

ACTIVE MEDIA

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Spectroscopic properties of erbium-doped yttria-stabilised zirconia crystals

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Abstract. **Yttria-stabilised zirconia crystals $ZrO_2-Y_2O_3$ (6 mol %) $-Er_2O_3$ (5.85 mol %) are grown by directional crystallisation in a cold container using direct RF melting. The spectral and luminescent properties of these crystals are studied in order to use them as active media of solid state lasers emitting in the wavelength range 1.5–1.7 μm.**

Keywords: *$ZrO_2-Y_2O_3-Er_2O_3$ crystals, luminescence spectrum, gain cross section.*

1. Introduction

Laser radiation in the near-IR spectral region (in particular, within 1.5–1.7 μm) is of interest for various practical applications – in range finding, lidars, etc. Most lasers of this wavelength range are based on crystals or glasses doped with Er^{3+} ions [1–4]. Recently, numerous publications have appeared on efficient 1.5-micron lasers operating according to a three-level scheme under selective laser pumping of Er^{3+} ions directly to the upper $^4I_{13/2}$ laser state. These lasers are based both on well-known Er^{3+}-doped $Y_3Al_5O_{12}$ crystals and on new laser materials [5–9].

The search for new active media for this type of lasers still remains a topical problem. Resonance pumping to the upper laser level decreases the thermal load on the active element, which allows one to use materials with lower thermal conductivity, including crystals with disordered structures. Due to the inhomogeneous broadening of the absorption and luminescence lines of these crystals, it is possible to considerably extend the wavelength tuning range and reduce the requirements to the pump diode spectrum. Papers [10–13] present the results of investigations of the spectral and luminescent characteristics of disordered-structure $Er:Ca_3(NbGa)_5O_{12}$ crystals. The yttria-stabilised zirconia crystals doped with rare-earth ions also have a disordered structure. The authors of [14–16] present the spectral, luminescent, and lasing characteristics of yttria-stabilised zirconia crystals doped with Yb^{3+}, Nd^{3+}, and Tm^{3+} ions. In [17], three-micron lasing at the $^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition of Er^{3+} ions in $ZrO_2-Y_2O_3-Er_2O_3$ crystals was obtained under lamp pumping.

The specific features of the Stark splitting of multiplets of rare-earth ions in $ZrO_2-Y_2O_3-Yb_2O_3$ and $ZrO_2-Y_2O_3-Tm_2O_3$ crystals lead to a shift of the luminescence spectra of the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transitions of Yb^{3+} ions, as well as of the $^3F_4 \rightarrow {}^3H_6$ transition of Tm^{3+}, to long wavelengths with respect to the similar spectra in other oxide crystals, for example, in $Y_3Al_5O_{12}$ and $Ca_3(NbGa)_5O_{12}$ garnets. Therefore, tunable lasing in yttria-stabilised zirconia crystals can be obtained in a longer wavelength region. In particular, under diode pumping we obtained lasing in $ZrO_2-Y_2O_3-Tm_2O_3$ crystals at a wavelength of 2.046 μm [18].

In the present work, we study the spectral and luminescent characteristics of $ZrO_2-Y_2O_3-Er_2O_3$ crystals to use them as a basis for experiments on lasing in the range 1.5–1.7 μm on the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ions.

2. Methods of growth and investigation of $ZrO_2-Y_2O_3-Er_2O_3$ crystals

The yttria-stabilised zirconia crystals of the composition $ZrO_2-Y_2O_3$ (6 mol %)$-Er_2O_3$ (5.85 mol %) were grown by the cold container method in a Kristall-407 apparatus. The absorption spectra of the crystals were measured on a PerkinElmer Lambda 950 spectrophotometer, and the luminescence spectra of Er^{3+} ions in these crystals were recorded using an automated system based on an MDR-23 monochromator. As radiation detectors, we used a FEU-100 photomultiplier and an FD-7G germanium photodiode with an SR810 lock-in amplifier. Luminescence was excited by a laser diode at the wavelength $\lambda_{ex} \approx 970$ nm.

