

Spectroscopic and Lasing Properties of Highly Concentrated Glasses

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Abstract—A method has been advanced for the quantitative separation of the degradation channels of the electron-excitation energy of rare-earth activators, which is based on measurements of the duration of activator luminescence and of the absorption coefficient of OH-groups in concentration series of glasses. The optimal neodymium concentration has been established for obtaining the maximum gain in phosphate glasses. Preliminary lasing tests of the concentration series of phosphate and also silicate glass with a neodymium concentration of approximately 2.3×10^{20} ions cm^{-3} have been performed.

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Nonradiative deactivation of the excited levels of rare-earth activators (REA) with a growth in the concentration of the latter and an enhancement of the excitation-energy migration is determined chiefly by two factors: the exchange of excitation energy for valence vibrations of impurity OH-groups and the quenching of the luminescence of the REA according to the cross-relaxation scheme. The physical mechanisms of these processes have been investigated in detail in [1, 2].

The present communication advances a method for the quantitative separation of each of the degradation channels indicated above for the electron-excitation energy. The method is based on measuring the duration T of the activator luminescence and the absorption coefficient of the OH-groups in concentration series of glasses, each of which includes a glass having a constant activator concentration and a variable concentration of the OH-groups. Moreover, the possibility is investigated of obtaining continuous-wave lasing on neodymium glasses with high and low cross sections of stimulated radiation over a wide range of concentrations.

Figure 1 displays the dependences of $1/\tau$ on the absorption coefficients K_{OH} for glasses activated with Nd^{3+} and $\text{Yb}^{3+}-\text{Er}^{3+}$. From Fig. 1a, it is evident that for each fixed concentration N of neodymium, the dependence of $1/\tau$ on K_{OH} is linear. The slope angles of the straight lines increase with increasing N . The tangents of the slope angles made by the straight lines with the axis of ordinates characterize the quenching of neodymium luminescence by the OH-groups which is due to migration of the excitation along the activator ions to the OH-groups. The values of $1/\tau$ intercepted

by the straight lines on the axis of ordinates, less the probability $1/\tau_0$ of radiative transitions, characterize the quenching of neodymium via the cross-relaxation scheme. Under these conditions, the value of $1/\tau$ corresponding to the minimum activator concentration

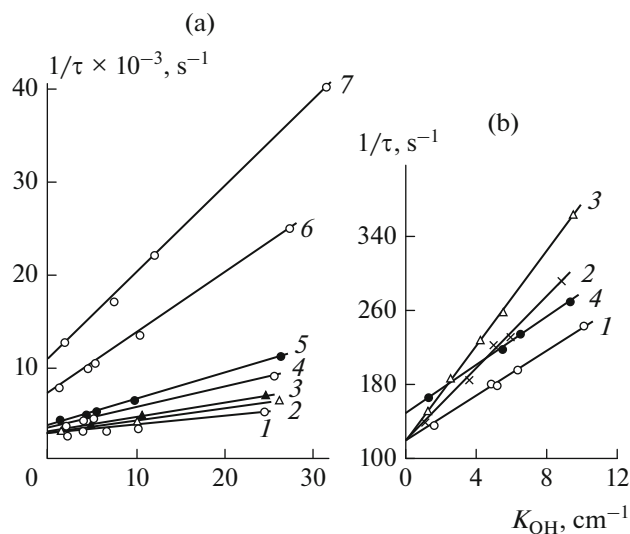


Fig. 1. Dependence of the probability of deactivation of the ${}^4\text{F}_{3/2}$ level of neodymium (a) and the ${}^4\text{I}_{13/2}$ level of erbium (b) on the absorption coefficient of OH-groups in phosphate glass at a wavelength of approximately $3.4 \mu\text{m}$: (a) neodymium concentration $N \times 10^{-20} \text{cm}^{-3}$: (1) 0.56; (2) 1.12; (3) 2.24; (4) 3.37; (5) 4.3; (6) 9.3; (7) 12.95; (b) erbium concentration $N \times 10^{-19} \text{cm}^{-3}$: (1) 4.7; (2) 8; (3) 12; (4) 4.7; neodymium concentration $N \times 10^{-19} \text{cm}^{-3}$; (4) 2.

$N \sim 0.5 \times 10^{20}$ ions cm^{-3} coincides with the radiative probability of $1/\tau$ of neodymium which is equal to 2500 s^{-1} and has been calculated for barium-lead-phosphate glass of the GLS 22 type according to the Judd theory [3] and from the q/τ relationship.

