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Frequency upconversion involving triads and quartets of ions in a $\text{Pr}^{3+}/\text{Nd}^{3+}$ codoped fluoroindate glass

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Frequency upconversion (UC) processes involving energy transfer (ET) among Nd^{3+} and Pr^{3+} ions in a fluoroindate glass are reported. In a first experiment, the excitation of Pr^{3+} [transition $^3H_4 \rightarrow ^1D_2$] and of Nd^{3+} [transition $^4I_{9/2} \rightarrow ({}^2G_{7/2} + {}^4G_{5/2})$] was achieved with a dye laser operating in the 575–590 nm range. In a second experiment, the Nd^{3+} ions were excited with the second harmonic of a Nd:YAG laser at 532 nm. The ET processes leading to UC in both experiments were studied by monitoring the blue fluorescence decay at 480 nm due to the transition $^3P_0 \rightarrow ^3H_4$ in Pr^{3+} . In the more relevant UC process, quartets of ions (Nd-Nd-Pr-Pr) are excited due to absorption of three laser photons by two Nd^{3+} ions which transfer their energy to two Pr^{3+} ions. Each Pr^{3+} ion promoted to the 3P_0 level decays to the ground state emitting one photon in the blue region. This conclusion was achieved investigating the dependence of the UC fluorescence intensity as a function of laser intensity, samples concentrations, and temporal behavior of the UC signal. Other UC processes involving nonisoionic groups of three ions are also reported. © 2002 American Institute of Physics. [DOI: 10.1063/1.1501757]

I. INTRODUCTION

Studies of energy transfer (ET) in rare-earth (RE)-doped solids have attracted a continuous research effort after the seminal works of Förster¹ and Dexter.² Nowadays, it is well known that the phenomenon of ET may lead to frequency upconversion (UC) emission in compounds containing trivalent RE ions. Particularly Pr^{3+} , Nd^{3+} , Er^{3+} , and Tm^{3+} have been incorporated in various materials and UC has been demonstrated.^{3,4} As a consequence, a number of studies were presented which provide a basis for the characterization of materials for photonics.

From a basic point of view, studies of ET in RE-doped solids provide information relative to ion-ion interactions. Also, such studies allow one to understand the behavior of excited states of RE, providing valuable information for the construction of lasers, quantum counters, and optical amplifiers. In particular, materials doped with Pr^{3+} or Nd^{3+} have attracted much attention because of their absorption and fluorescence bands in the visible and in the ultraviolet region.

UC processes involving pairs of Pr^{3+} or pairs of Nd^{3+} were first reported a long time ago. For instance, in crystals doped with Pr^{3+} , a process was identified by which two Pr^{3+} ions in the excited state 1D_2 exchange energy in such way that one of the ions decays nonradiatively to the ground state while the other is promoted to state 3P_0 , and from there, blue emission is observed due to decay to the ground state.^{5–7} In glasses, this effect was reported, for example, in

Refs. 8–10. ET among pairs of Nd^{3+} ions was also studied in crystals^{11,12} and, recently, in fluoride glasses,^{13–17} where efficient UC emission was detected.

Experiments were also reported involving triads ($\text{Nd}^{3+}-\text{Pr}^{3+}-\text{Pr}^{3+}$) in LaF_3 (Ref. 18) and UC due to triads of Pr^{3+} was observed in $\text{LaF}_3:\text{Pr}^{3+}$.^{19,20} More recently, UC due to Nd^{3+} triads was investigated in crystals²¹ and glasses.²²

From a practical point of view, the characterization of UC processes involving pairs, triads, and quartets of RE ions is desirable as it may help to identify appropriate hosts for frequency UC lasers. For example, laser emission due to UC involving Er^{3+} pairs in CaF_2 was presented.²³ More recently, the efficient ET process in ($\text{Nd}^{3+}-\text{Pr}^{3+}$) pairs was exploited to obtain blue laser emission in fluorozirconate glass.²⁴ The operation of UC lasers based on triads and quartets of Er^{3+} ions in fluoride crystals was also reported.^{25,26}

