

PROGRESS IN LASER GLASSES ACTIVATED BY CHROMIUM

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Results of systematic investigations of spectral and kinetic properties of Cr^{3+} ions as well as energy transfer peculiarities for the $\text{Cr}^{3+} - \text{Nd}^{3+}$ and $\text{Cr}^{3+} - \text{Yb}^{3+} - \text{Er}^{3+}$ systems in a number of phosphate glasses are discussed in detail. The efficiency of using the chromium as a sensitizer of Nd^{3+} and Yb^{3+} ion emission has proved to be strong-dependent on glass composition. The direct correlation between the extent and intensity of long-wave wing of ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ chromium absorption band, on the one hand, and the rate of back-transfer processes on the other hand, is fixed. The essential improvement of emission efficiency of the lamp-pumped erbium laser based on new triple-activated phosphate glass is reported finally.

Recent achievements in the development of glass lasers with high average power^{1,2} showed that possibilities of laser glasses have not so far been exploited to the full. The promising direction of their further improvement is connected with using of trivalent chromium as a sensitizer of rare-earth emission. Similar attempts were made earlier³⁻⁵ but up to now they were unsuccessful. Of particular interest is the paper [5] whose authors report that one can achieve quantum efficiency of sensitization exceeding 50% at high concentration of Nd^{3+} ions in phosphate glasses. However, the authors have observed first the back transfer of excitation from Nd^{3+} to Cr^{3+} which cancels the advantages due to sensitization.

The present paper reports new results of systematic investigations of spectral and kinetic properties of chromium as well as nonradiative energy transfer processes in $\text{Cr}^{3+} - \text{Nd}^{3+}$ and $\text{Cr}^{3+} - \text{Yb}^{3+} - \text{Er}^{3+}$ systems in a number of phosphate glasses. The purpose of these investigations was to define mechanisms of energy loss at low and high excitation levels to reveal the ways of their diminution.

Base compositions of investigated glasses are given in Table 1. Rare-earths and chromium were introduced in required concentration substituting La. The glasses were prepared from reagents of 99.999% purity in platinum crucibles of 200ml in a nitrogen atmosphere. Special conditions were created to remove hydroxyl groups whose content was tested measuring infrared absorption at 2800 nm which did not exceed 1 cm^{-1} .

Table 1. Some spectral parameters of chromium doped phosphate glasses. The k_{max} , $k(890)$, and $k(975)$ are the absorption coefficients at the maximum (λ_{max}) of ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ band, 890 nm and 975 nm respectively. τ_e is a time of decay in 2.72 times from starting intensity. $\tau = \int I(t) t dt / \int I(t) dt$. $N_{\text{Cr}} = 1.10^{20} \text{ cm}^{-3}$.

NN	Glass	$\lambda_{\text{max}}, \text{nm}$	$k_{\text{max}}, \text{cm}^{-1}$	$k(890), \text{cm}^{-1}$	$k(975), \text{cm}^{-1}$	$\tau_e, 10^{-6} \text{ s}$	$\tau, 10^{-6} \text{ s}$
1	Na-La-phosphate	~660	9.75	0.017	0.005	5.3	19.2
2	Pb-La-phosphate	~660	10.0	0.04	0.02	4.1	16.5
3	Ba-Al-La-phosphate	~660	9.1	0.19	0.1	3.9	15.6

The results obtained are listed below.

(1). Fig. 1 shows the optical absorption spectra of Cr^{3+} ions in investigated glasses. These spectra are similar to Cr^{3+} spectra in glasses of other compositions reported and interpreted earlier.^{6,7} While accepting this interpretation, we nevertheless should remark that there are no visible changes in spectral location of maximum of three particular absorption bands of Cr^{3+} connected to vibrationally broadened

