Temperature-dependent stimulated-emission cross section and concentration quenching in Nd^{3+}-doped phosphate glasses

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Measurements are reported of the spectroscopic properties of phosphate glasses doped with 3-, 5-, and 10-wt. % Nd^{3+} in the temperature range 70–300 K. The stimulated-emission cross sections of these glasses were determined by use of the Füchtbauer–Ladenburg formula at each temperature. The absorption spectra at room temperature were used to calculate the ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ stimulated-emission cross section and the ${}^4F_{3/2}$ radiative lifetime according to Judd–Ofelt theory. Good agreement was obtained between measured and calculated stimulated-emission cross sections at room temperature. As the temperature decreased, the emission cross section increased while the emission lifetime remained constant for all the samples. The temperature dependences of the stimulated-emission cross sections for the differently doped glasses are in good agreement with earlier predictions. © 2004 Optical Society of America

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1. INTRODUCTION

Neodymium-doped phosphate glasses are of interest for use in high-energy and high-peak-power laser systems.[1–3] There are a number of characteristics that distinguish glass from other solid-state laser host materials: Its properties are isotropic. It can be doped with high concentrations with excellent uniformity, and it can be made in large pieces that have diffraction-limited optical quality.[4] In addition, glass lasers have been made, in a variety of shapes and sizes, from fibers a few micrometers wide that support only a single dielectric waveguide mode, to rods 2 m long and 7.5 cm in diameter and disks as much as 90 cm in diameter and 5 cm thick. Energy can be efficiently stored and extracted from these glasses,[5,6] and high-energy storage densities can be achieved.[2,5] The thermal conductivity of glass is considerably lower than that of most crystal hosts, and the emission lines of Nd^{3+} in glasses are inherently broader than in crystals. However, a broader emission feature makes possible obtaining and amplifying shorter light pulses and permits storage of large amounts of energy in the amplifying medium.

In this paper we present evidence of the dependence on temperature of stimulated-emission cross sections of Nd^{3+} doped into phosphate glasses at different concentrations. We also report on concentration quenching in these materials.

2. EXPERIMENTS

Phosphate glasses were prepared by a semicontinuous melting technique. The compositions examined belong to the P_2O_5–Al_2O_3–BaO–K_2O–Li_2O–Nb_2O_5–La_2O_3 system and were doped with Nd_2O_3 to concentrations of 3, 5, and 10 wt. % Nd^{3+}. Phosphate glasses were melted at 1500–1600 K in a platinum crucible in air and then poured onto a stainless plate and cooled to room temperature. Finally, the samples were polished to produce 1-mm-thick samples for optical measurements.

The room-temperature absorption spectra were measured with a Cary 500 Scan UV-Vis-NIR spectrophotometer. Emission spectra were measured at 850–1100 nm with a fiber-coupled diode laser operating at 804 nm as the excitation source. Nd^{3+} ions were pumped into their ${}^4F_{3/2}$ states, from which they relaxed to the ground ${}^4I_{11/2}$ manifold. The excitation signal was monitored during the experiment with a silicon detector. An indium gallium arsenide (InGaAs) detector located at the output slit of a 25-cm focal-length Jarell-Ash monochromator was used to detect the fluorescence emission intensity. With 50-μm slits the resolution of this detection system was ~0.4 nm. Before their use in calculating the stimulated-emission cross section, the recorded spectra were corrected for the spectral response of the detector and of the monochromator grating. We achieved calibration of the detection system by recording its response to the light from a tungsten–iodine white-light source that had been calibrated at the National Institute for Standards and Testing.

The emission lifetime measurements employed excitation from a tunable optical parametric oscillator (e.g., Quanta Ray Model MOPO-SL) set such that the idler wavelength was 804 nm that was itself pumped by the third harmonic of a *Q*-switched Nd:YAG laser. The opti-

cal parametric oscillator's linewidth was ~0.2 cm^{-1}, and its pulse duration was ~5 ns. The energy of the idler pulse at 804 nm was <2 mJ. Fluorescence was collected with a 5-cm focal-length lens and spectrally dispersed with the monochromator. An InGaAs photodiode connected to a preamplifier was used to detect the pulse excited fluorescence and to monitor its decay with time. Decay curves were recorded with a Tektronix 2440 500-Ms/s digital oscilloscope and a computer-controlled data acquisition system. The emission spectra and lifetime measurements were carried out at temperatures from 70 to 300 K in a temperature-controlled compressed-helium cryostat.

3. RESULTS AND DISCUSSION

Room-temperature absorption spectra of the Nd^{3+}-doped phosphate glasses studied are shown in Fig. 1. All the absorption band shapes and their wavelengths were found to be the same, except for differences in the measured absorption strengths that resulted from the various Nd^{3+} concentrations. Because of inhomogeneous broadening in glasses, the Stark structure is poorly resolved. Adjacent energy levels often overlap and appear as one in the spectrum.