The identification of new RE host materials for UC is still of much interest and among the new materials available, fluoroindate glasses have emerged as promising candidates. Previous work has shown their large potential as devices because of the lower multiphonon emission rates and higher fluorescence efficiencies of RE ions in this material compared to other hosts.^{9,13–15,22,27–35}

In this letter, we report studies of ET involving groups of Nd^{3+} and Pr^{3+} resulting in UC in the blue-ultraviolet region in fluoroindate glasses. The samples were excited using light in the red-green range. The behavior of the upconverted luminescence is investigated as a function of the laser intensity and time, and as a function of RE concentration. The results allowed us to understand the dynamics of the UC processes.

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FIG. 1. Absorption spectrum of the sample with $x=0.2$. Sample thickness: 1.4 mm. The peaks marked with* are associated with Pr^{3+} transitions while the others refer to Nd^{3+} transitions.

II. EXPERIMENT

The samples used have the following compositions in mol %: $38 \text{ InF}_3-20 \text{ SrF}_2-20 \text{ ZnF}_2-(15.8-x) \text{ BaF}_2-2 \text{ NaF}-4 \text{ GaF}_3-0.2 \text{ PrF}_3-x \text{ NdF}_3$, where $x=0, 0.1$, and 0.2 . To prepare the samples, all the fluoride components were mixed and heated in a dry box under an argon atmosphere at 700°C for melting and 850°C for finning. The melt was poured and cooled into a preheated brass mold. Finning, casting, and annealing were carried out under a dry argon atmosphere in a way similar to standard fluoride glasses. Samples of good optical quality and which were stable against atmospheric moisture were obtained.

The Nd:YAG pumped dye laser, used in the first experiment, operates at 5 Hz with ~ 8 ns pulses, peak power of ~ 20 kW, linewidth of $\sim 0.5 \text{ cm}^{-1}$, and could be tuned over the 575–590 nm range. In the second experiment, the light beam used was the second-harmonic radiation at 532 nm, obtained from a Q-switched Nd:YAG laser delivering ~ 10 ns pulses with peak power of ~ 200 kW at 5 Hz.

In both experiments, the linearly polarized excitation beam was focused into the sample with a 10 cm focal length lens and the fluorescence was collected along a direction perpendicular to the incident beam direction by a 5 cm focal length. The fluorescence signal was analyzed in a spectrometer with $5 \text{ \AA}$ resolution equipped with a GaAs photomultiplier. The signal was processed using a digital oscilloscope connected to a computer.

The samples with dimensions of $1.0 \times 1.5 \times 0.14 \text{ cm}$ were studied at room temperature.

III. RESULTS AND DISCUSSION

The absorption spectrum in the visible range, obtained with the $x=0.2$ sample, is shown in Fig. 1. The broad features can be identified with transitions originating from the Pr^{3+} ground state (3H_4) and from the Nd^{3+} ground state ($^4I_{9/2}$). The spectrum obtained for the $x=0.1$ sample is similar, with no changes in the wavelengths of the absorption peaks. However, the intensities of the bands are dependent on the ions concentrations as expected. The spectrum of the

FIG. 2. Energy level diagram of Nd^{3+} and Pr^{3+} . The transitions indicated correspond to UC emissions in the blue-ultraviolet range.

sample with $x=0$ was previously reported.⁹ For the measurements, the spectrophotometer bandwidth (0.05 nm) was smaller than the absorption transitions linewidths (10 to 100 nm). These values, typical for RE ions in glasses, indicate that all transitions are inhomogeneously broadened.

A simplified energy level diagram of Nd^{3+} and Pr^{3+} is presented in Fig. 2.

A. Upconversion due to excitation in the red range

The emission spectrum for excitation at 588 nm is shown in Fig. 3 for the sample with $x=0.1$. The four bands located from 350 to 460 nm are due to Nd^{3+} transitions, and the peaks at ~ 470 and ~ 480 nm are due to Pr^{3+} ions. The states involved in the transitions are indicated in Fig. 3. The

FIG. 3. Frequency UC spectrum for excitation at 588 nm (sample with $x=0.1$). The peaks marked with* refer to Pr^{3+} .

