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On the kinetics of nonradiative energy transfer in Yb – Er phosphate glasses excited by a diode laser

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***Abstract*. The luminescence of a Yb – Er phosphate glass excited by a diode laser is studied as a function of the density of energy absorbed by a sample and the pump radiation intensity. An abrupt change in the depopulation rate of the $Yb^{3+}(^2F_{5/2})$ level was observed after switching off the pump laser. This effect is explained qualitatively based on the kinetics of nonradiative energy transfer in glasses and crystals.**

Keywords: *nonradiative energy transfer, phosphate glasses, diode-laser pumping*.

1. Introduction

Crystals and glasses doped with trivalent erbium ions for the use in lasers emitting at a wavelength of ~ 1.5 μm attract special attention because, first, this wavelength is optimal for fibreoptic communication and, second, emission at ~ 1.5 μm is the least eye hazardous (the damage threshold is 0.8 J cm^{-2}) and, therefore, is promising for applications in ophthalmology, laser ranging, material machining, ets.

It is known [1]* that the upper Er ($^4I_{11/2}$) laser level of Er is predominantly populated due to the Yb $\rightarrow$ Er ($^4I_{11/2}$) $\rightarrow$ Er ($^4I_{13/2}$) sensitising, when Yb^{3+} ions are excited upon optical pumping and then nonradiative energy transfer occurs to the $^4I_{11/2}$ level of Er^{3+} ions, which is resonant with the metastable $^2F_{5/2}$ level of ytterbium. For this reason, the energy parameters of ytterbium – erbium lasers are mainly determined by the efficiency of nonradiative energy transfer from the $Yb^{3+} \rightarrow Er^{3+}$ ions.

Because generation in erbium lasers occurs in accordance with a three-level scheme, the upper laser level should be strongly populated for producing the population inversion in the active element. The main problem encountered in attempts to increase the efficiency of Yb – Er lasers is related to the active parasitic processes that are developed in Yb – Er glasses upon the intense pumping of donors. These processes include accumulation of the excitation energy, reverse energy transfer, absorption of the pump energy at inactive transitions, nonlinear quenching, etc. All these processes prevent the efficient population of the upper Er ($^4I_{13/2}$) laser level of Er.

The probability of the Yb ($^2F_{5/2}$) $\rightarrow$ Er ($^4I_{11/2}$) energy transfer is proportional to the product $[N_{Yb}][N_{Er}]$. The efficient energy transfer with the quantum yield of luminescence $\eta_q > 0.9$ at the erbium concentration $\sim 10^{19}$ cm^{-3} is achieved at high concentrations of Yb (above 2×10^{21} cm^{-3}). Note that at high excitation energies, the efficiency of nonradiative energy transfer substantially decreases due to the accumulation of Er^{3+} ions in a metastable state during the action of the pump pulse. The spectral and luminescent characteristics of the glass and their variation under these conditions give information on the above processes and allow one to estimate the influence of these processes on the laser efficiency.

2. Experimental

Active elements of the Yb – Er laser were made of a Ba – Li – Al phosphate glass, in which the weight content of Yb_2O_3 and Er_2O_3 was 17 % and 0.13 %, respectively. The active elements were rectangular parallelepipeds of size $2.5 \times 2.5 \times 20$ mm. The optical scheme of the experiment is shown in Fig. 1.The active elements were pumped at 957 nm by a 1-cm long array of diode lasers mounted vertically. The pulsed power of this array did not exceed 45 W for a pulse duration of $\tau_p \leqslant 400$ μs.

The radiation from diode lasers was focused by cylindrical lenses (*2*) and short-focus objective (*3*) on active element (*4*), which was placed in the image plane of diode array (*1*), in the form of a narrow vertical strip of size $\sim 0.4 \times 3.5$ mm. The radiation intensity distribution in this strip is shown in Fig. 2. The pump radiation was focused in such a way that the width of the narrow strip almost did not change over the active element thickness and was equal to ~ 0.4 mm. The distance from the strip edge to the active element end did not exceed 0.5 mm. This eliminated the effect of reabsorption on the luminescence intensity distribution over the active element end.

The luminescence intensity distribution was determined

*In monograph [1], rather detailed data on Yb – Er glasses are presented. In later papers, the positions of energy levels are determined more exactly, the improved technologies of the glass synthesis are described, etc. However, these papers do not change essentially the main results reported in [1].