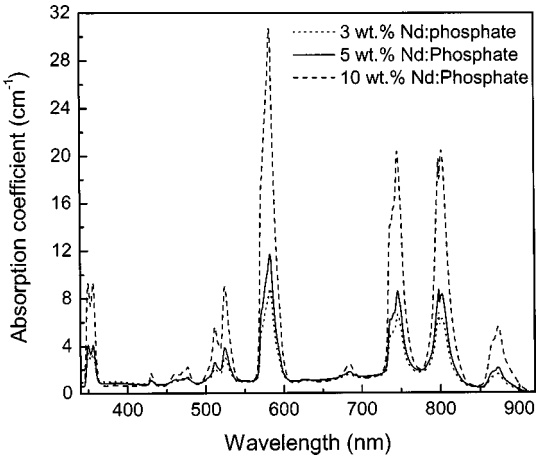

Fig. 1. Absorption spectra of Nd^{3+}-doped phosphate glasses at room temperature.

Table 1. Measured Line Strengths of Nd:Phosphate Glasses with Different Nd^{3+} Concentrations

		Line Strength ($\times 10^{-20}$ cm^2)		
λ (nm)	Excited State	3 wt. %	5 wt. %	10 wt. %
873	$^4F_{3/2}$	0.789	0.861	1.093
802	$^2H_{9/2}$, $^4F_{5/2}$	3.564	3.728	3.876
746	$^4S_{3/2}$, $^4F_{7/2}$	3.621	3.607	3.808
684	$^4F_{9/2}$	1.050	1.003	0.652
583	$^2G_{7/2}$, $^4G_{5/2}$	5.222	5.434	6.638
524	$^4G_{9/2}$, $^4G_{7/2}$, $^2K_{13/2}$	2.667	2.522	2.242
476	$^2G_{9/2}$, $^2D_{3/2}$, $^4G_{11/2}$, $^2K_{15/2}$	1.484	1.293	0.881
430	$^2P_{1/2}$, $^2D_{5/2}$	0.421	0.379	0.240
355	$^4D_{1/2}$, $^4D_{3/2}$, $^4D_{5/2}$, $^2I_{11/2}$	2.285	2.070	2.184

Table 2. Room-Temperature Emission Properties of Nd^{3+} in Phosphate with Various Nd^{3+} Concentrations

Sample	λ (nm)	Δλ (nm)	τ_R (μs)	τ_{exp} (μs)
3-wt. % Nd	1052.8	23.4	332	300
5-wt. % Nd	1052.8	24.3	336	280
10-wt. % Nd	1053.4	25.7	326	160

Table 3. Calculated Judd–Ofelt Parameters for the Nd:Phosphate Glasses in Table 2

	Nd Concentration (wt. %)		
Parameter	3	5	10
Ω_2 (10^{-20} cm^2)	2.471	2.857	3.983
Ω_4 (10^{-20} cm^2)	4.245	3.940	4.073
Ω_6 (10^{-20} cm^2)	5.295	5.438	5.632
$Q = \Omega_4/\Omega_6$	0.802	0.724	0.723
n	1.57	1.57	1.57
N_0 (10^{20} ions/cm^3)	4.286	5.357	10.714

Table 4. Calculated Branching Ratios of the Fluorescence Transitions to the Lower-Lying Manifold of Nd^{3+} Ion in the Phosphate Glasses in Table 2

	Branching Ratio, β (%)		
$^4F_{3/2}$ to	3 wt. %	5 wt. %	10 wt. %
$^4I_{15/2}$	0.5	0.6	0.6
$^4I_{13/2}$	8.9	10.5	10.5
$^4I_{11/2}$	49.7	50.3	50.5
$^4I_{9/2}$	40.9	38.6	38.4

We used the measured absorption spectra from Fig. 1 in Eq. (1) of Ref. 7 to find the oscillator strength of each line, and the resultant values are given in Table 1 for each glass studied. We also used these data to calculate the radiative lifetime of the $^4F_{3/2}$ excited state (see Table 2) according to Judd–Ofelt theory[8,9] (the calculated Judd–Ofelt parameters for the glasses considered are listed in Table 3) and the branching ratios of the fluorescence transitions to the lower-lying ^4I_J (J = 15/2, 13/2, 11/2, 9/2) manifold (Table 4).

