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Frequency upconversion of orange light into blue light in Pr^{3+}-doped fluoroindate glasses

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Excitation of the transition $^3H_4 \rightarrow {}^1D_2$ in a Pr^{3+}-doped fluoroindate glass at ~588 nm results in efficient blue emission at ~480 nm which is ascribed to the $^3P_0 \rightarrow {}^3H_4$. The upconversion process is due to an energy transfer involving a pair of Pr^{3+} ions. The dynamical behavior of the anti-Stokes emission is described using a rate-equation model which allows one to obtain the energy-transfer rates involving the pair states which contribute to the upconversion process.

I. INTRODUCTION

Laser spectroscopic studies of energy transfer involving rare-earth (RE) ions in solids have helped to establish a broad understanding of these processes. Among the several phenomena already investigated, the cooperative energy transfer between ions in pairs or larger aggregates has been demonstrated in a large number of compounds.[1] This is a multipolar interaction through which a number of ions de-excite simultaneously and transfer the released energy to a nearby ion which is promoted to an excited state of high energy. Subsequent emission from that higher excited state produces photons with higher energy than the energy of the absorbed photons (anti-Stokes emission). This effect, known as a frequency upconversion, is attracting a great interest because of the possibility of fluoride-crystal-based upconversion lasers.[2] Recently, fluoride glasses became available with large upconversion efficiencies and fluorozirconate fiber lasers have been reported.[3]

Fluoroindate glasses are now emerging as a promising group of halide glasses for optical amplifiers and also for fibers lasers.[4–6] These glasses present higher transparency in the mid-infrared range (up to 8 μm) compared to fluorozirconate glasses and are more stable against atmospheric moisture. Studies of their optical properties in the visible region have also attracted attention since rare-earth ions can be easily incorporated in these compounds. It is now well established that the nonradiative relaxation rates of dopant ions levels in fluoroindate glasses are small due to their smaller phonon energies in comparison with other fluoride-based glasses.[7–11]

In this paper we report frequency upconversion studies in fluoroindate glasses doped with Pr^{3+}. The generation of anti-Stokes fluorescence ($^3P_0 \rightarrow {}^3H_4$) excited via the $^3H_4 \rightarrow {}^1D_2$ transition is studied. The phenomenon, which corresponds to a two-ion cooperative energy-transfer process involving Pr^{3+} ions, is described by $^1D_2 + {}^1D_2 \rightarrow {}^3P_0 + {}^1G_4 + \text{phonons} \rightarrow {}^3P_0 + {}^3H_4 + \text{phonons}$.

The energy transfer is followed by blue emission corresponding to the transition from level $^3P_0$ to the ground state. The observation of this kind of process in $LaF_3:Pr^{3+}$ was due to Zalucha, Wright, Fong;[12] afterwards it was extensively studied by other groups in a variety of crystalline systems.[13–18] The effect was also investigated in borate glasses[19] and more recently in silica-based fibers doped with Pr^{3+}.[20]

Here we exploit the upconversion effect as a spectroscopical probe to investigate some characteristics of Pr^{3+}-doped in the fluoroindate matrix. In particular, the dynamics of the upconverted fluorescence is studied to evaluate upconversion transfer rates.

II. EXPERIMENTAL

The glass samples studied have the following compositions: (mol. %) (39-x)InF_3-20 ZnF_3-16BaF_2-20SrF_2-2GdF_3-2NaF-1GaF_3-$x$$PrF_3$ ($x=0.05$; 0.1; 0.2; 1; 2).

InF_3 was obtained by fluoration of In_2O_3 at 400 °C with NH_4F and HF in a platinum crucible. Then, all the fluoride components were mixed and heated in a dry box under argon atmosphere at 700 °C for melting and 800 °C for fining. After the fining process the melt was poured and cooled into a preheated brass mold. The obtained samples have a good optical quality and are nonhygroscopic. Previous studies with this material have been reported recently.[4,7,9–11]

The excitation within the $^1D_2$ band of Pr^{3+} was achieved with a Nd:YAG pumped dye laser which produces 8-ns pulses of ~20 kW (linewidth of ~0.5 cm^{-1}).

The linearly polarized excitation beam was focused into the sample with a 15-cm focal length lens and the emitted fluorescence was collected along a direction perpendicular to the incident beam. The signal was analyzed in a 0.5-m spectrometer equipped with a photomultiplier tube.

Optical-absorption measurements were made with a double-beam spectrophotometer. For all measurements the spectra resolution was much greater than the observed linewidths. All the data was taken at room temperature.