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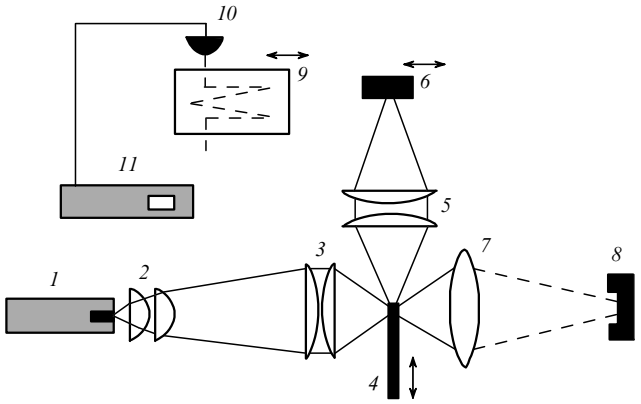

Figure 1. Optical scheme for measuring spectral and luminescent characteristics: (*1*) diode laser array; (*2*) cylindrical lenses; (*3*) short-focus objective; (*4*) active element; (*5*) objective; (*6*) pyroelectric matrix; (*7*) lens; (*8*) pyroelectric power meter; (*9*) monochromator; (*10*) photodiode; (*11*) oscilloscope.

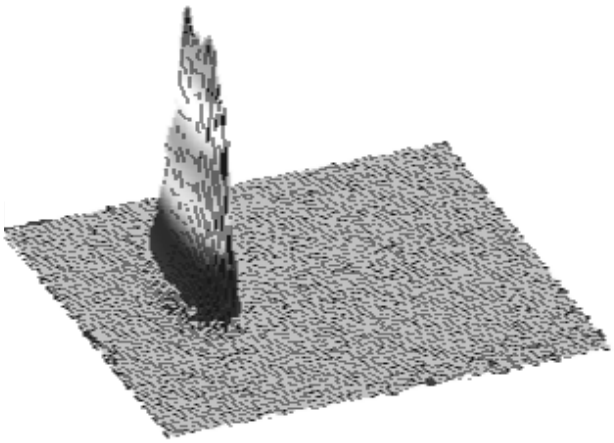

Figure 2. Distribution of the radiation intensity of a diode laser in the active element.

by the imaging of the end of a glass sample by objective (*5*) on the surface of a Pyrocam pyroelectric matrix (*6*) (the spatial resolution was 100 μm). Fig. 3 shows the typical distribution of the luminescence intensity obtained by this method. The decay of luminescence of Er^{3+} and Yb^{3+} ions was detected by focusing the image of the sample end at the entrance slit of an MDR-3 monochromator (*9*), which was placed instead of the pyroelectric matrix.

The radiation that have passed through the entrance slit of width 500 μm corresponded to the region shown by a rectangle in Fig. 3. The energy of this radiation could be readily measured and was used for calculating the energy density absorbed in this region of the active element. The radiation intensity was detected with a germanium photodiode (*10*), which was placed directly behind the monochromator exit slit of width 300 μm. The output signal of the photodiode was displayed with a Tektronix-360 oscilloscope. The energy absorbed by the sample was measured with a pyroelectric power meter (*8*) (Molectron). The pump energy was varied by changing the duration of diode laser pulses (100, 200, and 400 μs) and by changing the pump current (35, 50, 75, and 100 A).

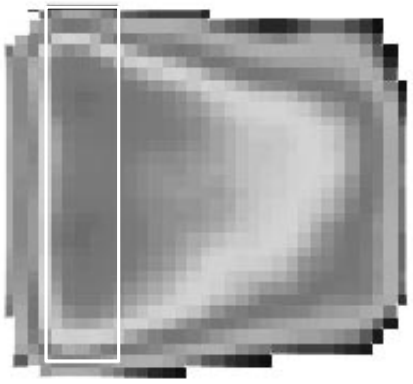

Figure 3. Distribution of the luminescence intensity over the active-element cross section.

3. Experimental results

We studied the decay of luminescence of Er^{3+} ions at a wavelength of 1536 nm. A simple analysis showed that the luminescence decay under our experimental conditions was not strictly exponential at the initial stage. In this case, the luminescence lifetime t_{lum} can be conventionally defined as a period of time from the end of the diode laser pulse to the instant when the luminescence intensity falls to the value $I = I_0/e$ (I_0 is the maximum luminescence intensity).