The radiative lifetimes determined from Judd–Ofelt theory and listed in Table 2 are nearly the same for the several Nd^{3+} concentrations in phosphate glass, i.e., ~332 μs. The fluorescent decay of each sample studied was found experimentally to be given by a nearly single exponential function at all temperatures and concentrations. This behavior is demonstrated in Fig. 2, where the decay is plotted logarithmically for each sample at room temperature. When this type of data was fitted with an exponential decay function the measured room-temperature lifetimes were found to be 300, 280, and 160 μs for the 3-, 5-, and 10-wt. % samples, respectively. The measured lifetime for 3-wt. % Nd-doped phosphate glass is in good agreement with the Judd–Ofelt model predic-

tion. However, concentration quenching caused by cross relaxation and energy migration results in shorter measured lifetimes than predicted for the higher-Nd-concentration glasses. The observed concentration quenching effect is in good agreement with published values for LG-760 phosphate laser glass manufactured by Schott Glass Technologies, Inc.

The variation of the measured lifetimes with concentration is related to the nonradiative Nd–Nd relaxation processes through the relation

$$\tau_{\mathrm{exp}}{}^{-1} = \tau_R{}^{-1} + W_{\mathrm{Nd-Nd}}$$

where τ_{exp} is the measured fluorescence lifetime, τ_R is the radiative lifetime of Nd^{3+} ions in phosphate glass, and $W_{\mathrm{Nd-Nd}}$ is the probability of nonradiative Nd–Nd concentration quenching. From our data we found $W_{\mathrm{Nd-Nd}}$ for 3-, 5-, and 10-wt. % Nd:phosphate glasses to be 321, 559, and 3238 s^{-1}, respectively.

The measured fluorescence lifetimes are plotted in Fig. 3 versus temperature for each concentration, where it is clear that they are nearly independent of temperature.

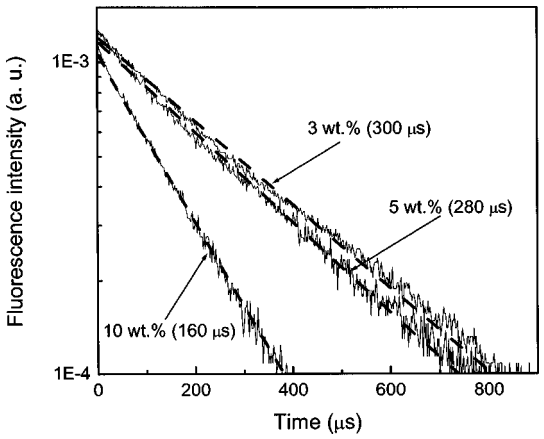

Fig. 2. Emission signal detected at 1.053 μm after excitation by a 5-ns pulse at 804 nm at room temperature for three concentrations of Nd^{3+} phosphate glasses. The experimental data are represented by the thin jagged curves. Exponential decays with lifetimes of 300, 280, and 160 μs for three samples are also plotted (thick dashed curves).

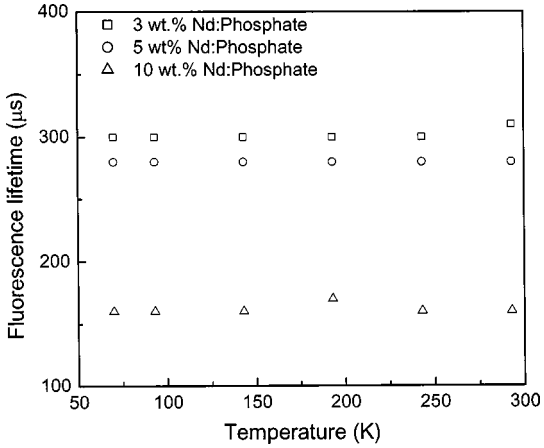

Fig. 3. Variation of the fluorescence lifetime of Nd:phosphate glasses with temperature.

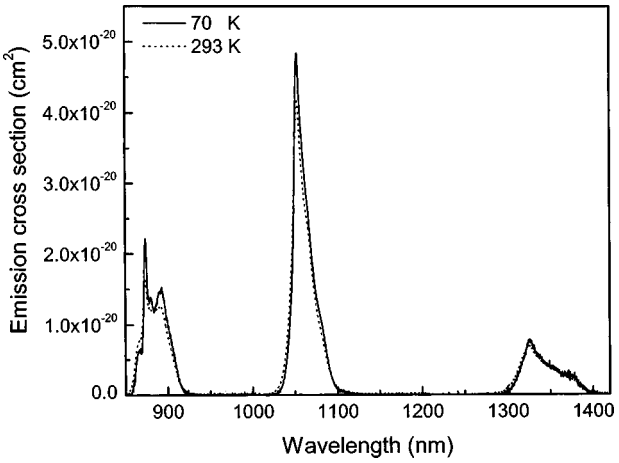

Fig. 4. Stimulated-emission cross section of 3% Nd^{3+} in phosphate glass as a function of wavelength at room temperature (293 K) and near liquid-nitrogen temperature (70 K).

