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Energy transfer and frequency upconversion involving triads of Pr^{3+} ions in (Pr^{3+}, Gd^{3+}) doped fluoroindate glass

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Blue and ultraviolet luminescence in (Pr^{3+}, Gd^{3+}) doped fluoroindate glass is studied for excitation in the red region (≈590 nm). Frequency upconversion (UC) is observed due to energy transfer (ET) among three Pr^{3+} ions initially excited to the $^1D_2$ state corresponding to the ET process $^1D_2+{}^1D_2+{}^1D_2 \rightarrow {}^1S_0+{}^3H_5+{}^3H_5$. Additionally, UC luminescence from states $^6P_{7/2}$ and $^6I_{7/2}$ of Gd^{3+} is observed for an excitation wavelength resonant with transitions of the Pr^{3+} ions. The characterization of the luminescence signals allowed to determine ET rate among the Pr^{3+} ions and provides evidence of interconfigurational ET between Gd^{3+} and Pr^{3+} ions. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2189207]

I. INTRODUCTION

The investigation of energy transfer (ET) processes is important to understand the mechanisms of interaction between atoms or molecules in condensed matter. The phenomenon was originally studied by Förster[1] who considered that the electronic energy of excited atoms or molecules (donors) can be transferred to nearby acceptors. On the other hand, from a practical point of view, ET studies may allow the discovery of systems for photonic applications such as lasers and sensors based on the excitation of rare earth (RE) ions.

Several mechanisms for ET among RE ions are known.[2–5] One possibility is the occurrence of ET to an acceptor through the absorption of the donor photoemission. ET may also occur due to exchange or superexchange mechanisms when donor and acceptor are at very short distances, inside wave functions overlap. However, the more frequently observed cases involving RE ions in solids are ET processes due to electric interaction with ion-ion distance dependence following an inverse power law which differs for dipole-dipole, dipole-quadrupole, or higher-order multipolar interactions. In these cases the donor and the acceptor are coupled not only to the electromagnetic field but also to each other. The dipole-dipole interaction mechanism is the most important and it is stronger if the corresponding dipole transitions in the donor and the acceptor are allowed. Larger ET rates are obtained when there is a spectral overlap between the transitions in the donor and in the acceptor. Phonon-assisted ET processes are also observed when there is no resonance between the donor and the acceptor transitions.[4,5]

Experiments illustrating ET processes involving pairs, triads, and quartets of RE ions in crystalline and amorphous solids were reported. Fluoride crystals are particularly interesting for such studies due to the high luminescence efficiency of RE hosted in these materials. Reports of processes involving pairs of Pr^{3+} in LaF_3 crystals exemplify well such studies. For instance, ET process followed by frequency upconversion (UC) luminescence was identified by which two Pr^{3+} ions in the $^1D_2$ state exchange energy in such way that one ion decays to the ground state while the other is finally promoted to the $^3P_0$ state; from there, blue emission occurs due to Pr^{3+} ion decay to the ground state.[6–8] Processes involving isoionic triads of RE ions were also studied in doped fluoride crystals[9–11] and ET processes involving groups of different RE species have been observed in different systems.[3–5,12]

From the applied point of view the characterization of ET processes involving pairs, triads, and quartets of RE ions is desirable because it may help to identify appropriate hosts for UC lasers. For example, laser emission due to UC involving Er^{3+} pairs in CaF_2 was presented in Ref. 13. The operation of UC lasers based on triads and quartets of Er^{3+} ions in fluoride crystals was also reported.[14,15]

In fluoride glasses, many ET processes were observed and successfully exploited.[3–5,16–23] For example, the efficient ET process in Nd^{3+}–Pr^{3+} pairs was exploited to obtain blue laser emission in fluorozirconate glass.[16] In fluoroindate glasses, besides the observation of ET involving RE pairs,[17–20] ET processes involving triads and quartets of ions were investigated in samples doped with Er^{3+} (Ref. 18) and Nd^{3+},[21] and samples codoped with Yb^{3+}/Tb^{3+} (Ref. 22) and Pr^{3+}/Nd^{3+}.[23] A process involving ET among three excited Er^{3+} ions was used to construct a practical temperature sensor.[24]

The studies of UC due to ET in fluoroindate glasses have demonstrated the large potential of these materials for devices because of their large transparency window, the low multiphonon emission rates, and the high fluorescence efficiency of RE ions hosted in these glasses.[17–23] Furthermore, it is possible to incorporate large concentration of RE ions inside the glass matrix and as a consequence many efficient ET processes can be observed. Moreover, a method to fabri-