UC spectra observed for excitation from 577 to 588 nm did not change as a function of laser wavelength.

To characterize the UC pathways, the intensity of each band was measured as a function of the laser intensity. The fluorescence signals present a quadratic dependence on the laser intensity, which indicates that two laser photons are required to generate each UC photon emitted. Time-resolved fluorescence measurements were also performed, varying the wavelength of the dye laser between 577 and 588 nm. No changes in the temporal behavior of the fluorescence signal was observed. Considering this result together with the quadratic intensity dependence, we conclude that the emissions from 350 to 460 nm are due to ET in a pair of Nd^{3+} ions in a way similar to Ref. 13 where Nd^{3+} -doped samples, without Pr^{3+} , were studied. The contribution of the Pr^{3+} ions for these emissions is not relevant, all it does is to introduce a small decrease in the decay time of the fluorescence signals, due to a lifetime reduction of the Nd^{3+} states in the codoped samples.

Based on the signal behavior as a function of laser intensity, we first investigate the possibility that the fluorescence emission at ~ 470 and ~ 480 nm could be produced via the process reported in Ref. 9, where a pair of Pr^{3+} ions excited to levels 1D_2 exchange energy in such a way that one atom is promoted to multiplet ($^3P_J, ^1I_6$), $J=0,1,2$, while the other decays to ground state. The emission at 480 nm is due to transition $^3P_0 \rightarrow ^3H_4$ while the weak emission at 470 nm is due to transition ($^3P_1, ^1I_6$) $\rightarrow ^3H_4$. However, although ET among two Pr^{3+} ions may be involved in the process that enables emission at 480 and 470 nm, the Nd^{3+} ions play an important role in the process. This was verified by comparing the UC efficiency of the ($\text{Nd}^{3+}/\text{Pr}^{3+}$) codoped samples with the efficiency of a sample with 0.2% of Pr^{3+} only ($x=0$). An enhancement of the UC intensity at 480 and 470 nm by two orders of magnitude with respect to the sample with $x=0$ was observed in the codoped samples. This is understood considering that: (i) the presence of Nd^{3+} increases the number of possible excitation pathways; (ii) the oscillator strength of the $^4I_{9/2} \rightarrow ({}^2G_{7/2} + {}^4G_{5/2})$ transition in Nd^{3+} is approximately five times larger than for transition $^3H_4 \rightarrow ^1D_2$ in Pr^{3+} ; and (iii) the ET efficiency among Nd^{3+} and Pr^{3+} ions is large.^{18,24} Thus, although the upconverted emission at 480 and 470 nm may be due to processes involving pairs ($\text{Pr}-\text{Pr}$), triads ($\text{Nd}-\text{Pr}-\text{Pr}$), or quartets ($\text{Nd}-\text{Pr}-\text{Pr}-\text{Nd}$), the last two processes are more probable because of the enhancement factor of $\sim 10^2$ observed in the UC emission for samples containing both Nd^{3+} and Pr^{3+} . The absorption of laser photons occurs mainly through Nd^{3+} ions. Afterward, two Nd^{3+} ions in the (${}^2G_{7/2} + {}^4G_{5/2}$) states transfer their energy to a Pr^{3+} pair in a resonant process where the acceptors make transition $^3H_4 \rightarrow ^1D_2$ while the donors decay to the ground state. Following this step, two Pr^{3+} acceptors in state 1D_2 exchange energy and one of them is promoted to the multiplet ($^3P_1, ^1I_6$). The other ion decays to the ground state. Finally, emissions corresponding to $^3P_0 \rightarrow ^3H_4$ at 480 nm and ($^3P_J, ^1I_6$) $\rightarrow ^3H_4$ at 470 nm are observed.