The dependence of the maximum luminescence intensity of Er^{3+} ions at 1536 nm on the energy density absorbed by the active element is also nonlinear. As the energy density was increased from 0.16 to 2.37 J cm^{-3}, the intensity I_0 increased by more than ten times, showing the tendency to saturation at the high energy density. The luminescence lifetime t_{lum} changed in this case considerably slower, from 8.4 ms for E = 0.16 J cm^{-3} to 8.8 ms for $E = 2.37$ J cm^{-3}. This is probably explained by a much more noticeable change in the luminescence rise time t_{fl} (the rise time of luminescence of Er^{3+} ions at 1536 nm was determined before the instant of the maximum luminescence intensity), which increased from 0.7 to 1.2 ms in this range of variation of E.

Fig. 4 shows the dependence of the relative conversion efficiency η of the pump energy spent for the population of the Er^{3+} ($^4I_{13/2}$) level of Er^{3+} on the specific energy input (the conversion efficiency is normalised to the maximum efficiency; the concentrations of Yb and Er in the phosphate

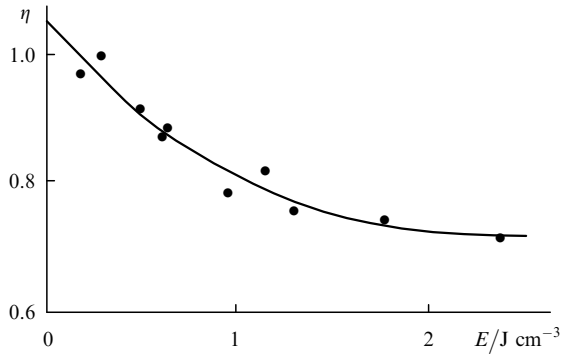

Figure 4. Dependence of the relative conversion efficiency of the pump radiation on the energy density absorbed by an active element.

glass used in our study are close to optimal ones and the quantum yield is $\eta_q \approx 0.9$ for $E \to 0$ [1]). In this case, η is defined as the ratio of the fixed fraction of the luminescence energy at $\lambda = 1536$ nm to the density of absorbed energy.

The luminescence energy was determined by the integration of the total curve (rise and decay) of the luminescence intensity at 1536 nm over time, so that we can say that the conversion efficiency η decreases with increasing pump energy to the densities required for producing population inversion. Our estimates showed that, if we assume that $\eta = 0.6$ for the active element under study, then the energy density required for producing population inversion will be ~ 2 J cm^{-3}.

In glasses containing only erbium, the long-wavelength edge of the luminescence spectrum of Er^{3+} ions is near 1050 nm. For this reason, we studied the decay of luminescence of Yb^{3+} ions at 1063 nm. Analysis of the data in Fig. 5 showed that the decay of luminescence of Yb^{3+} ions was always nonexponential. The luminescence lifetime τ defined as a period of time for which the luminescence intensity decreases by a factor of e depends on the specific energy input. This dependence is shown in Fig. 5.

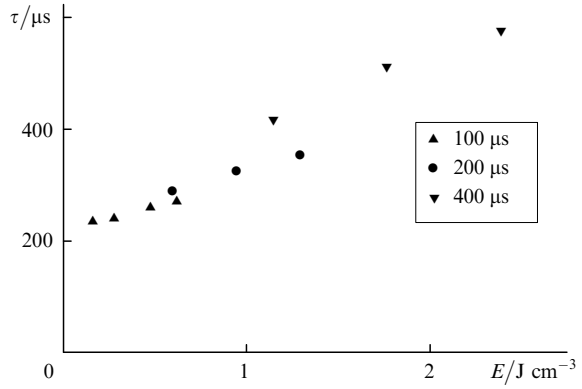

Figure 5. Dependence of the decay time of luminescence of Yb^{3+} ions on the energy density absorbed by an active element for different τ_p.

The luminescence lifetime for Yb^{3+} ions noticeably increases with increasing the density of energy absorbed by the sample. This well-known effect [1] is mainly explained by the fact that the efficiency of nonradiative energy is strongly reduced at high excitation energies due to accumulation of Er^{3+} ions in a metastable state. This is caused by the depletion of the ground state and also, which is more important, by the fact that Yb^{3+} ions, which provide the maximum probability of donor–acceptor interactions (the limiting factor of quenching is the rate of the $Yb^{3+} \to Er^{3+}$ energy transfer) are leaving the quenching process first of all. Because we can assume that migration of energy is virtually absent at such concentrations of Er^{3+} ions in the acceptor system, the effective rate of nonradiative energy transfer decreases much more rapidly than could be expected from the dynamics of a decrease in the ground-state population of erbium ions.