transitions ${}^4A_2 - {}^4T_2$; ${}^4A_2 - {}^4T_1(t_2e^2)$. More appreciable changes may be observed in relative intensity of transitions and their halfwidth. Apparently the later is determined by inhomogeneous broadening of bands which is the least in alkali glasses. Most important for further discussion are the extent and intensity of long-wave wing of ${}^4A_2 - {}^4T_2$ absorption band. These features are strongly dependent on glass composition. In Table 1 there are Cr^{3+} -absorption coefficients on wavelengths corresponding to maximum of Nd^{3+} and Yb^{3+} emission bands ($N_{Cr} = 10^{20} cm^{-3}$). The differences in these coefficients exceed 20 times in a number of investigated glasses. As it will be shown later, it is this difference that mainly determines whether a certain glass composition can serve as a host for activation by $Cr^{3+} - Nd^{3+}$, or $Cr^{3+} - Yb^{3+} - Er^{3+}$ systems.

(2). In Fig. 2 are given the decay curves of Cr^{3+} emission in the samples with low concentration of the activator ($10^{17} cm^{-3}$ or less). It allows to cancel the distortions due to $Cr^{3+} - Cr^{3+}$ interactions. The measurements were made in analog regime under the pulsed laser excitation ($\lambda = 532nm$, $\Delta t = 30ns$) using cooled photomultiplier and a boxcar integrator (time resolution - 100ns). The above luminescence decay curves turned out highly nonexponential, their appearance being slightly dependent on the wavelength of emission. However, it should be noted that the initial ($t \rightarrow 0$) decay rate of 4T_2 emission proved much less and the effective decay time (see Table 1) was greater than those reported by Avanesov et al.⁸ for Li-La-phosphate glass. On the other hand, the effective values of $\bar{\tau}$ are close to ones presented in [7]. It might be also noted that a trend has been towards the increase of decay rate in glasses with the greater intensity of the long-wave wing of ${}^4A_2 - {}^4T_2$ band.

(3). In Fig. 3 we demonstrate the efficiency dependence of Cr^{3+} emission concentration quenching on glass composition at 300K. In the glass with less intensive long-wave edge (composition 1) this quenching is much weaker and should be taken into account only for big concentrations of Cr^{3+} exceeding $(7-8) 10^{19} cm^{-3}$. Obviously, the differences in concentration quenching appearance are due to changes in an overlap of emission and absorption spectra of Cr^{3+} ions in glasses of various compositions. It gives rise to changes in the effective rates of the energy migration to the most quenched centers.

(4). Previously it was shown that the most dangerous quenchers of rare-earth emission were admixed hydroxyl groups. To examine their influence on Cr^{3+} emission, some samples were prepared for glass of composition 1 with hydroxyl concentration ranging from 10^{18} to $6 \cdot 10^{20} cm^{-3}$. However, at room temperature even at maximum OH^- concentration we failed to detect any visible changes in decay kinetics. Only at 4.2K a sharp decrease of the decay rate enables us to detect the weak quenching and to determine its parameters. The quenching was of electrical dipole-electrical dipole nature, and we obtained that $C_{da} = 10 nm^6 s^{-1}$, where $C_{da} = W_{da} R_0^6$ is the rate of pair interaction at a unit distance. So, for usual concentrations of hydroxyls in phosphate glasses not exceeding $1 \cdot 10^{20} cm^{-3}$ their influence can be neglected.

(5). In Figs. 4 and 5 are shown the efficiencies of Cr^{3+} -emission quenching by the Yb^{3+} and Nd^{3+} ions respectively. Judging by the relation of areas under decay curves, one may suppose that the quantum efficiency of sensitization η in both cases should exceed 0.9 at Nd^{3+} or Yb^{3+} concentration greater than $(6-8)wt\%$. However, the direct measurements of the η by the way of laser excitation of Cr^{3+} and Yb^{3+} or Nd^{3+} ions one after another and observation of relative intensities of acceptor's emission showed that η value does not exceed 60% in all cases. The understanding of this result is not clear up to date. The more careful investigations of the excitation transfer mechanisms have presumably helped in this question. Here we note only that we discovered a sufficiently strong dependence of decay kinetics on the emission wavelength in the presence of quenchers mentioned above. This dependence is particularly pronounced at low temperatures. The dependence of sensitization efficiency on glass composition was evaluated in terms of a relative decrease of area under decay curves at the same emission wavelength and appeared to be negligible.