Figure 4 illustrates the UC process for the quartet case with the relevant states written, in a first approximation, as a direct product of the ions states. The triad and dyad cases can

FIG. 4. Energy levels scheme describing the UC pathway associated with ($\text{Nd}-\text{Pr}-\text{Pr}-\text{Nd}$) quartets. Excitation wavelength: 588 nm.

be represented in an analogous way. The rate equations for the density of populations, n_i ($i=1,2,3$), in the quartets levels can be written as:

$$dn_1/dt = \sigma_0 \Phi \cdot n_0 - W_{12} \cdot n_1 - \gamma_1 \cdot n_1, \quad (1)$$

$$dn_2/dt = W_{12} \cdot n_1 - W_{23} \cdot n_2 - \gamma_2 \cdot n_2, \quad (2)$$

$$dn_3/dt = W_{23} \cdot n_2 - \gamma_3 \cdot n_3, \quad (3)$$

where Φ is the photon flux; σ_0 is the absorption cross section; W_{nm} is the ET rate from state $|n\rangle$ to state $|m\rangle$; and γ_n is the relaxation of state $|n\rangle$, $n=1-3$, to state $|0\rangle$.

The system of Eqs. (1)–(3) has the following solution for $t > \tau$, where τ is the laser pulse duration:

$$\begin{cases} n_2(t) = n_2(\tau) \cdot e^{-(W_{23} + \gamma_2)t}, \\ n_3(t) = \frac{n_2(\tau) \cdot W_{23}}{(W_{23} + \gamma_2) - \gamma_3} \cdot [e^{-\gamma_3 t} - e^{-(W_{23} + \gamma_2)t}]. \end{cases} \quad (4)$$

$$n_3(t) = \frac{n_2(\tau) \cdot W_{23}}{(W_{23} + \gamma_2) - \gamma_3} \cdot [e^{-\gamma_3 t} - e^{-(W_{23} + \gamma_2)t}]. \quad (5)$$

Figure 5 shows the measured fluorescence temporal profile for the sample with $x=0.1$ where the solid line represents a fitting of the $n_3(t)$ function as given in Eq. (5). The numerical fitting gives a reasonable set of parameters, where it is possible to identify the 3P_0 lifetime $\gamma_3^{-1} \sim 14 \mu\text{s}$ and the 1D_2 lifetime $(W_{23} + \gamma_2)^{-1} \sim 106 \mu\text{s}$. The values obtained are

FIG. 5. Temporal evolution of the emission at 480 nm pumped at 588 nm. The circles represent the experimental data and the solid line represents the predictions of the model with $\gamma_3^{-1} \sim 14 \mu\text{s}$ and $(W_{23} + \gamma_2)^{-1} \sim 106 \mu\text{s}$ (sample with $x=0.1$).

FIG. 6. Frequency UC spectrum for excitation at 532 nm (sample with $x=0.1$). Inset: sample with 0.5% of Nd^{3+} only.

comparable with the observed rise and decay times reported in Ref. 9, i.e., 16 μs and 126 μs , respectively. Unfortunately, it was not possible to obtain a value for the ET rate from Nd^{3+} to Pr^{3+} , because the nonradiative transition rate between levels 1 and 2 is very large due to the small energy gap of $\sim 650\text{ cm}^{-1}$ between the two levels. Also, it is impossible to determine unambiguously the main UC mechanism (i.e., whether it is due to triads or quartets) via the temporal fluorescence analysis because the estimated differences in the time evolution for triads or quartets is less than 1 ns, which is below the resolution of our data acquisition system. Moreover, it is not possible to infer from the statistical distribution of ions which contribution is more important because, although the number of quartets would be smaller than the number of triads for a homogeneous distribution of RE ions, the probability of quartets excitation is at least five times larger than that of triads. Clustering of RE ions is another possibility which makes the analysis more difficult. The results reported in the next section provide supporting evidence for a quartet process.