Along with the dependence of τ on the specific energy input E, we found the influence of the radiation intensity of diode lasers on the decay time of luminescence of Yb^{3+} ions at constant E (Fig. 5). Under our experimental conditions, the characteristic decay time is comparable with the pump-pulse duration τ_p. For $E \sim 1$ J cm^{-3}, the levels Yb^{3+} ($^2F_{5/2}$), Er^{3+} ($^4I_{13/2}$) and Er^{3+} ($^4I_{11/2}$), which are located directly above the ground levels, are already sufficiently populated, so that the dependence of the decay time on the pump intensity can be explained by a change in the rate of energy migration over the energy levels of the Er^{3+} ion and by the dependence of this process on the radiation intensity.

The system of kinetic equations describing a change in the population of energy levels of Yb^{3+} and Er^{3+} ions during population of the $^4I_{13/2}$ metastable level is quite complicated because it should describe in the general case many processes affecting the population of the metastable level. However, in the case of excitation of phosphate glasses, the population of the $^2F_{5/2}$ level of ytterbium can be described by one equation

$$\frac{dN}{dt} = q_0 - \frac{N}{\tau} - W_{da}(t)N, \qquad (1)$$

where N is the population of the $^2F_{5/2}$ level of Yb^{3+}; τ is the radiative lifetime of the $^2F_{5/2}$ state of ytterbium ions; $W_{da}(t)$ is the rate of the $Yb^{3+}(^2F_{5/2} \to {}^2F_{7/2})$ – $Er^{3+}(^4I_{15/2} \to {}^4I_{11/2})$ nonradiative energy transfer [we assume below that $W_{da}(t)$ is a slowly varying function of time]; and q_0 is the rate of population of the $^2F_{5/2}$ level of Yb^{3+} upon pumping.

Equation (1) is not exact because it neglects some processes involving $Yb^{3+}(^2F_{5/2})$ and $Er^{3+}(^4I_{11/2})$ ions. However, taking into account that the $^4I_{11/2} \to {}^4I_{13/2}$ multiphonon relaxation rate of Er^{3+} is $\sim 10^6$ s^{-1}, we can neglect these processes, assuming that the kinetics of the $^2F_{5/2}$ state of Yb^{3+} is completely described by the following processes. The $^2F_{5/2}$ level is populated only due to absorption of the 957-nm radiation from the diode laser by the ytterbium ions, whereas it is depleted due to nonradiative energy transfer to the $^4I_{11/2}$ level of Er^{3+} and due to radiative decay. The $^4I_{11/2}$ and $^4I_{13/2}$ levels are assumed to be 'short out', and no reverse energy transfer from erbium ions to ytterbium ions occurs.

The oscillograms of luminescence of ytterbium ions were processed using equation (1) for the period of time both during pumping and after pumping. The shape of the diode laser pulse was assumed strictly rectangular (real durations of the leading and trailing edges of the pulse did not exceed several microseconds).

Fig. 6 shows the time dependences of the effective depopulation rate

$$W = 1/\tau + W_{da}(t)$$

of the $^2F_{5/2}$ level for different intensities of the pump radiation ($\tau_p = 200$ μs). The arrow in the Fig. 6 shows the instant of the diode laser switching off. Similar dependences were observed for $\tau_p = 100$ and 400 μs.

Fig. 7 shows the time dependence of W for the constant intensity $I = 1.7$ kW cm^{-2} and different durations of the diode laser pulse. The main feature of these dependences is the abrupt decrease in W after the laser switching off. The drop ΔW depends both on the pump intensity and on the energy absorbed by the sample, the dependence of ΔW on the pump intensity being more strong, as one can clearly see from Fig. 8.

