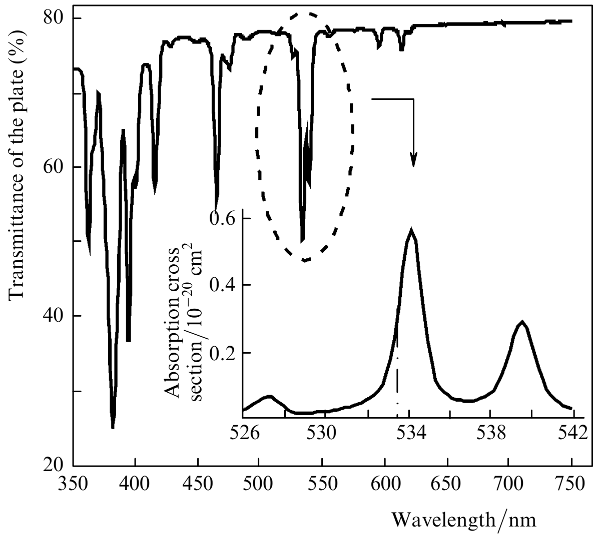

Figure 2. Fragment of the general transmission spectrum of a 1.9-mm-thick 25 %Eu^{3+} : KGW plate; the inset shows the wavelength dependence of the absorption cross section of the $^7F_0 \rightarrow {}^5D_1$ transition; the dash-and-dot line corresponds to the pump wavelength.

Figure 3 shows the polarisation anisotropy of the 25 %Eu^{3+} : KGW crystal absorption at this wavelength. The crystal is rotated around the N_p axis, which coincides with the direction of the pump beam propagation. Due to the low symmetry of the monoclinic KGW crystal, the absorption coefficient reaches the maximum value (2.6 cm^{-1}) when the electric vector E of the pump field is directed along the N_m axis and becomes minimum (0.5 cm^{-1}) in the case of $E||N_g$. Taking into account the polarisation anisotropy of the 25 %Eu^{3+} : KGW crystal absorption, all the experiments described below were performed at the crystal orientation corresponding to the maximum absorption of the pump radiation, the pump beam propagating along the N_p axis.

Figure 4 demonstrates the decay kinetics of the $^5D_0 \rightarrow {}^7F_4$ transition luminescence at room temperature. The oscillogram is obtained by averaging over 32 realisa-

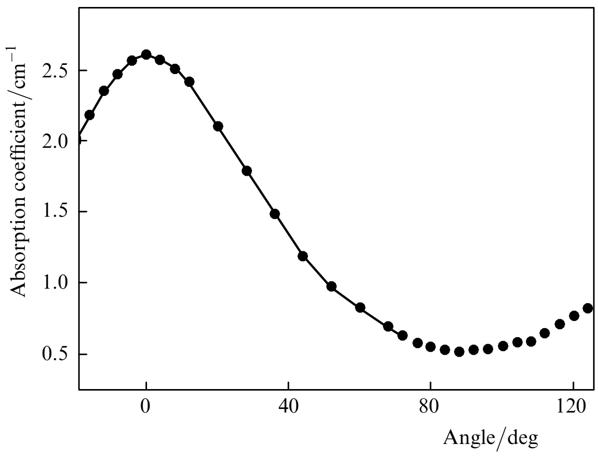

Figure 3. Dependence of the absorption coefficient of the 25 %Eu^{3+} : KGW crystal at $\lambda = 533.6$ nm on the angle between the electric field vector E of the incident beam and the axis N_m of the optical indicatrix of the crystal rotated around the N_p axis.

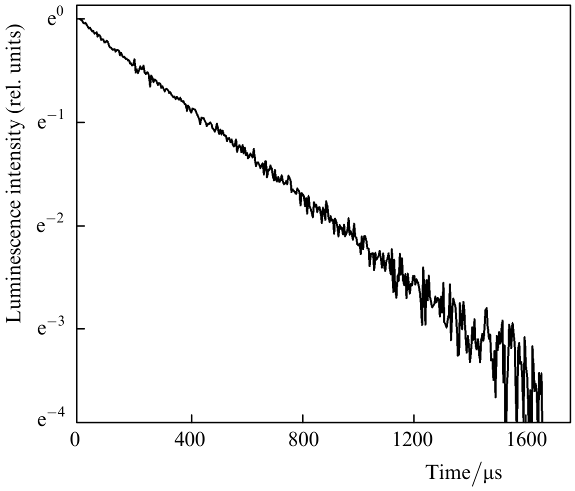

Figure 4. Luminescence kinetics for the $^5D_0 \rightarrow {}^7F_4$ transition at room temperature.