(6). In Fig. 6 we indicate the back-quenching efficiency of Nd^{3+} and Yb^{3+} ions as a function of Cr^{3+} concentration in glasses of different composition. There is an essential difference between the appearance of these dependences for glasses of composition 1 and 3. In the former backquenching can be ruled out up to $N_{Cr} = 1 \times 10^{20} cm^{-3}$, but in the latter it becomes appreciable starting from $N_{Cr} = (2-3) \times 10^{19} cm^{-3}$, and for $N_{Cr} = 1 \times 10^{20} cm^{-3}$ it results in the reduction of Yb^{3+} emission duration up to 6 times. To define mechanisms and characteristics of ion-ion interaction, there were prepared samples with the very small Nd^{3+} and Yb^{3+} concentration (less than $10^{18} cm^{-3}$) and Cr^{3+} concentrations equal to $9 \cdot 10^{19} cm^{-3}$ and $1.78 \times 10^{20} cm^{-3}$. The analysis of the emission decay curves showed that the back transfer is due to dipole-dipole interactions. The parameters of these interactions are given in Table 2. Their comparison confirms the essential dependence

Table 2. Rates of interion energy transfer on unit distance for the systems of $Nd^{3+} \rightarrow Cr^{3+}$ and $Yb^{3+} \rightarrow Cr^{3+}$ in phosphate glasses.

Glass Number	1	2	3
$C_{da} (Nd \rightarrow Cr), 10^2 nm^6 s^{-1}$	<1.3	5-6	10-12
$C_{da} (Yb \rightarrow Cr), 10^2 nm^6 s^{-1}$	<0.1	0.5-0.8	1.2-1.6

of back quenching rate on the extent and the intensity of long-wave wing of ${}^4A_2 - {}^4T_2$ absorption band.

Thus, among the phosphate glasses there are compositions with sharply different characteristics of the emission back quenching in $\text{Cr}^{3+} - \text{Nd}^{3+}$ and $\text{Cr}^{3+} - \text{Yb}^{3+}$ systems.

(7). The mechanism of back quenching influence on the inverse energy accumulation and laser action in Nd^{3+} -glasses is obvious. For $\text{Cr}^{3+} - \text{Yb}^{3+} - \text{Er}^{3+}$ triple system this problem is more complicated because in erbium glasses relatively small additional quenching of Yb^{3+} , which may accompany the admixture of chromium in moderate concentration (less than $(5-8) \times 10^{19} \text{cm}^{-3}$), can not at first change essentially the quantum efficiency of $\text{Yb}^{3+} \rightarrow \text{Er}^{3+}$ sensitization. However, as we mentioned previously [10], $\text{Yb}^{3+} \rightarrow \text{Er}^{3+}$ energy transfer rate sharply diminishes with the energy accumulation. Thus, a competition between the Yb^{3+} emission quenching by Er^{3+} and Cr^{3+} ions may lead to the increasing influence of the latter process. The data given in Fig. 7 confirm this competition does exist. For example, in glass of composition 3 at $N_{\text{Cr}} = 4.10^{19} \text{cm}^{-3}$ one can observe an essential slowdown of the inverse energy accumulation at excitation levels exceeding $(0.3-0.4) N_{\text{Er}}$. On the contrary, in the glass of composition 2 the chromium influence can be neglected up to $N_{\text{Cr}} > 10^{20} \text{cm}^{-3}$.