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III. RESULTS AND DISCUSSION

Figure 1 shows the absorption spectrum in the visible range, obtained with the $x=0.2$ sample. The broad features of several Angstroms bandwidth can be easily identified with transitions from the ground state ($^3H_4$) to the excited states of the Pr^{3+} ion. The bands positions and the relative intensities observed agree with previous reports on Pr^{3+} ions in other fluoride hosts.[21,22] The large bandwidths result from the site-to-site variation of the crystalline-field strength. The spectra obtained for the other studied samples are similar, except for the bands intensities and their linewidths which are dependent on the Pr^{3+} concentration. No changes in the wavelengths of maxima were observed. This is because the absorption bands are due to electronic transitions within the $4f$ shell which is not very sensitive to the crystalline field.

Figure 2 shows the upconverted fluorescence spectrum obtained for one of the samples. The band peaking at ~ 480 nm (transition $^3P_0 \rightarrow {}^3H_4$) was obtained by exciting the $^3H_4 \rightarrow {}^1D_2$ transition at 588 nm. The small feature centered around 468-nm corresponds to transition $({}^3P_1, {}^1I_6) \rightarrow {}^3H_4$. Similar spectra was observed when exciting with the laser wavelength tuned from 586 to 590 nm.

The intensity of the upconverted fluorescence exhibits a quadratic dependence with the Pr^{3+} concentration and with the laser intensity. This behavior indicates that two Pr^{3+} ions and two incident photons participate in the process which generates each photon of the upconverted fluorescence signal. The results are explained according to the following process: A pair of neighboring Pr^{3+} ions are both excited to the $^1D_2$ state by the laser pulse. Then cross relaxation takes place and the energy stored in the two ions is redistributed inside the pair in such way that one of the ions is promoted to the $^3P_2$ state; afterwards a blue fluorescence is observed to arise from the $^3P_0$ state.[13–18] A fraction of the energy stored in the pair is dissipated by emission of phonons.

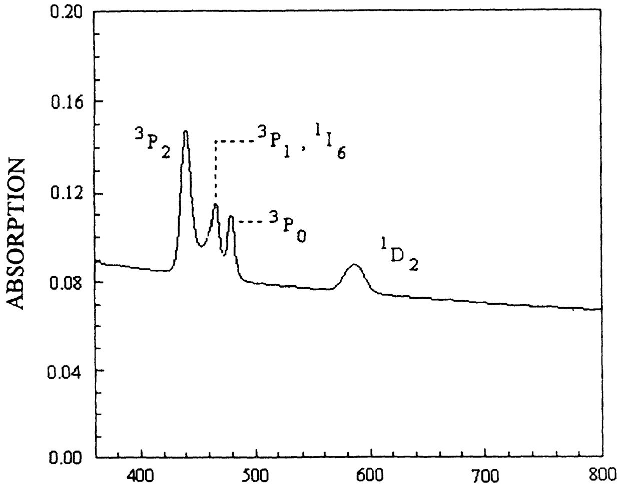

FIG. 1. Absorption spectrum of Pr^{3+} in fluoroindate glass at room temperature (sample with $x=0.2$).

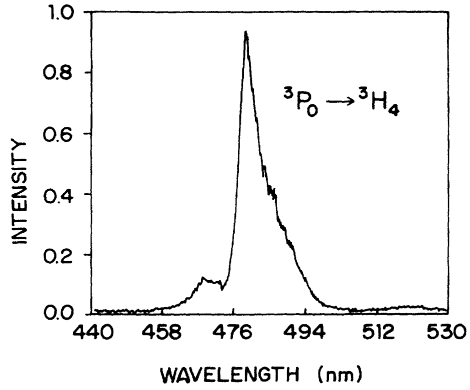

FIG. 2. Fluorescence spectrum corresponds to the transition $^3P_0 \rightarrow {}^3H_4$. The excitation wavelength was in resonance with the transition $^3H_4 \rightarrow {}^1D_2$. (Sample with $x=0.2$).