The abrupt change in the effective depopulation rate of the $^2F_{5/2}$ level of Yb^{3+} can be explained by considering processes that affect the population of the $^4I_{11/2}$ level of Er^{3+} ions involved in nonradiative energy transfer. As

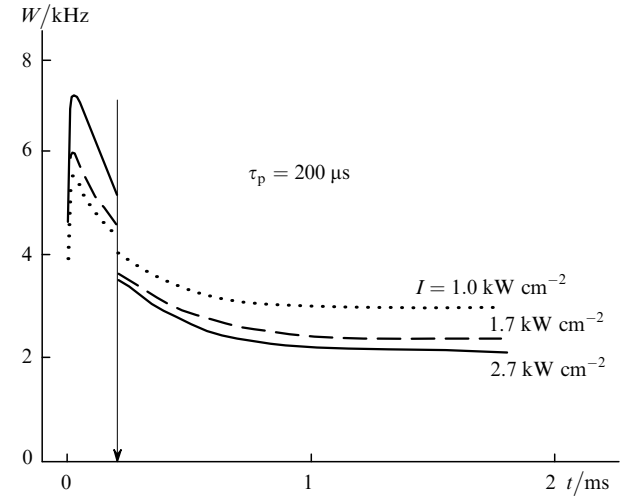

Figure 6. Time dependences of the effective depopulation rate of the $Yb^{3+}(^2F_{5/2})$ level for different intensities of pump radiation.

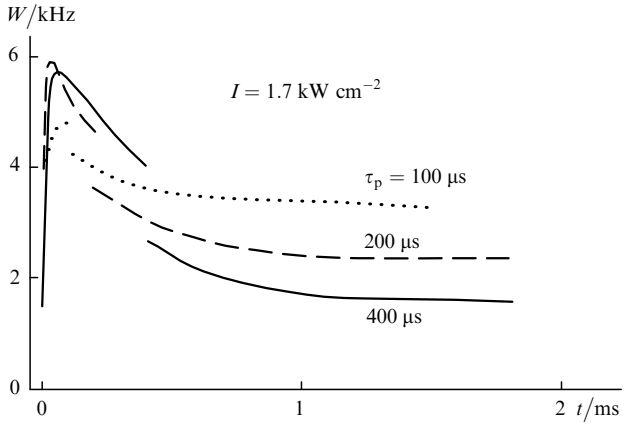

Figure 7. Time dependences of the effective depopulation rate of the $Yb^{3+}(^2F_{5/2})$ level for the constant intensity of pump radiation and different τ_p.

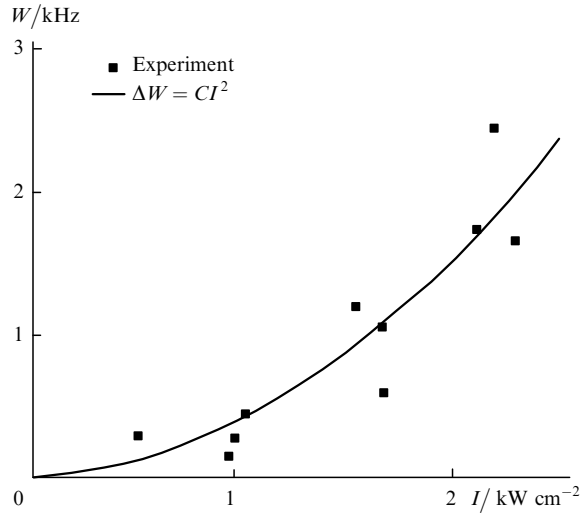

Figure 8. Dependence of the drop ΔW of the effective depopulation rate of the $Yb^{3+}(^2F_{5/2})$ level after the pump switching off on the diode-laser radiation intensity.

mentioned above, the quenching of Yb^{3+} ions that located most closely to Er^{3+} ions ceases first of all. Although at such concentrations of Er^{3+} ions, the migration of energy in the acceptor system is almost absent, one of the processes that returns these ions to the ground state can be the induced absorption of the diode laser radiation, which results in the transition of Er^{3+} ions to the $^4F_{7/2}$ state (the resonance $^4I_{11/2} \rightarrow {}^4F_{7/2}$ transition) accompanied by fast multiphonon relaxation to the low-lying levels and by the radiative decay [2] (probably, from the $^4S_{3/2}$ level).

