# Avalanche upconversion in $Er^{3+}$ doped fluoroindate glass

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Avalanche upconversion is reported for $Er^{3+}$ doped fluoroindate glass pumped at 633.5 nm. Strong frequency upconversion signals and intensity dependent transmittances are observed. The results of the transient and steady-state measurements agree well with the predictions of a rate-equation model which take into account cross-relaxation processes among pairs of erbium ions.

The upconversion mechanism called photon-avalanche (PA), first discovered in the study of $Pr^{3+}$-based infrared quantum counters,[1] occurs when the pump laser frequency is far away from ground state absorption to electronic states but it is in resonance with a transition between a pair of excited states. When the excitation power exceeds a certain value, the samples transmittance decreases and the upconversion signal grows nonlinearly with increasing pump power. Also, the signal risetime is pump dependent and it is often longer than the lifetimes of the fluorescing levels involved.

Recently much attention has been dedicated to the study of PA because of the basic research interest in the phenomenon and because of its usefulness as an excitation mechanism for upconversion lasers. Accordingly, efficient PA processes were reported for a number of rare earth (RE) doped crystals.[2] The effect was first observed for RE doped glasses a few years ago[3,4] and its investigation in ZBLAN and BiGa ZYTZr glasses doped with RE was further reported.[5,6] In fact, vitreous materials have the advantage that some compositions can be fibered which is a convenient mean for the operation of upconversion lasers.

Among the new glasses which can be fibered, the fluoroindate glasses are promising materials for laser applications because of their large transparency window (250 nm to 8 $\mu$m), small sensitivity to atmospheric moisture, capability of incorporating large concentrations of RE ions, and possibility to be processed for integrated optics devices.[7] Recently we have shown that these materials present large efficiency as light frequency unconverters from infrared to visible,[8] from infrared to ultraviolet,[9] and from orange to blue[10] using $Er^{3+}$, $Nd^{3+}$, and $Pr^{3+}$ as the doping ions, respectively. In this letter we report, for the first time to our knowledge, the observation of avalanche upconversion in $Er^{3+}$ doped fluoroindate glass.

The sample used, prepared following the procedure described in Refs. 8–12, has the composition in mol %: $36InF_3 - 20ZnF_2 - 20SrF_2 - 16BaF_2 - 2GdF_3 - 2NaF - 1GaF_3 - 3ErF_3$.

The linear absorption spectrum was measured using a commercial spectrophotometer. The PA measurements were made using a cw dye laser ($\leq$45 mW) as the excitation source operating in the range 632 to 635 nm. The beam was focused on the sample using a focal length lens of 2.5 cm and the fluorescence signal, dispersed by a 0.25 m spectrometer, was detected by a photomultiplier using either a lock-in or a digital oscilloscope. For the transmittance measurements the laser beam was split into two beams and the ratio between the intensity transmitted through the sample and the intensity of the reference beam was recorded.

Figure 1 shows the absorption spectrum in the wavelength range of 500 to 700 nm. The bands shown can be identified with transitions from the ground state to the excited states of $Er^{3+}$: ~651 nm ($^4I_{15/2} \rightarrow {}^4F_{9/2}$), ~540 nm ($^4I_{15/2} \rightarrow {}^4S_{3/2}$), and ~521 nm ($^4I_{15/2} \rightarrow {}^2H_{11/2}$).

Figure 2 shows the behavior of the intensity dependent transmittance of the sample when the laser wavelength was set at 633.5 nm. Notice the large reduction of $\approx$23% in the sample transmittance when the laser intensity is changed from 2 to 24 mW. The solid line in Fig. 2 was obtained assuming an intensity dependent transmission given by $T = (1-R)^2 e^{-\alpha_0 L}[1 + (\alpha_2/\alpha_0)(1-R)I_0(1-e^{-\alpha_0 L})]^{-1}$, where $I_0$ is the incident intensity at the sample front surface, $\alpha_0 = 0.33$ cm$^{-1}$, obtained from the linear absorption spectrum, $R = 0.04$ is the sample reflectance, $L$ is the sample length, and $\alpha_2 = 5.3 \times 10^{-5}$ cm/W is the nonlinear absorption coefficient. It is important to recall (see Fig. 1) that there is no resonant electronic transition at 633.5 nm in $Er^{3+}$ from the