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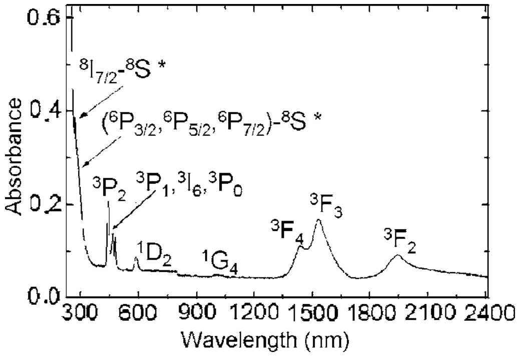

FIG. 1. Absorption spectrum of the sample (thickness: 1.4 mm). The states marked with (*) are associated with Gd^{3+} transitions while the others refer to Pr^{3+} transitions starting from the ground state.

cate waveguides on fluoroindate substrates was presented[25] and monomode fibers can be made with basis on fluoroindate glasses.[26]

In this work, we report on the observation of ET involving groups of three Pr^{3+} ions resulting in UC emission in a fluoroindate glass. The luminescence behavior of the sample was investigated as a function of the laser intensity and its optical frequency. The results allowed us to understand the dynamics of the UC emission observed and to determine rates for the ET processes. The ET from Pr^{3+} to Gd^{3+} ions is also reported.

II. EXPERIMENTAL DETAILS

The sample was prepared following the procedure given in Ref. 20 and has the following compositions in mol %: $40InF_3-20SrF_2-20ZnF_2-16BaF_2-2NaF-1GdF_3-1PrF_3$. The glass synthesis was made using proanalysis oxides and fluorides as starting materials. The fluoride powders used were mixed together and heat treated first at 700 °C for melting and then 800 °C for refining. The melt was finally poured between two preheated brass plates to allow the preparation of samples of different thickness. Fining, casting, and annealing were carried out in a way similar to standard fluoride glasses under a dry argon atmosphere.

Optical absorption measurements in the 250–2400 nm range were made using a double-beam spectrophotometer.

For excitation of the luminescence spectra two light sources were used. A dye laser (pulses of ≈ 8 ns; ≈ 20 kW peak power) was used for excitation in the red spectral region. It was transversely pumped by the second harmonic of a pulsed Nd:YAG (yttrium aluminum garnet) laser and consisted of an oscillator plus one stage of amplification. The oscillator, operating with a grazing incidence grating, was tunable from 560 to 610 nm, with linewidth of ≈ 0.5 cm^{-1}. For excitation in the UV (180–375 nm) a 300 W lamp was used connected to a monochromator. For both excitation conditions the light beam was focused into the sample with a 10 cm focal length lens and the luminescence, collected along a direction perpendicular to the incident beam, was sent to a monochromator attached to a GaAs photomultiplier tube and lock-in amplifier. The temporal behavior of the fluorescence signal was determined using a fast digital oscilloscope. Samples with dimensions of $10 \times 15 \times 1.4$ mm^3 were studied at room temperature.

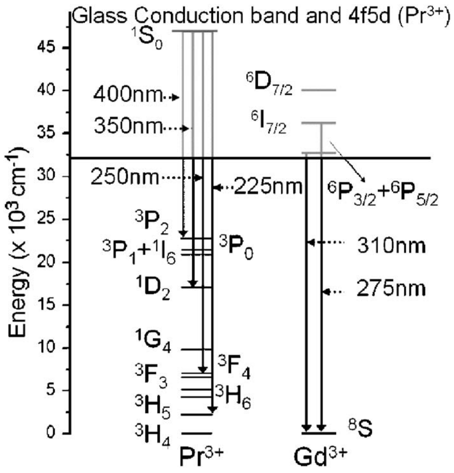

FIG. 2. Energy level schemes of Pr^{3+} and Gd^{3+} ions. The transitions indicated correspond to UC emissions in the blue-ultraviolet range. The energy of level $^1S_0$ was deduced from the luminescence spectrum.