It is obvious that this process results in a loss of two photons and reduces the pumping efficiency. This assumption is confirmed by the green emission of the excited region of the sample that we observed in experiments. It was assumed in paper [2], where the dynamics of fluorescence of Yb, Er : Y_2SiO_5 crystals was studied, that the Er^{3+} ($^4I_{11/2} \rightarrow {}^4F_{7/2}$) transition in Er^{3+} ions can occur either due to direct absorption of diode laser radiation by the $Er^{3+}(^4I_{11/2})$ ion or after energy transfer according to the scheme

$$Yb^{3+}(^2F_{5/2} \rightarrow {}^2F_{7/2}) \rightarrow Er^{3+}(^4I_{11/2} \rightarrow {}^4F_{7/2}).$$

The authors of paper [3] reported that they failed to observe the direct absorption of the 970-nm radiation from a diode laser by $Er^{3+}(^4I_{11/2})$ ions in an Er^{3+} : YSO silicate crystal because of a short lifetime of this ion state. The experimental data obtained in our paper can be explained by the excitation mechanism proposed in paper [4], where the neodymium laser-stimulated energy transfer from Yb^{3+} ions to Tb^{3+} ions in silicate glass was observed. Under our conditions, the energy transfer is described by the reaction

$$h\nu + Yb^{3+}(^2F_{5/2}) + Er^{3+}(^4I_{15/2}) \rightarrow Yb^{3+}(^2F_{7/2}) + Er^{3+}(^4F_{7/2}).$$

In addition, in this case, to observe an abrupt change in the effective depopulation rate for the $Yb^{3+}(^2F_{5/2})$ level, the condition $\Delta W \sim IN^* \sim I^2$ should be satisfied (where N^* is the concentration of ytterbium ions at the $^2F_{5/2}$ level).

The solid curve in Fig. 8 is the approximation of the experimental data by the function $y = Cx^2$, and we can consider that this condition is well satisfied. After the end of the diode laser pulse, this channel of supplying the ion–ion system with Er^{3+} ions, which have the greatest probability of donor-acceptor interactions, disappears, resulting in the abrupt decrease in W.

Fig. 9 shows the dependence of the effective depopulation rate of the $Yb^{3+}(^2F_{5/2})$ level on the absorbed energy density for the values of W corresponding to the end of luminescence decay curves. In this case, unlike the data presented in Fig. 5, the dependence on I is absent, and W depends only on one argument – the absorbed energy density.

The above results show that real lasing thresholds of diode-pumped erbium lasers prove to be considerably higher than the calculated values, which should be taken into account in the development of these lasers.

The required concentration of activators in laser glasses was determined by one of the authors of this paper based on the condition that the efficiency of energy transfer from Yb ions to Er ions should be no less than 0.8. However, the luminescent properties of glasses were measured for low pump energies. The same method was used in papers of

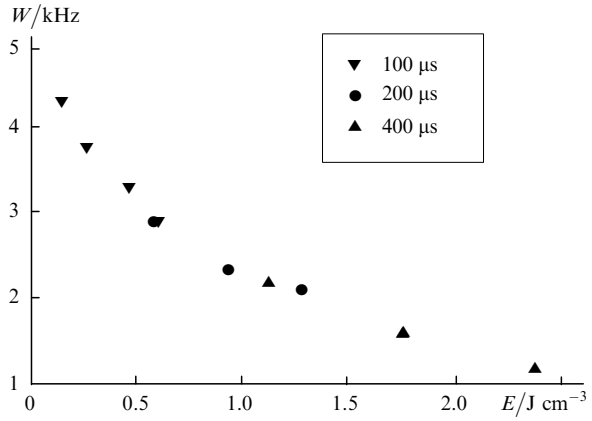

Figure 9. Dependence of the effective depopulation rate of the $Yb^{3+}(^2F_{5/2})$ level on the absorbed energy density corresponding to the end of luminescence decay curves for $\tau_p = 100, 200$, and 400 μs.

other researchers. The use of diode pumping for measuring the luminescent properties of glasses and crystals at high levels of excitation of erbium ions allows one to determine the optimal concentrations of activators in these materials for applications in free-running or *Q*-switched lasers.

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References

1. Alekseev N.E., Gapontsev V.P., Zhabotinskii M.E., Kravchenko V.B., Rudnitskii Yu.P. *Lazernye fosfatnye stekla* (Laser Phosphate Glasses) (Moscow: Nauka, 1980).
2. Li C., Wyon C., Moncoge R. *IEEE J. Quantum Electron.*, **28**, 1209 (1992).
3. Schweizer T., Jensen T., Heumann E., Huber G. *Opt. Commun.*, **118**, 557 (1995).
4. Bilak V.I., Zverev G.M., Karapetyan G.O., Onishchenko A.M. *Pis'ma Zh. Eksp. Teor. Fiz.*, **14**, 301 (1971).