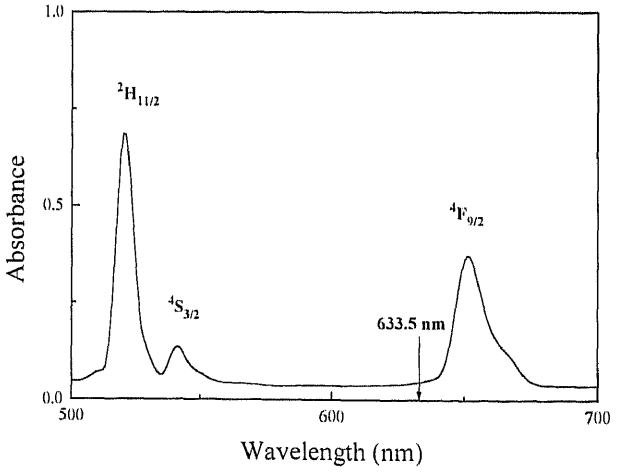


FIG. 1. Absorption spectrum in the 500–700 nm range. Length of the sample: 0.26 cm. The solid arrow indicates the laser wavelength used in the experiments.

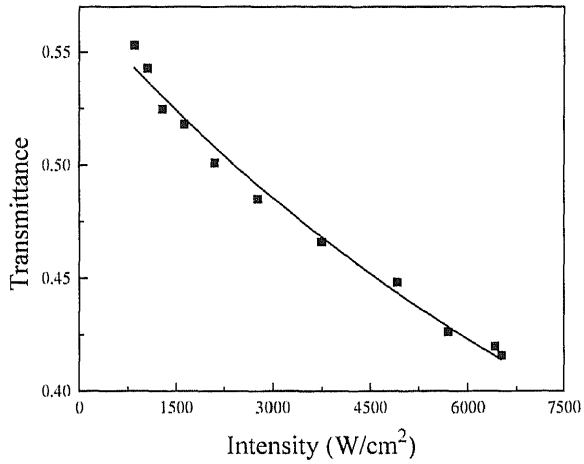


FIG. 2. Transmittance of the sample as a function of the laser intensity. Laser wavelength: 633.5 nm.

ground state. The laser frequency detuning to the level $^4F_{9/2}$ is ~440 cm$^{-1}$ and the absorption corresponding to $^4I_{15/2}\rightarrow{}^4F_{9/2}$ is simultaneous with the excitation of one phonon. Following the excitation to state $^4F_{9/2}$ nonradiative decay to states $^4I_{9/2}$, $^4I_{11/2}$, and $^4I_{13/2}$ occur due to multiphonon relaxation. The following steps in the excitation process are the resonant excited state absorptions (ESA) $^4I_{9/2}\rightarrow{}^2K_{15/2}$, $^4I_{11/2}\rightarrow{}^4G_{11/2}$, and $^4I_{13/2}\rightarrow{}^4F_{5/2}$. These transitions are responsible for the nonlinear behavior of the transmittance.

The frequency upconversion spectrum obtained shows emission bands at ~530 nm and ~550 nm which correspond to transitions $^2H_{11/2}\rightarrow{}^4I_{15/2}$ and $^4S_{3/2}\rightarrow{}^4I_{15/2}$, respectively. Weaker bands corresponding to transitions $^4F_{9/2}\rightarrow{}^4I_{15/2}$ (~670 nm), $^2H_{9/2}\rightarrow{}^4I_{15/2}$ (~407 nm), and $^4G_{9/2}\rightarrow{}^4I_{13/2}$(~475 nm) were also observed. The green fluorescence was so intense that it was seen by naked eyes. The dependence of the upconverted signal with the incident laser intensity is quadratic indicating that two laser photons are required to generate each photon of the upconverted green fluorescence. Similar behavior was observed for the blue and red bands.

Figure 3 shows the temporal behavior of the upconverted signal at ~550 nm, studied with the laser beam chopped at 25 Hz. The resolution of the detection system is better than 0.1 ms. There is a clear dependence of the transient data with the laser intensity. Signal rise times between 9.3 and 18 ms were observed while the decay time varied between 2.0 and 2.9 ms for laser power between 45 and 2 mW. The transient behavior also indicates that long lifetime states contribute as intermediate states in the upconversion process because the green fluorescence decay time is longer than the lifetime of the emitting level [$\tau(^4S_{2/3})=86$ $\mu$s] as measured previously.[12]

The dynamical behavior of the signal was described using rate equations for a three-level system taking into account the contributions from all relevant levels. Using the symbols $n_1$, $n_2$, and $n_3$ for the population density of states $^4I_{15/2}$ (level 1), $^4I_{13/2}$, $^4I_{11/2}$, and $^4I_{9/2}$ (level 2), and $^4S_{3/2}$ together with all levels above it (level 3), the rate equations describing the evolution of the level's populations are