The luminescence decay kinetics for the $^4I_{13/2}$ level of Er^{3+} was recorded at a wavelength of 1535 nm upon excitation by a colour centre laser ($\lambda_{ex} \approx 965$ nm).

3. Experimental results

The panoramic absorption spectrum of the $ZrO_2-Y_2O_3$ (6 mol %)$-Er_2O_3$ (5.85 mol %) crystal is shown in Fig. 1. The absorption bands in this spectrum belong to the transitions from the ground $^4I_{15/2}$ state to the excited $^2H_{9/2}$, $^4F_{5/2}$, $^4F_{3/2}$, $^4F_{7/2}$, $^2H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$, $^4I_{11/2}$, and $^4I_{13/2}$ multiplets of Er^{3+} ions.

The absorption and luminescence spectra at the $^4I_{15/2} \leftrightarrow {}^4I_{13/2}$ transitions were studied in most detail because it is these transitions that are responsible for lasing in the range 1.5–1.7 μm. The absorption and luminescence spectra of Er^{3+} in cross section units are given in Fig. 2.

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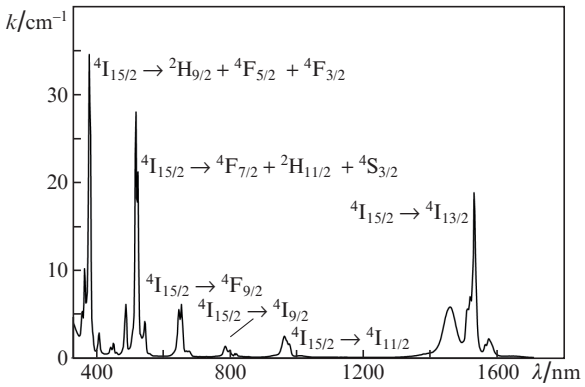

Figure 1. Absorption spectrum of Er^{3+} ions in a ZrO_2–Y_2O_3 (6 mol %) –Er_2O_3 (5.85 mol %) crystal at $T = 300$ K.

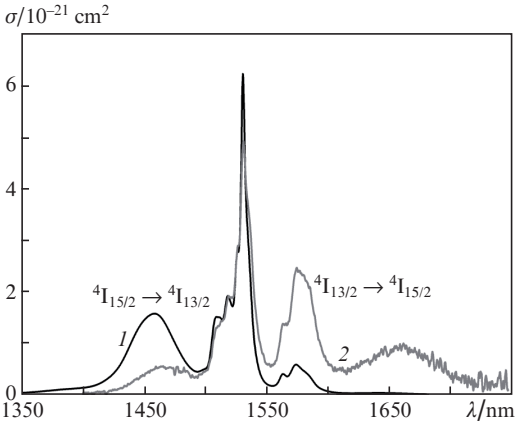

Figure 2. Absorption (*1*) and luminescence (*2*) spectra in cross section units for the $^4I_{15/2} \rightarrow {}^4I_{13/2}$ and $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transitions of Er^{3+} ions in a ZrO_2–Y_2O_3 (6 mol %)–Er_2O_3 (5.85 mol %) crystal at $T = 300$ K.

The spectral dependence of the luminescence cross section for the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition was determined by the Fuchtbauer–Ladenburg formula

$$\sigma_{em} = \frac{\lambda^5}{8\pi c n^2} \frac{1}{\tau_{rad}} \frac{I(\lambda)}{\int \lambda I(\lambda) d\lambda}, \quad (1)$$

where τ_{rad} is the radiative lifetime of the level, n is the refractive index of the material, λ is the wavelength, and I is the luminescence intensity in relative units. For calculations, we used $\tau_{rad} = 1/A = 5.9$ ms, where A is the probability of the radiative transition from the $^4I_{13/2}$ level determined by the formula

$$A = \frac{8\pi n^2}{N\lambda^4} \frac{2J' + 1}{2J + 1} \int k(\lambda) d\lambda \quad (2)$$

[$k(\lambda)$ is the absorption coefficient at the given wavelength; J' and J are the total angular momenta of 4f electrons in the ground and excited states, which in our case are 15/2 and 13/2, respectively; and N is the concentration of Er^{3+} ions].