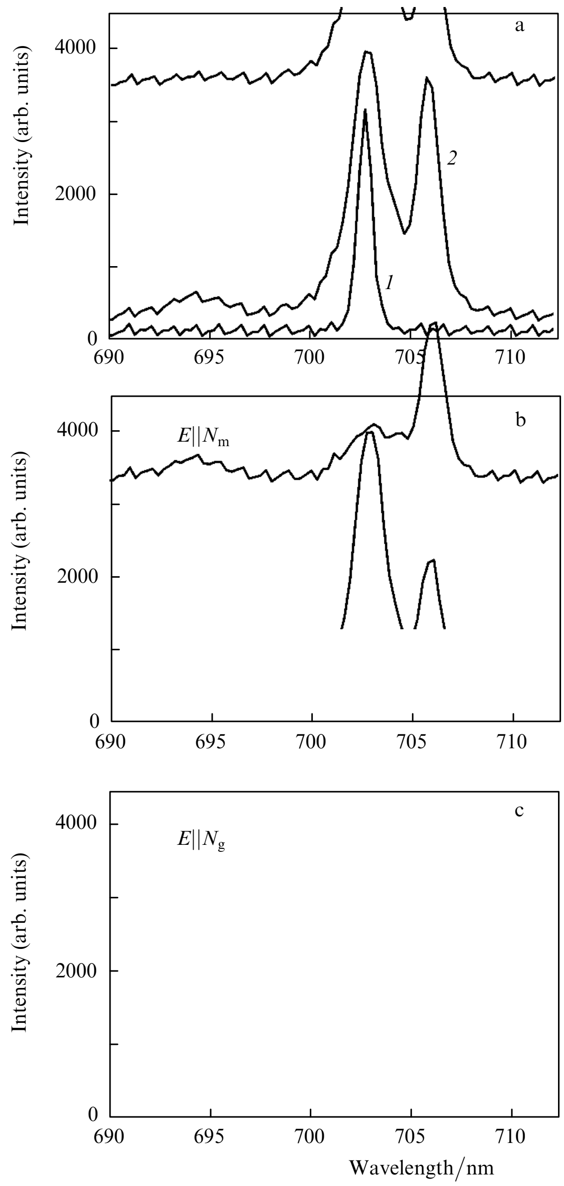

Figure 5. Spectra of the laser radiation (*1*) and natural luminescence in the $^5D_0 \rightarrow {}^7F_4$ channel (*2*), as well as polarised luminescence spectra for this channel (b, c).

tions. One can see that the decay is exponential in a dynamic range of 10^3 with the decay constant of ~ 463 μs.

In laser experiments, the linear laser cavity was formed by a concave spherical output mirror and a plane crystal surface with a coating highly reflecting in the region of 700 nm; the cavity length did not exceed 15 mm. The optical axis of the cavity coincided with the N_p axis. The crystal was studied in natural air at room temperature. The laser was excited from the side of the plain mirror of the cavity; the longitudinal pump radiation was focused in front of the crystal by a lens with a focal distance of 60 mm. The pump beam diameter at the entrance to the crystal was 0.87 mm (the diameter was measured by the moving edge method). The laser characteristics were studied at the output mirror reflectances of 97.8 % and 99.4 %, the output mirror curvature radii being 50 and 100 mm, respectively.

In the free-running regime, the 25 %Eu^{3+} : KGW laser operating on the $^5D_0 \rightarrow {}^7F_4$ transition emitted at a wavelength of 702.8 nm [Fig. 5a, curve (*1*)]. The output radiation was linearly polarised along the N_m axis. Figure 5a also presents the spectrum of natural luminescence at the $^5D_0 \rightarrow {}^7F_4$ transition [curve (*2*)]. The polarised luminescence spectra shown in Fig. 5b, c show that the radiation in the short-wavelength region of this transition is most intense, and it is this region that is responsible for the generation of stimulated emission polarised along the N_m axis.

The dependence of the free-running energy E_{gen} on the pump pulse energy E_{pump} is shown in Fig. 6. Each point is a result of averaging over 30 measurements performed at a pump pulse repetition rate of 0.5 Hz. The almost strictly linear dependence $E_{gen}(E_{pump})$ indicates that the laser medium is far from saturation. In the case of the output mirror with the reflectance $R = 97.8$ %, the laser oscillation threshold was 5.53 mJ (or 93 MW cm^{-2}). The slope efficiency $\delta\eta = \delta E_{gen}/\delta E_{pump}$ was 2.2 %. At the maximum pump energy (16.3 mJ), the free-running energy reached 244 μJ, and, hence, the optical efficiency of the laser $\eta = E_{gen}/E_{pump}$ was 1.5 %. The use of the mirror with the higher reflectance $R = 99.5$ % lead to an almost threefold decrease in the oscillation threshold (to 37 MW cm^{-2}), but worsened the other characteristics of the laser ($\delta\eta = 0.82\%$, $\eta = 0.73\%$).