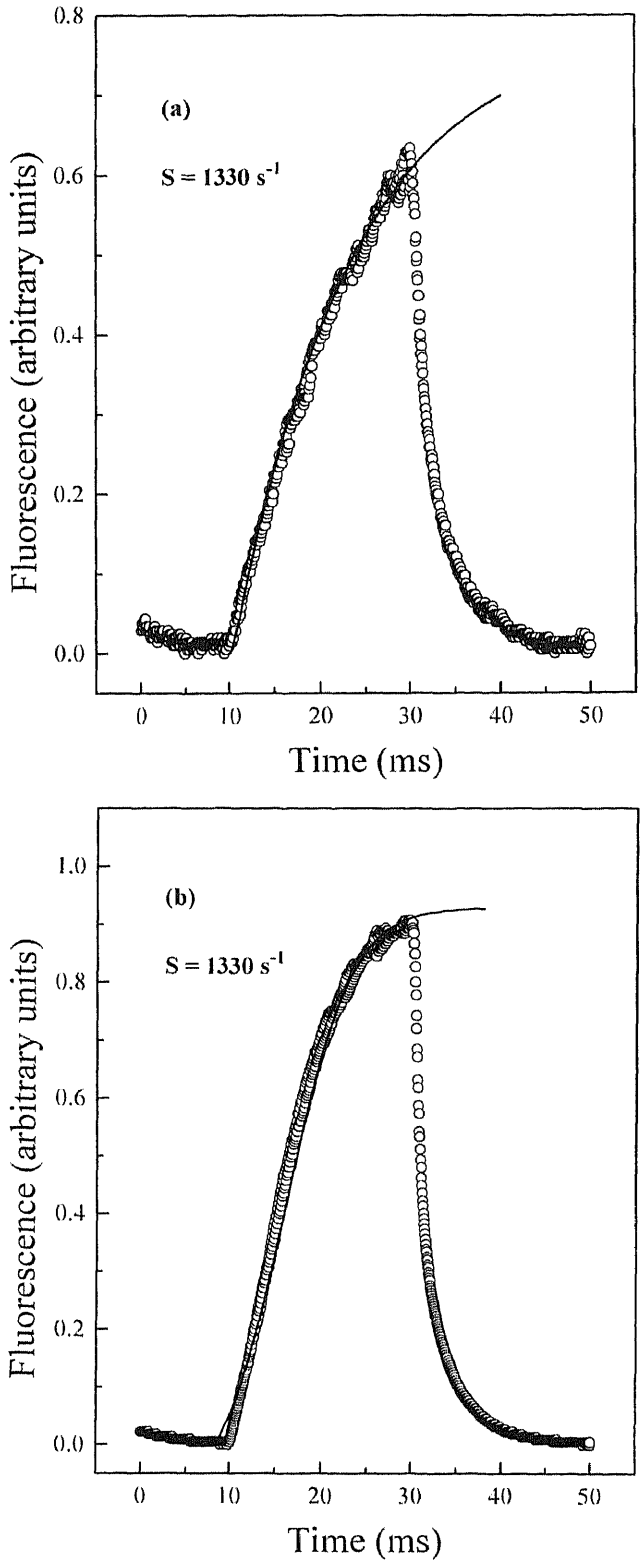


FIG. 3. Transient behavior of the upconversion fluorescence from level $^4S_{3/2}$ to $^4I_{15/2}$ for an incident laser power of (a) 2.1 mW and (b) 45 mW.

$$\dot{n}_1=-R_1n_1+W_{21}n_2+W_{31}n_3-Sn_1n_3, \quad (1)$$

$$\dot{n}_2=+R_1n_1-R_2n_2-W_{21}n_2+W_{32}n_3+2Sn_1n_3, \quad (2)$$

$$\dot{n}_3=+R_2n_2-(W_{31}+W_{32})n_3-Sn_1n_3, \quad (3)$$

with $n_1+n_2+n_3=1$.Three ESA processes [$^4I_{13/2}\rightarrow$

$(^4F_{3/2}, {}^4F_{5/2})$, $^4I_{11/2} \rightarrow {}^4G_{11/2}, {}^4I_{9/2} \rightarrow {}^2K_{15/2}]$ and cross relaxations involving the relevant levels may contribute to the nonlinear absorption. However, to simplify our model we considered only the contribution due to the excited state absorption with the largest cross section ($^4I_{13/2} \rightarrow {}^4F_{5/2}$) and one effective cross-relaxation process. Accordingly, the pumping rates $R_1$ and $R_2$ correspond to transitions $^4I_{15/2}$+phonon$\rightarrow {}^4F_{9/2}$+phonon and $^4I_{13/2} \rightarrow {}^4F_{5/2}$, respectively. $W_{ij}, i, j = 1, 2, 3$, represents the relaxation rate involving levels $i$ and $j$, while $S$ is the effective cross-relaxation parameter associated with processes involving one ion in the ground state (level 1) and another ion in the excited state (level 3). The upconverted fluorescence at ~550 nm is proportional to $n_3$ and thus the numerical results obtained using Eqs. (1)–(3) could be compared with the experimental results.