Analysis of the luminescence spectrum on the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ions in ZrO_2–Y_2O_3 (6 mol %)–Er_2O_3 (5.85 mol %) crystals shows that, similar to sesquioxide crystals $Er:Y_2O_3$ and Er_2O_3, the long-wavelength luminescence edge reaches 1.7 μm. The long-wavelength edge of this transition band of most oxide crystals doped with Er^{3+} ions lies at a wavelength no longer than 1.65 μm. This fact is illustrated in Fig. 3, which shows the luminescence spectra for the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} in the ZrO_2–Y_2O_3 (6 mol %)–Er_2O_3 (5.85 mol %) crystal and in the disordered-structure $Er:Ca_3(NbGa)_5O_{12}$ crystal.

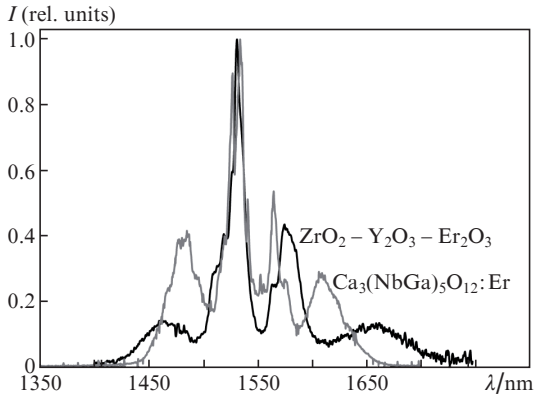

Figure 3. Luminescence spectra of ZrO_2–Y_2O_3 (6 mol %)– Er_2O_3 (5.85 mol %) and $Er:Ca_3(NbGa)_5O_{12}$ crystals ($T = 300$ K).

The luminescence of the ZrO_2–Y_2O_3 (6 mol %)–Er_2O_3 (5.85 mol %) crystal at wavelengths longer than 1.6 μm is caused by a significant splitting of the ground $^4I_{15/2}$ level of Er^{3+} ions. Since lasers based on the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ions operate according to the three-level scheme, an increase in the ground level splitting decreases the threshold laser power. This fact was previously noted and demonstrated in [19] in experiments on lasing at the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition of Yb^{3+} ions in ZrO_2–Y_2O_3 (10 mol %)–Yb_2O_3 (4 mol %) crystals.

We failed to detect luminescence in the spectral range 1.7–1.8 μm caused by the $^4S_{3/2} \rightarrow {}^4I_{9/2}$ transition of Er^{3+} ions under excitation both to the $^4I_{11/2}$ ($\lambda_{ex} \approx 970$ nm) and to the $^4S_{3/2}$ ($\lambda_{ex} \approx 532$ nm) levels.

The decay of luminescence of Er^{3+} ions from the $^4I_{13/2}$ level in ZrO_2–Y_2O_3 (6 mol %)–Er_2O_3 (5.85 mol %) crystals is shown in Fig. 4. The lifetime of Er^{3+} ions at the $^4I_{13/2}$ level determined by a decrease in the luminescence intensity $I(t)$ by