The temporal evolution of the blue emission is illustrated in Fig. 3 for the studied samples. As can be seen a similar behavior is observed for all samples, with rise and decay times which are Pr^{3+} concentration dependent. The solid lines represent the fitting to the expression $(e^{-t/\tau_d} - e^{-t/\tau_r})$ for each sample where τ_r and τ_d represent the rise and decay times of the upconverted fluorescence, respectively. The values obtained for τ_r and τ_d are shown in Table I. Their dependence with the Pr^{3+} concentration is due to energy transfer among the excited ions and their neighbors.[23]

The dynamical behavior of the anti-Stokes intensity signal can be derived from rate equations for the populations of the pair states involved in the process. The temporal evolution after excitation of the populations of the initial state of the pair (that is, the pair state directly pumped by the laser) and of its final fluorescent state (one ion in the $^3P_0$ state and another ion in the ground state) can be described by

$$\dot{n}_1 = -[W_{12}(x) + \gamma_1(x)]n_1 , \quad (1)$$

$$\dot{n}_2 = -\gamma_2(x)n_2 + W_{12}(x)n_1 , \quad (2)$$

when n_1 and n_2 are the populations of the pair states $|1\rangle = |{}^1D_2, {}^1D_2\rangle$ and $|2\rangle = |{}^3P_0, {}^3H_4\rangle$, respectively. $\gamma_1(x)$ represents the relaxation of state $|1\rangle$ due to all possible mechanisms except the transfer to state $|2\rangle$. $W_{12}(x)$ is the energy-transfer rate from state $|1\rangle$ to state $|2\rangle$, and $\gamma_2(x)$ is the total radiative relaxation rate from the state

TABLE I. Observed rise and decay times of the blue fluorescence $^3P_0 \rightarrow {}^3H_4$ for all studied samples.