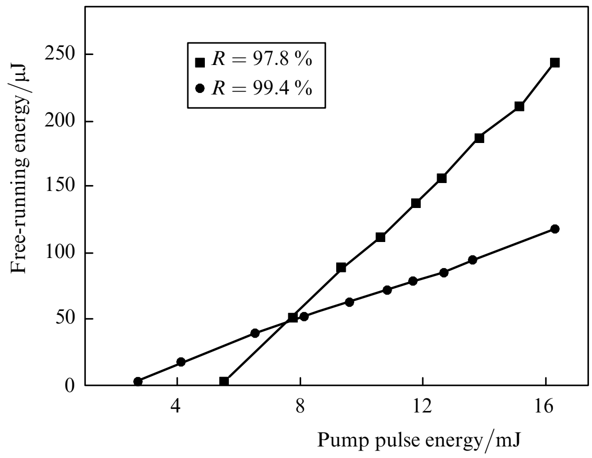

Figure 6. Dependences of the free-running lasing energy on the pump pulse energy at different output mirror reflectances.

Figure 7 shows a typical power oscillogram of a free-running pulse of the 25 %Eu^{3+} : KGW laser. The oscillogram demonstrates the so-called integral pulse, recorded when the entire beam spot hits the photodetector. In addition to the power oscillogram, Fig. 7 shows the oscillogram of luminescence at the $^5D_0 \rightarrow {}^7F_4$ transition in the absence of lasing. Both processes are recorded at the maximum pump power ($\sim$ 16 mJ) and synchronised by means of the pump pulse. One can see that the free-running oscillation starts even at the stage of luminescence buildup and lasts for $\sim$ 15 μs. The initial stage of oscillation on the $^5D_0 \rightarrow {}^7F_4$ transition is characterised by a relatively low modulation depth of the integral intensity.

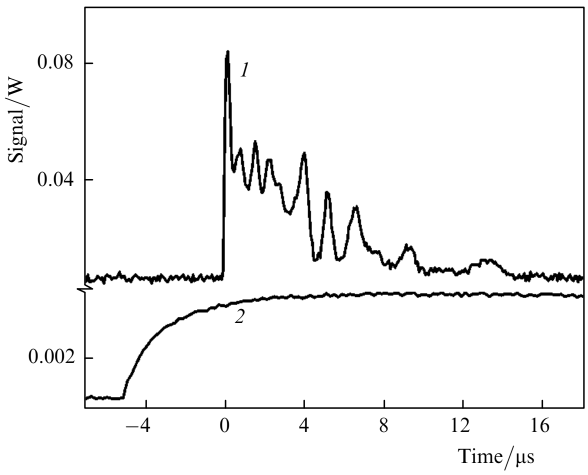

Figure 7. Power oscillograms of laser radiation (*1*) and luminescence (*2*).

It should be noted that, compared to the traditional UV excitation of E^{3+}-containing materials, pumping into the $^7F_0 \rightarrow {}^5D_1$ absorption band allows one to considerably decrease the Stokes losses S determined by the ratio of the pump frequency to the laser frequency. The decrease in the Stokes losses leads to an increase in the laser slope efficiency, a decrease in the oscillation threshold, and, what is most important, a decrease in the heat generated in the active element, since the fraction of energy transferred to heat is $1 - 1/S$. Probably, the relatively low experimental optical efficiency (with respect to the maximum possible, which is equal to $1/S$) is caused by uncompensated thermooptical distortions in the active element. However, note that the questions related to the thermooptics of the 25 %Eu^{3+} : KGW crystal are out of the scope of this work.

At present, we continue to study the mechanisms of energy transfer in the $^5D_1 \rightarrow {}^5D_0$ channel, the cross sections of stimulated transitions from the $^5D_0$ state, the gain curves, and the methods of compensation of thermal distortions for cw and pulsed regimes of Eu^{3+} : KGW lasers. The results of these investigations will be presented in future publications.

4. Conclusions

Thus, as far as we know, we obtained the stimulated emission on the $^5D_0 \rightarrow {}^7F_4$ transition in an Eu^{3+}-doped laser medium for the first time. A laser operating at room temperature is developed based on a 25 %Er^{3+} : KGW crystal grown by a modified Czochralski method. A *b*-cut active element was pumped into the $^7F_0 \rightarrow {}^5D_1$ absorption band of the Eu^{3+} ion by the second harmonic of a *Q*-switched Nd : KGW laser (λ_{pump} = 533.6 nm). The Eu^{3+} : KGW laser operated in the free-running regime at a wavelength of $\sim$ 703 nm with a pulse duration of $\sim$ 15 μs. At the active element length of 9.4 nm, the laser slope efficiency was 2.2 %, and the laser medium in this case was far from saturation. The maximum output energy was 244 μJ, which corresponds to the optical efficiency of 1.5 %. Some spectral and luminescent properties of the 25 %Eu^{3+} : KGW crystal were studied. The obtained experimental results allow us to conclude that the Eu^{3+} : KGW crystal is promising for the creation of solid-state pulsed and cw lasers operating in the region of 700 nm.

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