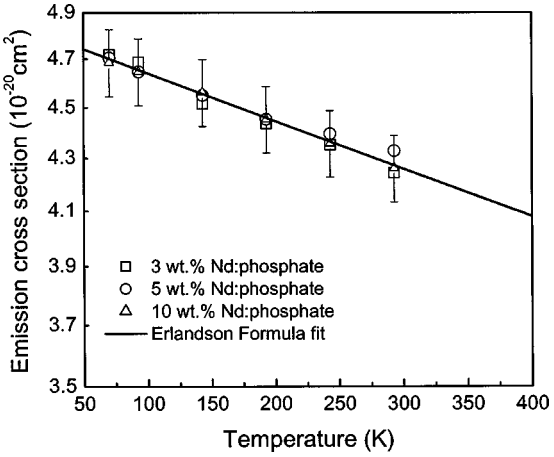

Fig. 5. Logarithm of the stimulated-emission cross section versus temperature for differently doped glasses. The data are indicated, and the straight line is the model of Erlandson *et al.* from Ref. 11.

However, the measured lifetime decreases with increasing concentration, as just discussed. The lifetime of the $^4F_{3/2}$ state of Nd^{3+} ions in phosphate glass should be governed by the sum of probabilities for several competing processes such as radiative decay, nonradiative decay by multiphonon emission, and energy transfer to other Nd^{3+} ions. Judd–Ofelt analysis allows us to assume that the purely radiative lifetime, τ_R, of the $^4F_{3/2}$ state is independent of Nd^{3+} concentration, as shown in Table 2. Comparing the lifetimes calculated by the Judd–Ofelt theory with those that we measured shows that the measured lifetime of 3-wt. % Nd^{3+}-doped phosphate glass is close to that calculated for the radiative lifetime. As a result, we use this measured value as the radiative lifetime with which to calculate the stimulated-emission cross section at different temperatures for all three samples by use of the Fuchtbauer–Ladenburg formula[10]

$$\sigma_{\mathrm{em}}(\lambda) = \frac{1}{8\pi}\frac{\lambda^5}{n^2 c\tau}\frac{I(\lambda)}{\int I(\lambda)\lambda\,\mathrm{d}\lambda}, \qquad (1)$$

where τ is the radiative lifetime of the upper laser level; c is the speed of light in vacuum; n is the refractive index at the emission wavelength, ~1.57; and $I(\lambda)$ is the corrected emission spectral intensity as a function of wavelength. Figure 4 shows the stimulated-emission cross section for the 3% Nd^{3+}-doped phosphate glass at both room and liquid-nitrogen temperatures obtained from our data and from the Fuchtbauer–Ladenburg formula.

The variation with temperature of the stimulated-emission cross section of the Nd:phosphate glasses studied here and calculated from our data and Eq. (1) is given in Fig. 5. The results show that the stimulated-emission cross section is nearly independent of Nd^{3+} concentration. The dependence of the emission cross section on the temperature will have a significant effect on the laser performance of Nd:phosphate glass–based high-power solid-state laser systems. Erlandson *et al.*[11] predicted the variation of the stimulated-emission cross section of Nd:phosphate glasses with temperature as

$$\sigma_{32}(T) = \sigma_{32}(T_0)\exp[b'(T_0 - T)], \qquad (2)$$

where T_0 is the temperature at which the stimulated-emission cross section, $\sigma_{32}(T_0)$, is known or measured; here $T_0 = 295\,\mathrm{K}$. They measured the stimulated-emission cross sections of Nd:phosphate glasses at temperatures in the range of 288–365 K. Our results extend theirs to the temperature range 70–400 K. As shown in Fig. 5, our temperature-dependent stimulated-emission cross section data give $b' = 4.3 \times 10^{-4}\,\mathrm{K}^{-1}$ for the Nd:phosphate glasses studied.

4. CONCLUSIONS

The emission spectra and lifetime of Nd^{3+}-doped phosphate glasses were measured in the temperature range 70–300 K. The results show that the measured emission lifetime of Nd^{3+}-doped phosphate glass is independent of temperature, though it decreases with Nd^{3+} concentration as a result of concentration quenching. Increasing temperature causes the emission cross sections of Nd^{3+}-doped phosphate glasses to decrease. The calculated radiative lifetime and stimulated-emission cross section are in agreement with our measured results at room temperature. Further, the measured temperature-dependent stimulated-emission cross sections of the Nd:phosphate glasses studied are in a good agreement with the prediction from Erlandson's temperature-dependent model for the stimulated-emission cross section. It is now possible to use Erlandson's model to predict the stimulated-emission cross sections from liquid-nitrogen temperature to 365 K and above. These results should be useful in designing high-power and high-energy Nd:phosphate glass lasers.

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