In the case of phosphate glasses that are doubly activated with $\text{Yb}^{3+}-\text{Er}^{3+}$ (Fig. 1b), the slope angles or the analogous straight lines likewise increase with a growth of erbium concentration, but the lines converge to one point on the axis of ordinates corresponding to the radiative probability of erbium which is equal to approximately 116 s^{-1} . When neodymium is introduced into glass containing erbium (Fig. 1b, the straight line 4), the quenching of erbium by hydroxyl groups is weakened, which is evidenced by the decrease in the slope angle of the straight line 4 with respect to the axis of ordinates, but the intercept of the indicated straight line on the axis of ordinates is shifted in the direction of increasing $1/\tau$. The difference between the values of $1/\tau$, (for $K_{\text{OH}} = 0$) for the straight lines 1–3 (Fig. 1b) and the straight line 4 characterizes the probability of erbium quenching by neodymium in the absence of hydroxyl groups in the glass.

Figure 2 shows the concentration dependences of the probability of nonradiative deactivation of the ${}^4\text{F}_{3/2}$ level of neodymium which were obtained from the data of Fig. 1a. Curve 1 (Fig. 2a) was plotted from points corresponding to the values of $1/\tau - 1/\tau_0$ for $K_{\text{OH}} = 0$ and characterizes the quenching of neodymium via the cross-relaxation scheme. Curves 2–4 were obtained from the difference between the values of $1/\tau$ taken from the dependence $1/\tau = 1/(K_{\text{OH}})$ at the values $K_{\text{OH}} = 5, 10, 20 \text{ cm}^{-1}$ and $K_{\text{OH}} = 0$ for each fixed activator concentration and characterize the concentration quenching of neodymium for a specified water content of the glass.

The probability of quenching via the cross-relaxation scheme depends quadratically on the Nd^{3+} concentration, although for values of $N \leq (3-4) \times 10^{20}$ ions cm^{-3} for which the migration of the excitation energy is still low, this dependence may be approximated as a linear dependence (curve 1, Fig. 2a) [4]. Quenching of neodymium luminescence by water (Fig. 2a, curves 2–4), on the contrary, corresponds to a linear dependence of W on N which for $N \leq (3-4) \times 10^{20}$ ions cm^{-3} and a reduction of the excitation-energy migration along neodymium ions goes over into a quadratic dependence. As a whole, it follows from Fig. 2a that in glass having a value of $K_{\text{OH}} \sim 5 \text{ cm}^{-1}$, the quenching of neodymium luminescence by hydroxyl groups predominates over quenching via the cross-relaxation scheme for an activator concentration of up to approximately 7×10^{20} ions cm^{-3} . At higher activator concentrations, cross-relaxation becomes predominant.

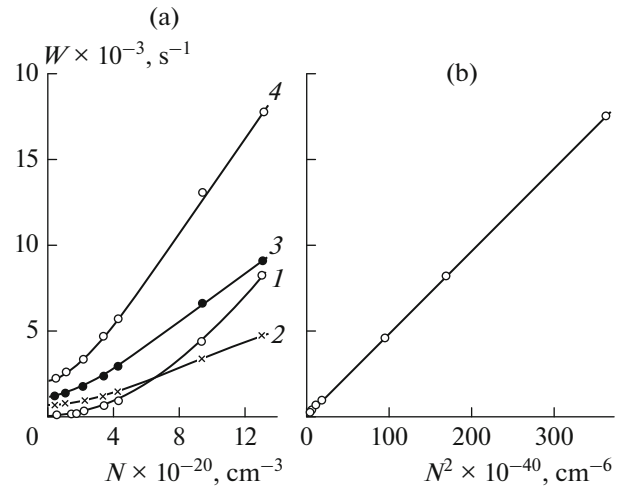


Fig. 2. Dependence of the deactivation probability W of the ${}^4\text{F}_{3/2}$ level of neodymium on Nd^{3+} concentration (a) and on the square of the concentration (b): (a) (1) $K_{\text{OH}} = 0$, $W = \frac{1}{\tau} - \frac{1}{\tau_0}$; (2) $K_{\text{OH}} = 5 \text{ cm}^{-1}$; (3) $K_{\text{OH}} = 10 \text{ cm}^{-1}$; (4) $K_{\text{OH}} = 20 \text{ cm}^{-1}$; (2–4) $W = \frac{1}{\tau} - \frac{1}{\tau_1}$, where τ is the measured lifetime of Nd (μs), τ_0 is the radiative lifetime of Nd (μsec), τ_1 is the lifetime of Nd (μs) for $K_{\text{OH}} = 0$ (Fig. 1a); (b) $K_{\text{OH}} = 0$. The absorption coefficients were calculated using common logarithms.