III. RESULTS AND DISCUSSION

The absorption spectrum of the sample is shown in Fig. 1. The broad spectral features are associated to transitions originating from the Pr^{3+} ground state ($^3H_4$) and from the Gd^{3+} ground state (^8S). For the measurements, the spectrophotometer bandwidth was much smaller than the absorption transition linewidths that are inhomogeneously broadened. Simplified energy level schemes of Pr^{3+} and Gd^{3+} ions are presented in Fig. 2. The energy of states $^1S_0$ (Pr^{3+}) and $^6I_{7/2}$, $^6D_{7/2,9/2}$, (Gd^{3+}) cannot be determined from Fig. 1 and the values indicated in Fig. 2 are the energies corresponding to Pr^{3+} and Gd^{3+} in LaF_3.[4] The energies of states associated to the $4f^{N-1}5d$ band are not known for the fluoroindate glasses but they are expected to overlap with the glass conduction band.

The frequency UC spectrum for excitation at ≈ 590 nm is shown in Fig. 3 and the states involved in the transitions are indicated. The emitted intensities from 200 to 420 nm

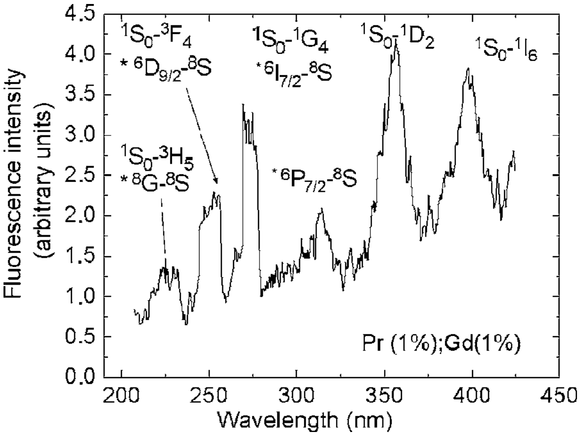

FIG. 3. Frequency UC spectrum for excitation at 590 nm. The peaks marked with (*) refer to Gd^{3+}.

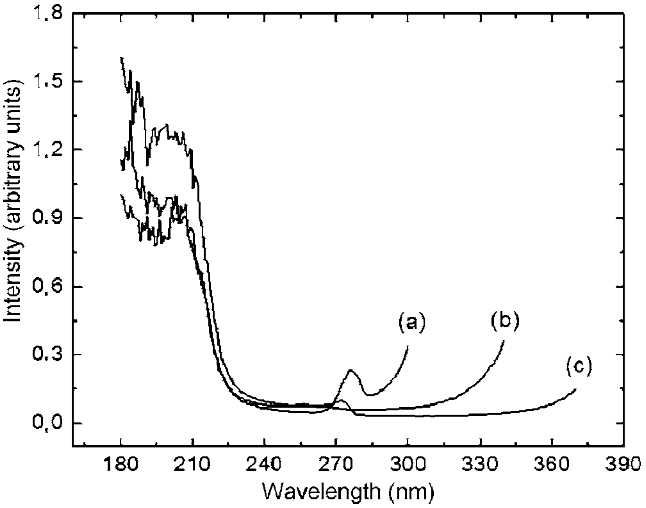

FIG. 4. Excitation spectra of the UV signals. Emission wavelength: (a) ≈396 nm, (b) ≈350 nm, and (c) ≈310 nm.

have the same order of magnitude but they are three orders of magnitude smaller than the UC blue emission (at 480 nm) due to the process $^1D_2 + ^1D_2 \rightarrow ^3P_0 + ^3H_4$ previously studied.[17]

To identify the origin of the UV emissions the excitation spectra of the luminescence bands were measured. Figure 4 shows that the signal at 396 nm [curve (a)] is larger for excitation with wavelengths smaller than ≈225 nm. Notice also that a spectral feature is observed for excitation at ≈275 nm. The excitation from 170 to 225 nm access a region that corresponds to the glass conduction band, states associated to the $4f5d$ band and $^1S_0$ state of Pr^{3+}, and states of Gd^{3+} associated to the $4f$ configuration. The highly shielded $4f$ states located inside the glass conduction band are discrete energy states. Evidences for transitions, whose $4f$ final states do not appear in the ground state absorption spectra due to overlap with the fundamental absorption of the glass host, were reported for RE ions in different materials;[27–29] thus we assume that ET from Bloch states in the conduction band to the RE $4f$ is negligible. The emission at 396 nm is attributed to transition $^1S_0 \rightarrow ^1I_6$ of Pr^{3+}. The increase observed in the Fig. 4 [curve (a)] for excitation at ≈275 nm can be attributed to absorption in Gd^{3+} ($^8S \rightarrow ^6I$) followed by ET to states of the $4f5d$ (Pr^{3+}) configuration and decay to $^1G_4$ (Pr^{3+}). Figure 4(b) [curve (b)] shows the excitation spectrum of the emission at 350 nm that is attributed to the $^1S_0 \rightarrow ^1D_2$ transition. In this case no enhancement is observed when the excitation wavelength is resonant with the Gd^{3+} transitions. The spectrum in Fig. 4 [curve (c)] is understood assuming that from 180 to 225 nm the absorption is mainly due to Pr^{3+} ($^3H_4 \rightarrow 4f5d$) followed by ET [$4f5d(Pr^{3+}) \rightarrow 4f(Gd^{3+})$], and absorption to excited Gd^{3+} $4f$ levels. The enhancement for excitation at ≈275 nm is due to the $^8S \rightarrow ^6I$ (Gd^{3+}) transition. The emission at ≈310 nm is attributed only to Gd^{3+} ($^3P_J \rightarrow ^8S$).