(8). In conclusion, we present the results of comparative laser tests in free operation with the lamp pumping of $5 \times 85 \text{ mm}$ rods of Yb-Er glass LGS-E1 and new experimental laser glass, activated with $\text{Cr}^{3+} (5.1 \times 10^{19} \text{cm}^{-3}) - \text{Yb}^{3+} - \text{Er}^{3+} (3.5 \times 10^{19} \text{cm}^{-3})$. The rods were placed in a cylindrical quartz reflector with silver cover and were excited by xenon flash-tube ($\Delta t_p = 650 \mu\text{s}$). In the Fabry-Perot resonator with reflection from an output mirror about 40% we managed to reduce the threshold in about 2 times (up to 80 J) and to improve the performance in 2.6 times with the efficiency up to 1.3% under the excitation energy 500 J. It is not limited obviously because the optical quality and losses in new erbium glass were not good enough.

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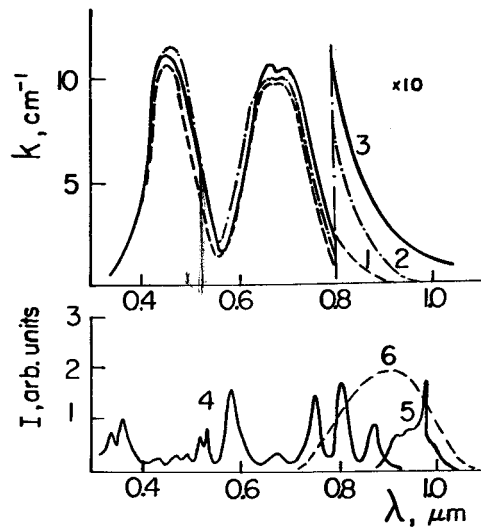


Fig. 1. Absorption spectra of Cr^{3+} ions (10^{20}cm^{-3}) in phosphate glasses of composition 1 (1), 2 (2), 3 (3) and typical absorption spectra of Nd^{3+} (4) and Yb^{3+} (5) compared with Cr^{3+} emission spectrum (6) in the glass of composition 3.

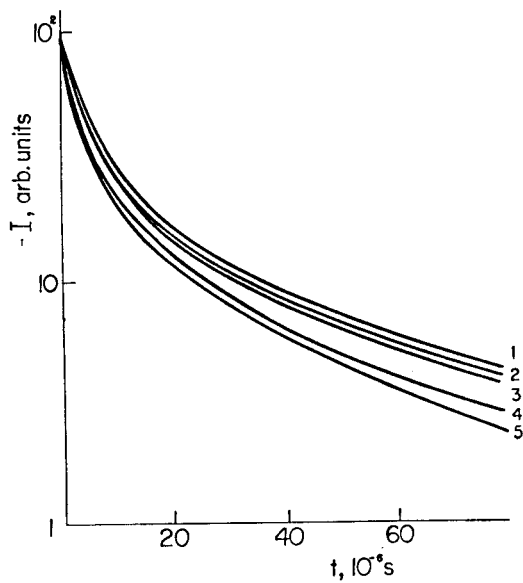


FIG. 2. Decay curves of Cr^{3+} emission ($N_{\text{Cr}} = 10^{17} \text{ cm}^{-3}$) in glasses of composition 1 ($\lambda = 750 \text{ nm}$ (1), 800 nm (2), 850 nm (3)) and compositions 2 (4) and 3 (5) at $\lambda = 800 \text{ nm}$.