The absorption cross-sections, the corresponding reduced matrix elements, and radiative relaxation rates were calculated using the Judd–Ofelt formalism.[13] The pumping rate $R_2 = \sigma_2 I / h\nu$ was determined considering the laser frequency $\nu = 4.7 \times 10^{14}$ Hz and $\sigma_2 = 5.8 \times 10^{-20}$ cm$^2$. The parameters used in the computer calculations are $W_{31} = 781$ s$^{-1}$, $W_{32} = 321$ s$^{-1}$, and $W_{21} = 109$ s$^{-1}$. The values for the cross-relaxation rate $S = 1330$ s$^{-1}$and $R_1$ were obtained by fitting the theoretical results to the experimental data. The agreement between the predicted time behavior (solid line in Fig. 3) in comparison with the experimental data for the range of intensities used indicates that the studied frequency upconversion signals are due to the PA process. The highly nonlinear intensity dependence sometimes associated with PA is not observed in the present case because $R_1 / R_2 = 6.1 \times 10^{-3}$ in agreement with the analysis of Ref. 14 which predicts that the PA threshold is not sharp when the ratio between resonant and nonresonant pumping rates is larger than $10^{-4}$.

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[1] J. S. Chivian, W. E. Case, and D. D. Eden, Appl. Phys. Lett. **35**, 124 (1979).
[2] H. Ni and S. C. Rand, Opt. Lett. **16**, 1424 (1991); *ibid.* **17**, 1222 (1992); T. Herbert, R. Wannemacher, R. M. MacFarlane, and W. Lenth, Appl. Phys. Lett. **60**, 2592 (1992); M. F. Joubert, S. Guy, and B. Jacquier, Phys. Rev. B **48**, 10 031 (1993); B. C. Collings and A. J. Silversmith, J. Lumin. **62**, 271 (1994).
[3] A. S. L. Gomes, G. S. Maciel, R. E. de Araújo, L. H. Acioli, and C. B. de Araújo, Opt. Commun. **103**, 361 (1993).
[4] F. Auzel, Y. H. Chen, and D. Meichenin, J. Lumin. **60 & 61**, 692 (1994).
[5] Y. H. Chen and F. Auzel, J. Phys., Condens. Matter. **7**, 3363 (1995).
[6] M. F. Joubert, S. Guy, C. Linarès, B. Jacquier, and J. L. Adam, J. Non-Cryst. Solids **184**, 98 (1995).
[7] R. P. de Melo, Jr., B. J. P. da Silva, E. L. Falcão-Filho, E. F. da Silva, Jr., D. V. Petrov, C. B. de Araújo, Y. Messaddeq, and M. A. Aegerter, Appl. Phys. Lett. **67**, 886 (1995).
[8] C. B. de Araújo, L. de S. Menezes, G. S. Maciel, L. H. Acioli, A. S. L. Gomes, Y. Messaddeq, A. Florez, and M. A. Aegerter, Appl. Phys. Lett. **68**, 602 (1996).
[9] L. de S. Menezes, C. B. de Araújo, G. S. Maciel, Y. Messaddeq, and M. A. Aegerter, Appl. Phys. Lett. **70**, 683 (1997).
[10] L. E. E. de Araújo, A. S. L. Gomes, C. B. de Araújo, Y. Messaddeq, A. Florez, and M. A. Aegerter, Phys. Rev. B **50**, 16 219 (1994).
[11] G. S. Maciel, C. B. de Araújo, Y. Messaddeq, and M. A. Aegerter, Phys. Rev. B **55**, 6335 (1997).
[12] R. Rieche, L. A. O. Nunes, C. C. Carvalho, Y. Messaddeq, and M. A. Aegerter, Solid State Commun. **85**, 773 (1993).
[13] B. R. Judd, Phys. Rev. **127**, 750 (1962); G. S. Ofelt, J. Chem. Phys. **37**, 511 (1962).
[14] Ph. Goldner and F. Pellé, Opt. Mater. **5**, 239 (1996).