To characterize the UC pathways for excitation at 590 nm, the intensity of each luminescence band was measured as a function of the laser intensity. The dependence of the UC signals with the laser intensity is shown in Fig. 5(a). The signals present an approximate cubic dependence with the laser intensity, indicating that three laser photons are required to generate each UC photon emitted. Figure 5(b) shows the excitation spectrum of the emission at 396 nm. It is observed that the signal amplitude is a maximum when the dye laser wavelength is ≈590 nm, in resonance with the transition $^3H_4 \rightarrow ^1D_2$. The excitation spectrum of the bands at 350, 310, and 275 nm exhibits a maximum also at 590 nm. These emissions correspond to the transitions indicated in Fig. 3. The emissions centered at ≈225, ≈250, and ≈275 nm can be due to Pr^{3+} and/or Gd^{3+} ions. The excitation of Gd^{3+} ions when the laser wavelength is in resonance with Pr^{3+} transitions is due to ET from Pr^{3+} to Gd^{3+} ions.

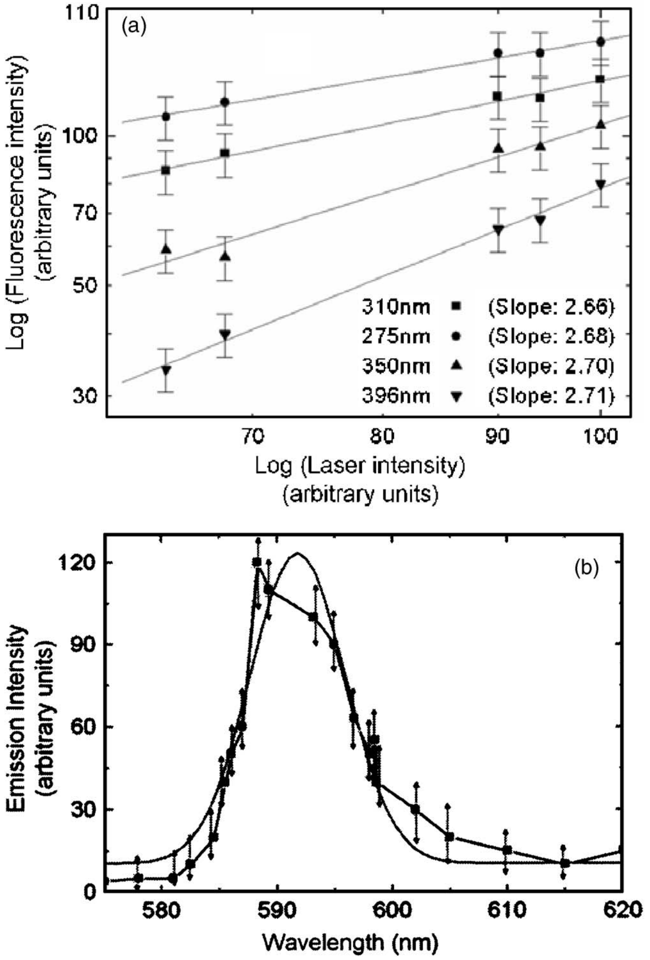

FIG. 5. UC luminescence emission for pumping wavelength at 590 nm: (a) dependence of the fluorescence signal with the laser intensity and (b) excitation spectrum of the signal at 396 nm (transition $^1S_0 \rightarrow ^1I_6$). The dotted line is a Gaussian curve that represents the best fit of the data.