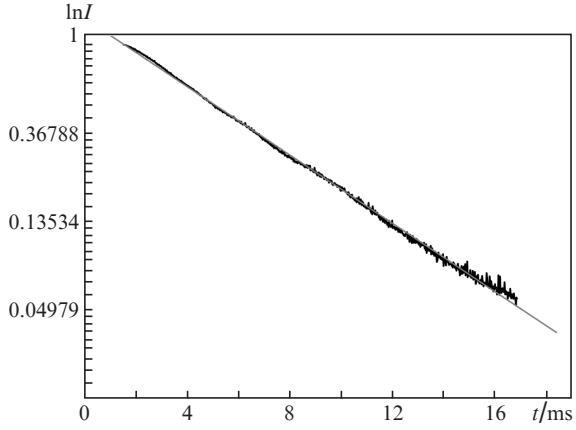

Figure 4. Luminescence decay kinetic of the $^4I_{13/2}$ level of Er^{3+} ions in a ZrO_2–Y_2O_3 (6 mol %)–Er_2O_3 (5.85 mol %) crystal.

e times was 5.4 ms, which agrees well with the lifetime 5.9 ms calculated by formula (2).

To analyse the possibility of lasing in the desired spectral region, it is convenient to use the spectral dependence of the gain cross section of the active medium at several values of the relative population inversion,

$$\sigma_g(\lambda) = p\sigma_{em}(\lambda) - (1-p)\sigma_{ab}(\lambda), \quad (3)$$

where σ_{em} and σ_{ab} are the luminescence and absorption cross sections at a chosen wavelength and $p = N_e/(N_e + N_f)$ is the relative population inversion (N_e and N_f are the populations of the $^4I_{13/2}$ and $^4I_{15/2}$ levels). Figure 5 shows the spectral dependences of the gain cross section for several values of relative population inversion.

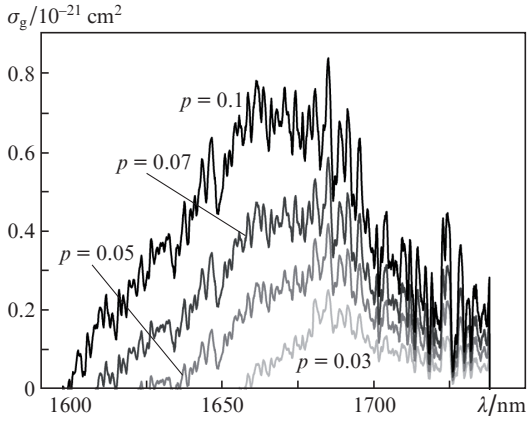

Figure 5. Spectral dependence of gain cross section for the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ions in a $ZrO_2-Y_2O_3$ (6 mol %)$-Er_2O_3$ (5.85 mol %) crystal at different values of relative population inversion.

Note in conclusion that yttria-stabilised zirconia crystals of the composition $ZrO_2-Y_2O_3$ (6 mol %)$-Er_2O_3$ (5.85 mol %) have been grown by direct RF heating in a cold container. The panoramic spectrum of absorption in this crystal from the ground $^4I_{15/2}$ state to the excited $^2H_{9/2}$, $^4F_{5/2}$, $^4F_{3/2}$, $^4F_{7/2}$, $^2H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$, $^4I_{11/2}$, and $^4I_{13/2}$ multiplets is measured at T = 300 K. The spectral dependence of the luminescence cross section $\sigma_{em}(\lambda)$ for the stimulated $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ions is determined by the Fuchtbauer–Ladenburg formula.

From the spectral dependence of the absorption $\sigma_{ab}(\lambda)$ and luminescence $\sigma_{em}(\lambda)$ cross sections for the $^4I_{13/2} \leftrightarrow {}^4I_{15/2}$ transitions of Er^{3+} ions, the gain cross section spectrum $\sigma_g(\lambda)$ for the expected laser transition $^4I_{13/2} \rightarrow {}^4I_{15/2}$ is calculated for relative population inversions of 0.03, 0.05, 0.07, and 0.1. Laser radiation of $ZrO_2-Y_2O_3$ (6 mol %)$-Er_2O_3$ (5.85 mol %) crystals can be tuned within the spectral range 1620–1700 nm.

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