The revealed regularities allowed establishment of an optimal neodymium concentration for obtaining the maximum gain K_{am} for dehydrated glasses and determining its dependence on their content of OH-groups. Figure 3 shows the dependence of the quantity Nq , which is proportional to the gain (for a pumping duration that is comparable with τ_{Nd}), on neodymium concentration in the investigated glass and in vitreous lanthanum pentaphosphate which has the lowest concentration quenching of the well-known glasses [5]. From Fig. 3, it follows that the maximum K_{am} is realized in all the glasses for $N \sim 8 \times 10^{20}$ ions cm^{-3} . In the glass having $K_{\text{OH}} = 5 \text{ cm}^{-1}$, the gain is reduced by a factor of 1.5 compared with the dehydrated glass, and its dependence on activator concentration is weakened. In the glass having the composition $\text{La}_2\text{O}_3 \cdot 5\text{P}_2\text{O}_5$ with $K_{\text{OH}} = 1 \text{ cm}^{-1}$, an increase in neodymium concentration from 8×10^{20} to 25×10^{20} ions cm^{-3} has practically no effect on the value of K_{am} .

Thus, a neodymium concentration $N = 8 \times 10^{20}$ ions cm^{-3} ensures the maximum gain in glasses having both conventional and reduced concentration quenching. For the condition requiring total utilization of the pumping light, this concentration is optimal for active elements having a diameter of 1–5 mm, and evidently for activated fibers. A further increase in

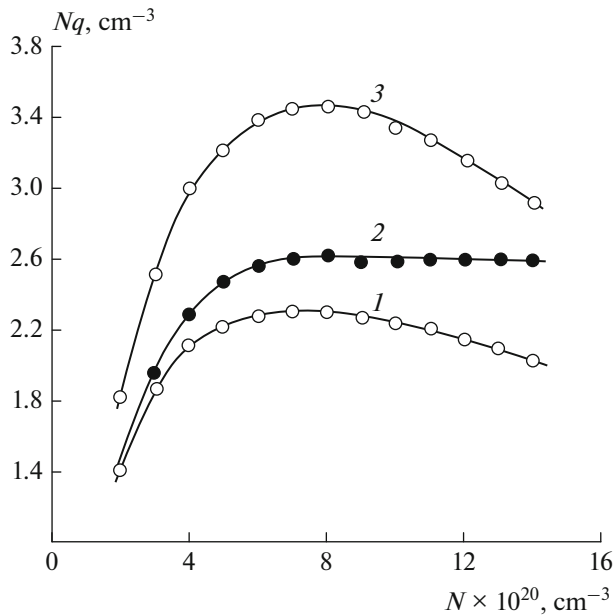


Fig. 3. Dependence of the quantity Nq , which is proportional to the gain K_{am} , on neodymium concentration: (1) for barium-lead-phosphate glass of the GLS-22 type, $K_{\text{OH}} = 5 \text{ cm}^{-1}$; (2) glass having a neodymium pentaphosphate composition, $K_{\text{OH}} = 1 \text{ cm}^{-1}$; (3) barium-lead-phosphate glass of the GLS-22 type, $K_{\text{OH}} = 0$.

neodymium content leads merely to a growth of the absorption in the region of $1.06 \mu\text{m}$, which for $N = 5.7 \times 10^{20} \text{ O ions cm}^{-3}$ (GLS-24) glass already amounts to $6 \times 10^{-4} \text{ cm}^{-1}$ [6]. Only in the case of activated films, where high activator absorption coefficients are required, does the introduction of ultrahigh neodymium concentrations become justified.

However, even here, one should take into account the fact that the cross sections σ of the stimulated emission in the $\text{La}_2\text{O}_3 \cdot 5\text{P}_2\text{O}_5$ glass and, for example, in the investigated barium-lead-phosphate glass of the GLS-22 type amount to 2.3×10^{-20} and $3.2 \times 10^{-20} \text{ cm}^2$, respectively [3, 6], according to the spectroscopic procedure for determining this cross section. Therefore, the advantage in quantum yield may not compensate the low value of σ .