x	τ_r (μs)	τ_d (μs)
0.05	17	224
0.1	17	193
0.2	16	126
1.0	4	50
2.0	1	22

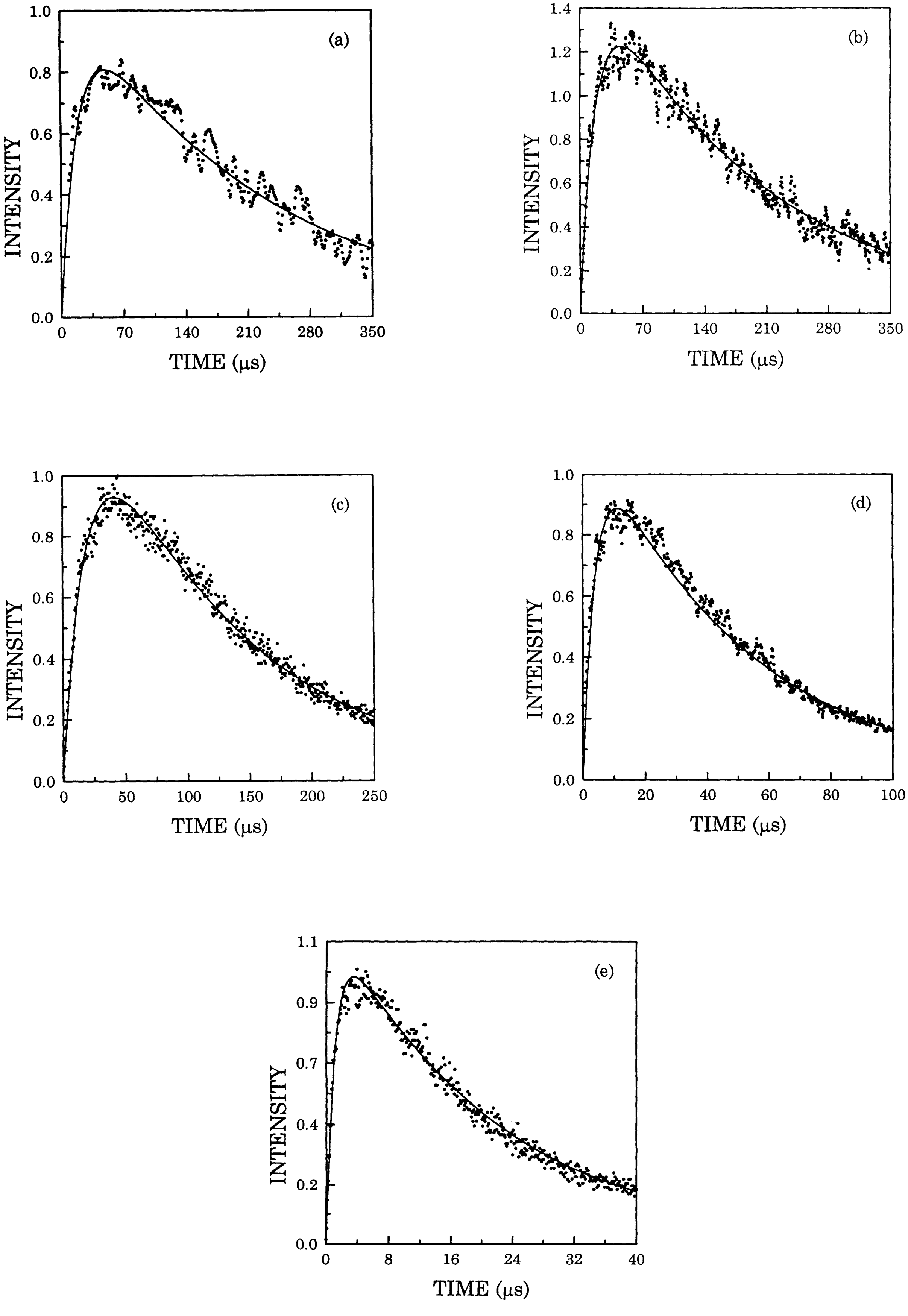

FIG. 3. Time evolution of the upconverted fluorescence: (a) $x=0.05$; (b) $x=0.1$; (c) $x=0.2$; (d) $x=1$; (e) $x=2$.

$|2\rangle$. The solutions for these equations are

$$n_1(t)=n_1(0)e^{-(W_{12}+\gamma_1)t} , \tag{3}$$

$$n_2(t)=\frac{n_1(0)W_{12}}{W_{12}+\gamma_1-\gamma_2}(e^{-\gamma_2 t}-e^{-(W_{12}+\gamma_1)t}) . \tag{4}$$

To compare with the measured rise and decay time we first note that τ_r^{-1} is the larger of the two rates (γ_1+W_{12}) and γ_2; τ_d^{-1} corresponds to the smaller rate.

Therefore, for long times, the fluorescence signal decays with an exponential decay time equal to τ_d and we have observed decay times which are about one order of magnitude longer than the lifetime of the $^3P_0$ state. Consequently, τ_d^{-1} must be identified with $(W_{12}+\gamma_1)$ and τ_r^{-1} is equal to γ_2. It is interesting to note that $(W_{12}+\gamma_1)$ is higher than $2\tau_D^{-1}$ [τ_D is the lifetime of state $^1D_2$ determined by resonance fluorescence measurements for isolated ions, $\tau_D=460$ μs (Ref. 23)]. This is a reasonable result since the decay rate of a pair state $|m\rangle=|i,j\rangle$ is determined by the relation $\gamma_m=\gamma_i+\gamma_j+W_T(i,j)$, where γ_i and γ_j are the ions relaxation rates and $W_T(i,j)$ is the total probability of transfer between the ions in the states i and j. The determination of $W_T(i,j)$ is only possible when $W_T(i,g)$ and $W_T(j,g)$ (g designates the ground state) are negligible compared to γ_i, γ_j and $W_T(i,j)$.[18] For example, in the specific case of state $|{}^1D_2,{}^1D_2\rangle$ resonant fluorescence measurements cannot provide reliable values to derive W_{12} and γ_1 because the τ_D value obtained in those experiments corresponds to isolated atoms. Moreover, the value of W_T $({}^1D_2,{}^3H_4)$ may be affected by the excitation power density.

It is important to emphasize that we do not expect that multiphonon processes give an important contribution to the lifetime of levels $^1D_2$ and $^3P_0$. As has been shown before[21,24] multiphonon decay rates exhibit an exponential dependence on the energy gap. In the present case, the energy difference between the centers of the $^3P_0$ and $^1D_2$ is $\Delta E\sim 3800$ cm^{-1}, while for the bands $^1D_2$ and $^1G_4$ we have $\Delta E\approx 6800$ cm^{-1}. Those energy gaps correspond to a large number of high-energy phonons and the corresponding decay rates are negligible in comparison with the values calculated from Table I.

Finally, it is worthwhile to note that the large efficiency observed for upconversion generation in the fluoroindate glasses deserves further investigation which is beyond the scope of the present work. In fact, considering a density of 5 g/cm^3 (Ref. 8) results in a distance of $\sim$39 Å between Pr^{3+} ions for a sample with 0.2 mol. %. On the other hand, the Forster's critical transfer distance[25] for two rare-earth ions is $\approx$20 Å. Therefore the large efficiency observed suggests clustering of the RE ions as proposed in Ref. 26 for other fluoride glasses. However more investigations are necessary to elucidate this point.

IV. CONCLUSION

Efficient blue upconversion was observed under excitation with an orange laser beam resonant with the $^3H_4\rightarrow{}^1D_2$ transition of Pr^{3+}. Fluorescence transients were investigated and their rise and decay times were fitted by a model which considers the energy transfer inside a pair of Pr^{3+} ions as the dominant mechanism for generation of the upconverted signal. The present results show the large potential of fluoroindate glasses to be used as efficient hosts for upconversion generation.

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