The temporal evolution of the UC signals at 350 and 396 nm for excitation at ≈590 nm is displayed in Figs. 6(a) and 6(b). The solid lines represent the fitting to the expression $[\exp(-t/\tau_d) - \exp(-t/\tau_r)]$, where τ_r and τ_d represent the rise and decay time of the UC signal, respectively. The values obtained for the signal at ≈350 nm were $\tau_r = 0.65 \pm 0.10$ μs and $\tau_d = 6.2 \pm 0.10$ μs. For the emission at ≈396 nm the values determined from the fitting procedure were $\tau_r = 0.58 \pm 0.10$ μs and $\tau_d = 5.5 \pm 0.6$ μs. The similar values for τ_r and τ_d for both transitions, as well as the behavior

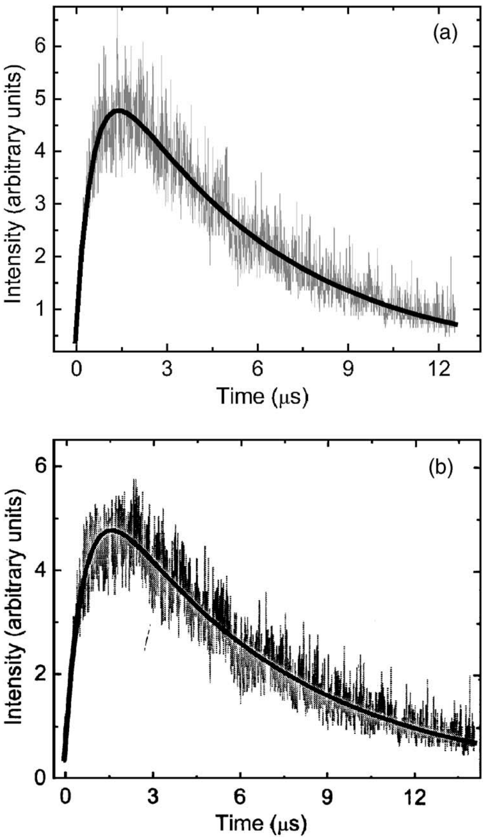

FIG. 6. Temporal behavior of the luminescence centered at (a) ≈350 nm and (b) ≈396 nm. Excitation wavelength: 590 nm.

of the excitation spectra of the signals at ≈350 and ≈396 nm, indicate that both transitions originate from the same excited state. Considering the energy levels scheme of Fig. 2 we attribute the emissions at ≈350 and ≈396 nm to the transitions $^1S_0 \rightarrow {}^1D_2$ and $^1S_0 \rightarrow {}^1I_6$, respectively.

Different mechanisms can be considered to understand the growth of the $^1S_0$ level population following the resonant excitation of the $^1D_2$ state. Figure 7 illustrates mechanisms that involve isolated ions, pairs, and triads, respectively. Mechanism (a) is a three-photon excitation process of an isolated Pr^{3+} ion with an intermediate real state ($^1D_2$). This mechanism corresponds to a one-photon transition within the $4f$ configuration ($^3H_4 \rightarrow {}^1D_2$) followed by a two-photon transition between the $4f$ and $4f5d$ configurations with no real intermediate state. The two-photon transition is parity forbidden and it is expected to have a small cross section. Moreover, this mechanism implies a fluorescence rise time of ≈8 ns (due to the laser pulse duration) but the measured rise time was $\geqslant 0.6$ μs. Consequently, mechanism (a) does not explain our observation. Mechanism (b) is a two-ion process where after excitation of both ions to the $^1D_2$ state the absorption of a third photon takes place simultaneously with a cooperative ET from the other ion in the pair. The process is followed by relaxation from the $4f5d$ band to the $^1S_0$ state. However, the transition $^1D_2 \rightarrow 4f5d$, involving one-photon absorption and cooperative ET, is expected to have a very small cross section. Also this process should occur during the laser pulse duration but, since the observed rise time is ≈0.6 μs, it has to be discarded.

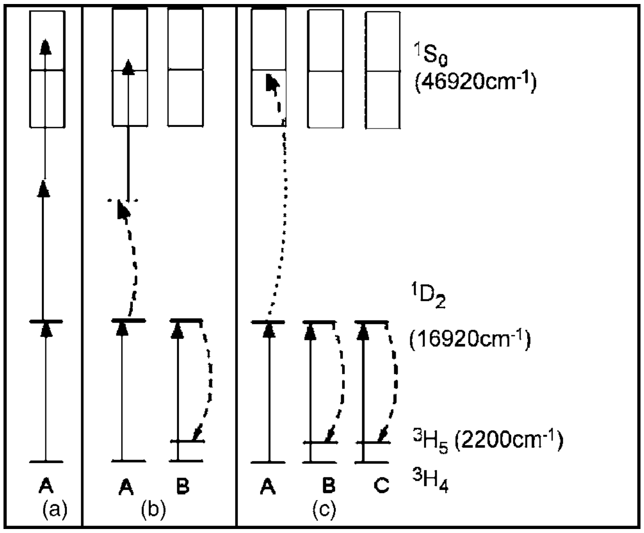

FIG. 7. Investigated mechanisms for populating the state $^1S_0$ after laser excitation of the $^3H_4 \rightarrow {}^1D_2$ transition. Mechanism (a) is a single-ion three-photon absorption; (b) is a two ion excitation followed by a cooperative absorption; and (c) is a three-ion absorption process followed by energy transfer.