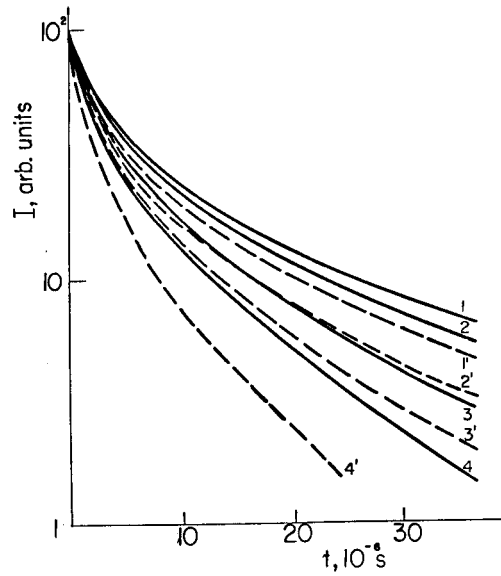


FIG. 3. Concentration quenching of Cr^{3+} emission in glasses of composition 1 ($N_{\text{Cr}} = 10^{17} \text{ cm}^{-3}$ (1), $5 \times 10^{19} \text{ cm}^{-3}$ (2), $1.5 \times 10^{20} \text{ cm}^{-3}$ (3), $2.5 \times 10^{20} \text{ cm}^{-3}$ (4)) and composition 3 ($N_{\text{Cr}} = 10^{17} \text{ cm}^{-3}$ (1'), $5 \times 10^{19} \text{ cm}^{-3}$ (2'), $1.4 \times 10^{20} \text{ cm}^{-3}$ (3'), $3.4 \times 10^{20} \text{ cm}^{-3}$ (4')).

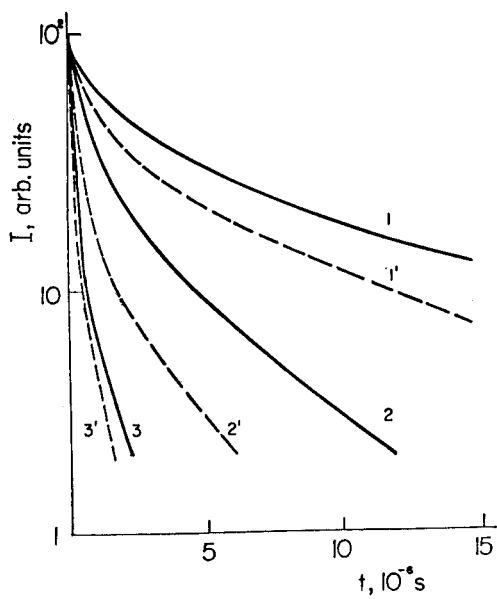


FIG. 4. Cr^{3+} -emission quenching by Yb^{3+} -ions in glass of composition 1 ($N_{\text{Cr}} = 3.2 \times 10^{19}$, $N_{\text{Yb}} = 0$ (1), 3.6×10^{20} (2), $1.3 \times 10^{20} \text{ cm}^{-3}$ (3)) and in glass of composition 2 ($N_{\text{Cr}} = 3.2 \times 10^{19}$, $N_{\text{Yb}} = 0$ (1'), 9×10^{20} (2'), $1.48 \times 10^{20} \text{ cm}^{-3}$ (3')).

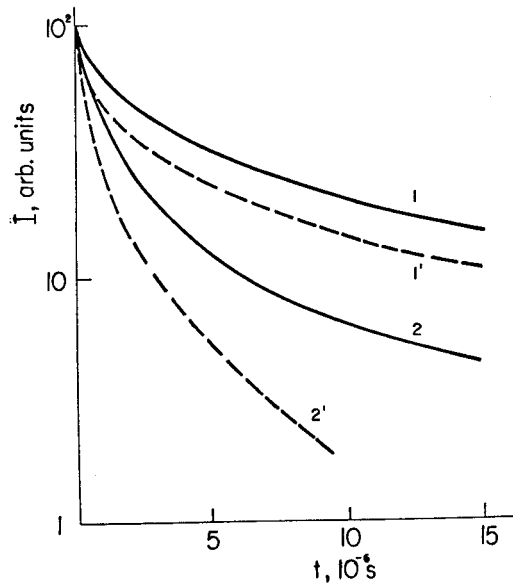


FIG. 5. Cr^{3+} -emission quenching by Nd^{3+} -ions in glass of composition 1 ($N_{\text{Cr}} = 3.2 \times 10^{19}$, $N_{\text{Nd}} = 0$ (1), $2.2 \times 10^{20} \text{ cm}^{-3}$ (2)) and in glass of composition 2 ($N_{\text{Cr}} = 3.2 \times 10^{19}$, $N_{\text{Nd}} = 0$ (1'), $5.2 \times 10^{20} \text{ cm}^{-3}$ (2')).