B. Upconversion due to excitation at 532 nm

The main part of Fig. 6 shows the UC spectrum for excitation at 532 nm of the $x=0.1$ codoped sample. The four bands are due to the Nd^{3+} ions as it is confirmed by the inset which shows the UC spectrum for a sample with 0.5% of Nd^{3+} , without Pr^{3+} . The UC spectrum for the sample without Pr^{3+} can be understood as due to a process where two photons are absorbed in two Nd^{3+} ions (transition $^4I_{9/2} \rightarrow ^4G_{7/2}$) to originate the emission of each UC photon. This process was studied in Ref. 14 in samples with Nd^{3+} but without Pr^{3+} ions. On the other hand, it can be seen by comparison between the two spectra that there is a contribution from Pr^{3+} in the codoped sample because its band I presents a tail that extends up to 490 nm.

The dependence of the signal intensity at 480 nm on pumping intensity, I_L , is shown in Fig. 7(a) for several values of x , and the time behavior is shown in Fig. 7(b) for the $x=0.1$ sample. An analogous temporal behavior is observed for $x=0.2$ and in both cases the temporal evolution is de-

FIG. 7. UC fluorescence emission at 480 nm—pumping wavelength: 532 nm: (a) intensity as a function of the laser intensity and (b) temporal evolution. The solid line is a fitting of the theoretical predictions. The corresponding intensities vary from 0.9 to 2.5 GW/cm^2 .

scribed by $\{\exp(-t/t_r) - \exp(-t/t_d)\}$, where the rise (t_r) and decay (t_d) times are dependent on the Nd^{3+} concentration.

The intensity of the blue emission is described by $I_{480} \propto I_L^n$ ($n=1.33$ and 1.36), which indicates again a UC process involving a group of four ions (Nd-Nd-Pr-Pr), where two Nd^{3+} ions absorb three incident photons making a cross relaxation to two Pr^{3+} ions which are then excited to the multiplet ($^3P_J, ^1I_6$) from where blue emission is observed. Since each Pr^{3+} emits one photon corresponding to 480 nm, the three photons absorbed in Nd^{3+} ions originate two photons in the blue. Thus, we expect that I_{480} should be proportional to $I_L^{1.5}$ in reasonable agreement with the observation. If the process originated from triads (Nd-Nd-Pr), it would correspond to $n=2$, since Pr^{3+} ions do not absorb at 532 nm and two photons would be absorbed by Nd^{3+} ions. Experiments with samples without Nd^{3+} , pumped at 532 nm, did not show emission at 480 nm.

The proposed mechanism for the generation of the UC signal at 480 nm is represented in Fig. 8(a), and the possible combinations of levels involved are listed in Table I. The variety of possible UC pathways is due to the large number of Nd^{3+} levels and the possibility of excitation to any level in ($^3P_J, ^1I_6$) multiplet of Pr^{3+} . Thus, the combination of this fact plus the large oscillator strength of transitions $^3P_J - ^3H_4$, the large laser peak power ($\sim 200\text{ kW}$) and the small

FIG. 8. (a) Quartet scheme representing the pathway for UC emission at 480 nm pumping at 532 nm. The dashed arrows represent nonradiative transitions due to cross relaxation between Nd³⁺ and Pr³⁺ and (b) energy levels scheme describing the UC pathway in the (Nd-Pr-Pr-Nd) quartets case. Excitation wavelength: 532 nm. The Nd³⁺ levels involved in the UC process are indicated in Table I.

phonon energy of the fluorindate matrix favor the UC process. Notice also that the signal at 468 nm due to transition $^4D_{3/2} \rightarrow ^4I_{15/2}$ and $^2P_{3/2} \rightarrow ^4I_{13/2}$ in Nd³⁺, shows a quadratic dependence on the pump intensity. Thus, the UC process leading to emission at 468 nm is the same identified in Ref. 14, where two Nd³⁺ ions are involved without cooperation with a Pr³⁺ ion.

To provide a quantitative description, we considered the energy level scheme of Fig. 8(b) where the quartet states are written, in a first approximation, as direct product of states associated to the individual ions. Then, the rate equations system for the levels represented in Fig. 8(b), can be written as:

$$dn_1/dt = \sigma_0 \Phi \cdot n_0 - W_{12} \cdot n_1 - \gamma_1 \cdot n_1, \quad (6)$$

TABLE I. Possible combinations of excited states of Nd³⁺ involved in the UC process which generates emission at 480 nm from Pr³⁺ ions when the laser wavelength is 532 nm.