Our observations can be understood considering the mechanism (c). In this case the energy is stored in Pr^{3+} ions excited in the $^1D_2$ state; afterwards ET among three Pr^{3+} ions takes place, transferring the excitation to one of the ions in the triad. The more probable ET channel is $^1D_2 + {}^1D_2 + {}^1D_2 \rightarrow {}^1S_0 + {}^3H_5 + {}^3H_5$. The final state $|{}^1S_0 + {}^3H_5 + {}^3H_5\rangle$ is reached after transitions involving intermediate electronic states with emission of phonons. Then, the UC emissions at ≈350 and ≈396 nm appear due to the decay from the $^1S_0$ state. The UC process based on mechanism (c) was first identified for Pr^{3+} doped LaF_3 crystals.[10]

The temporal evolution of the luminescence signals that originate from state $^1S_0$ can be described by

$$\dot{n}_0 = -(W_0 + W_t)n_0 \tag{1}$$

and

$$\dot{n}_1 = W_0 n_0 - W_1 n_1, \tag{2}$$

where n_0 and n_1 are the populations of the triad states $|0\rangle = |{}^1D_2 + {}^1D_2 + {}^1D_2\rangle$ and $|1\rangle = |{}^1S_0 + {}^3H_5 + {}^3H_5\rangle$, respectively. W_t is the energy transfer rate from state $|0\rangle$ to state $|1\rangle$; W_1 is the total radiative emission rate from the $^1S_0$ state; and W_0 is the relaxation rate of the state $|0\rangle$ due to all possible mechanisms except ET to state $|1\rangle$. The solutions of Eqs. (1) and (2) are

$$n_0 = N_0 e^{-(W_0 + W_t)t} \tag{3}$$

and

$$n_1 = \frac{N_0 W_t}{(W_r - W_d)}[e^{-W_d t} - e^{-W_r t}], \tag{4}$$

where N_0 is the population of $|0\rangle$ at $t=0$, W_r is the larger of the two transfer rates $W_0 + W_t$ and W_1, and W_d is the smaller transfer rate.

It is expected that $W_0 \approx 3(\tau_D)^{-1}$, where τ_D is the decay time of the $^1D_2$ state, and $W_1 \cong (\tau_S)^{-1}$, where τ_S corresponds to the $^1S_0$ state. The value $\tau_D = 32$ μs was determined exciting the transition $^3H_4 \rightarrow {}^1D_2$ (at 590 nm) and observing the signal decay corresponding to $^1D_2 \rightarrow {}^3H_5$ (at 688 nm). Thus the value obtained for W_0 is 9.4×10^4 s^{-1}.

To determine W_t we first recall that the lifetime of state $^1S_0$ determined for LaF$_3$:Pr^{3+} (Ref. 30) is ≈ 0.7 μs. This value is of the same order of magnitude than the observed risetime of the signals at 350 and 396 nm. Thus W_d cannot be associated to W_1. Therefore, we considered $W_d = (\tau_d)^{-1} = W_t + W_0$ and $W_r = (\tau_r)^{-1} = W_1$, and from this we obtain $W_t = 7.3 \times 10^4$ s^{-1}.

Therefore the spectral behavior of the UC processes as well as the dynamics of the signal indicate that ET involving triads of Pr^{3+} ions is the mechanism for emissions at 350 and 396 nm.

IV. CONCLUSION

In summary, processes of ET involving Pr^{3+} and Gd^{3+} ions in a fluoroindate glass were investigated. Mechanisms to explain the frequency upconversion luminescence considering different ET channels among the rare earth ions are proposed. The study of the phenomena observed allowed the estimation of the ET rate among Pr^{3+} ions excited to $^1D_2$ state. Processes between Pr^{3+} states associated to the $4f5d$ configuration and Gd^{3+} states of the $4f$ configuration were also observed and discussed.

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