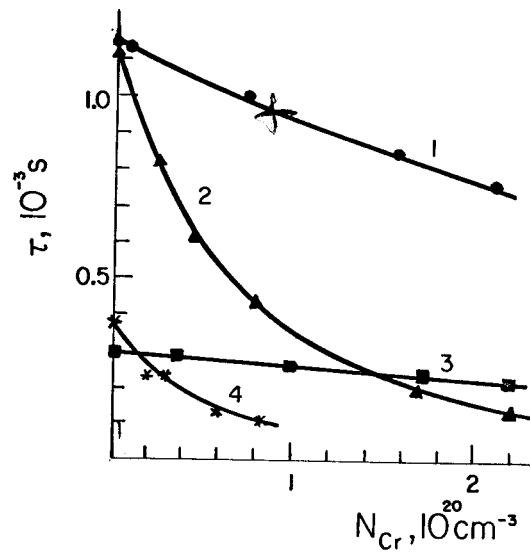


FIG.6. Back-quenching efficiency of Yb^{3+} ($1.2 \times 10^{21} \text{ cm}^{-3}$) and Nd^{3+} ($2.2 \times 10^{20} \text{ cm}^{-3}$) as a function of Cr^{3+} concentration in glasses of composition 1 (curves 1 and 3 respectively) and composition 3 (curves 2 and 4 respectively).

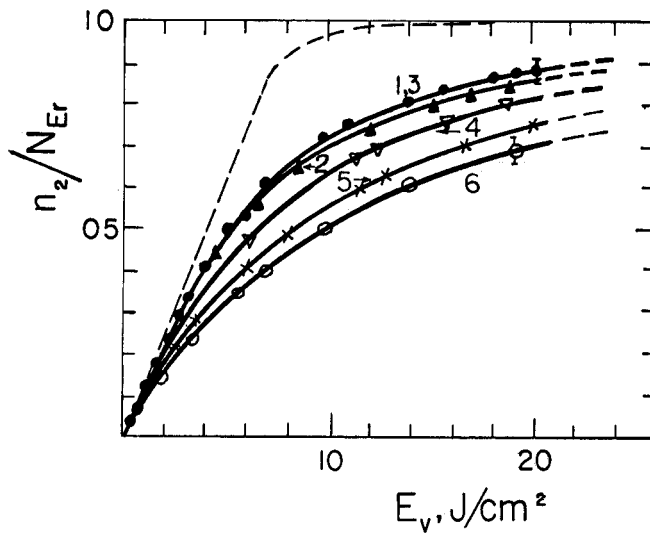


FIG.7. Relative metastable state population of Er^{3+} ions ($3.8 \times 10^{19} \text{ cm}^{-3}$) versus specific absorbed energy for glasses of composition 1 ($N_{\text{Cr}} = 1.7 \times 10^{19}$, $N_{\text{Yb}} = 1.2 \times 10^{21} \text{ cm}^{-3}$) (1); $N_{\text{Cr}} = 6.4 \times 10^{19}$, $N_{\text{Yb}} = 1.2 \times 10^{21} \text{ cm}^{-3}$ (2), and composition 3 ($N_{\text{Cr}} = 0$, $N_{\text{Yb}} = 1.3 \times 10^{21} \text{ cm}^{-3}$) (3); $N_{\text{Cr}} = 3.9 \times 10^{19}$, $N_{\text{Yb}} = 1.2 \times 10^{21} \text{ cm}^{-3}$ (4); $N_{\text{Cr}} = 5.1 \times 10^{19}$, $N_{\text{Yb}} = 1.52 \times 10^{21} \text{ cm}^{-3}$ (5); $N_{\text{Cr}} = 10.6 \times 10^{19}$, $N_{\text{Yb}} = 1.2 \times 10^{21} \text{ cm}^{-3}$ (6). The curve 7 is calculated for $\bar{w} \propto (N_{\text{Er}} - n_2)$.