Based on the concentration-quenching results obtained, a phosphate glass KGSS-083 was developed which allows the introduction of high concentrations of neodymium in place of lanthanum up to approximately $13 \times 10^{20} \text{ ions cm}^{-3}$ and has good technological properties. The processes of nonradiative deactivation of the ${}^4\text{F}_{3/2}$ level in these glasses are relatively weak, which makes them comparable to crystals which are being searched for in order to create miniature lasers. The glass has the following characteristics: refractive index $n_c = 1.5807$, $n_F = 1.5904$; number of neodym-

ium ions per cubic centimeter 12.7×10^{20} ; absorption index $K_{586} \sim 1.63$, $K_{874} \sim 0.300$; stimulated-emission cross section (spectroscopic measurements) approximately $3 \times 10^{-20} \text{ cm}^2$; duration or luminescence attenuation approximately $110 \mu\text{sec}$; optical stress coefficient $1.4 \text{ nm cm kg}^{-1}$; nonactive absorption $K_{1.06} = 0.002 \text{ cm}^{-1}$. Under production conditions, a concentration series has been synthesized on the basis of the given glass with a neodymium concentration or 2, 3, 4, 5, 6, 8, 10, and $12.7 \text{ ions cm}^{-3}$.

The lasing experiments were preliminary in character and had as their purpose confirmation of the possibility of continuous-wave lasing in a small volume using glasses activated with neodymium. Continuous-wave lasing in the presence of longitudinal pumping by a Spectra-Physics 171-01 Kr laser was obtained for all samples of the concentration series of phosphate glasses, and likewise for silicate glass with a neodymium concentration of approximately $2.3 \times 10^{20} \text{ cm}^{-3}$. In order to reduce the overheating of the samples with light, the $0.752 \mu\text{m}$ radiation line was mainly used for pumping. The absorption coefficient, on this wavelength varied from 2.0 to 12.7 cm^{-1} depending on neodymium concentration. In accordance with this, the thickness of the samples for the lasing experiments was chosen to range from 0.5 to 3 mm. The resonator, which was formed by two plane mirrors that were pressed directly against the surfaces of the samples, was retuned for each investigated sample. The reflection coefficient of the mirrors at the wavelength $1.06 \mu\text{m}$ amounted to approximately 98 and 99.5%. The transmission of the mirrors at the pumping wavelength amounted to approximately 70%. The lasing which was obtained was highly directional with a divergence of the order of several degrees and was registered by means of an image converter as well as by a Spectra-Physics 404 power meter on the decaying section of its spectral-sensitivity curve.

For samples having a neodymium concentration $N = 8 \times 10^{20} \text{ cm}^{-3}$ and higher, lasing was obtained for pumping with an unfocused laser using a spot of approximately 1.5 mm on the sample. The lasing threshold and yield depended essentially on the tuning and were determined by the losses in the resonator. For samples having a lower concentration, the radiation from the pumping laser was focused by a lens up to approximately $300 \mu\text{m}$. The continuous-wave character of the lasing, which was preserved for several hours without any signs of deterioration, allowed the lasing spectrum to be recorded on a SDL-1 spectrometer.

Figure 4 shows the luminescence and lasing spectra of a sample having $N = 8 \times 10^{20} \text{ cm}^{-3}$. The positions and intensities of the narrow lines in the lasing spec-

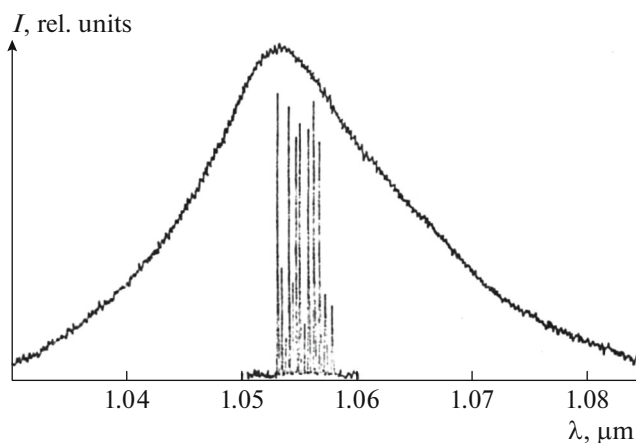


Fig. 4. Luminescence spectrum and lasing spectrum of phosphate glass having a Nd^{3+} concentration equal to $8 \times 10^{20} \text{ cm}^{-3}$.

trum turned out to be unstable in time as a consequence of the fluctuations of the resonator modes.

Thus, it has been demonstrated that continuous-wave lasing from Nd^{3+} on glasses in the presence of laser excitation may be obtained not only on high-concentration phosphate or tellurite glasses [7], but also on glasses having a low neodymium content, including silicate glasses, which have low stimulated-emission cross sections.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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