Nd ³⁺ levels	Pr ³⁺ final levels
$^2L_{15/2} + ^4F_{3/2}$	$^3P_0 + ^3P_0$
$^2L_{15/2} + ^4F_{3/2}$	$^3P_0 + ^3P_1, ^1I_6$
$^2L_{15/2} + ^4F_{5/2}, ^2H_{9/2}$	$^3P_1, ^1I_6 + ^3P_1, ^1I_6$
$^2L_{15/2} + ^4F_{7/2}$	$^3P_0 + ^3P_2$
$^2L_{15/2} + ^4S_{3/2}$	$^3P_1, ^1I_6 + ^3P_2$
$^2L_{15/2} + ^4F_{9/2}$	$^3P_2 + ^3P_2$
$^4D_{3/2} + ^4F_{7/2}$	$^3P_0 + ^3P_0$
$^4D_{3/2} + ^4S_{3/2}$	$^3P_0 + ^3P_0$
$^4D_{3/2} + ^4S_{3/2}$	$^3P_0 + ^3P_1, ^1I_6$
$^4D_{3/2} + ^4F_{9/2}$	$^3P_1, ^1I_6 + ^3P_1, ^1I_6$
$^4D_{3/2} + ^4F_{9/2}$	$^3P_0 + ^3P_2$
$^4D_{3/2} + ^2H_{11/2}$	$^3P_1, ^1I_6 + ^3P_2$
$^4D_{3/2} + ^2G_{7/2}, ^4G_{5/2}$	$^3P_2 + ^3P_2$

$$dn_2/dt = W_{12} \cdot n_1 - \gamma_2 \cdot n_2, \quad (7)$$

where the solution for n_2 when $t > \tau$ is:

$$n_2(t) = A \cdot e^{-(W_{12} + \gamma_1) \cdot t} + B \cdot e^{-\gamma_2 \cdot t}, \quad (8)$$

where A and B are expressed in terms of γ_1 , γ_2 , W_{12} , $\sigma_0 \Phi$, and τ .

The solid curve in Fig. 7(b) represents a fitting based on Eq. (8) for the $x=0.1$ sample. From this analysis, it was possible to infer the 3P_0 lifetime of Pr³⁺ ions in quartets, $(\gamma_2)^{-1} \sim 20 \mu s$, which is of the same order of magnitude as in the previous section. The value of $(W_{12} + \gamma_1)^{-1}$ was not determined because the time resolution of the data acquisition system was too low ($\sim 1 \mu s$) due to the small signal power.

IV. CONCLUSION

Two experiments were performed to study frequency UC processes due to ET among Nd³⁺ and Pr³⁺ ions in fluorindate glass samples. The ET process was monitored through the blue fluorescence at 480 nm, due to the transition $^3P_0 \rightarrow ^3H_4$ in Pr³⁺. In the first experiment, Pr³⁺ was excited through the transition $^3H_4 \rightarrow ^1D_2$ and of Nd³⁺ via the transition $^4I_{9/2} \rightarrow (^2G_{7/2} + ^4G_{5/2})$ by a dye laser operating in the 575–590 nm range. It was observed that the presence of Nd³⁺ contributes to an enhancement of two orders of magnitude in the fluorescence signal at 480 nm, relative to samples without Nd³⁺. In the second experiment, the excitation of the $^4G_{7/2}$ state of Nd³⁺ by the second harmonic of a Nd:YAG laser (532 nm) generates a blue signal due to a cross-relaxation process involving quartets of Nd³⁺ and Pr³⁺.

Frequency upconversion involving nonisoionic quartets of RE species is detected in a fluorindate glass. Detection of nonisoionic triads were reported previously in Yb³⁺/Tb³⁺ codoped fluorindate glass.³⁵

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