Infrared-to-visible upconversion of Er^{3+} ions in $\text{GeO}_2\text{-PbO-Nb}_2\text{O}_5$ glasses

Rolindes Balda*

Departamento de Física Aplicada I, Universidad del País Vasco, Alameda Urquijo s/n, 48013 Bilbao, Spain, Centro Mixto CSIC-UPV/EHU, and Donostia International Physics Center, San Sebastian, Spain

Angel J. Garcia-Adeva

Departamento de Física Aplicada I, Universidad del País Vasco, Alameda Urquijo s/n, 48013 Bilbao, Spain

Joaquín Fernández

Departamento de Física Aplicada I, Universidad del País Vasco, Alameda Urquijo s/n, 48013 Bilbao, Spain, Centro Mixto CSIC-UPV/EHU, and Donostia International Physics Center, San Sebastian, Spain

José M. Fdez-Navarro

Instituto de Optica, Consejo Superior de Investigaciones Científicas, Madrid, Spain

Received April 2, 2003; revised manuscript received October 3, 2003; accepted October 20, 2003

We report the infrared-to-visible upconversion luminescence of Er^{3+} -doped lead–niobium–germanate glasses ($\text{GeO}_2\text{-PbO-Nb}_2\text{O}_5$) with different Er_2O_3 concentrations (0.5, 1, 2, and 3 wt.%) under continuous-wave and pulsed-laser excitation in the near-infrared region inside the $^4I_{9/2}$ level. Intense green emission due to the $(^2H_{11/2}, ^4S_{3/2}) \rightarrow ^4I_{15/2}$ transitions was observed at room temperature together with a weak red emission corresponding to the $^4F_{9/2} \rightarrow ^4I_{15/2}$ transition. These upconversion emissions are attributed to a two-photon process. The time evolution of the green emission from the $^4S_{3/2}$ level indicates that energy-transfer upconversion and excited-state absorption are responsible for the upconversion luminescence. The increase of the weak red emission with increasing Er_2O_3 concentration, together with its temporal behavior under infrared excitation, suggests that for Er_2O_3 concentrations higher than 1 wt.%, the upconverted red emission is the result of multiphonon relaxation from the $^4S_{3/2}$ level and energy-transfer processes. © 2004 Optical Society of America

OCIS codes: 160.5690, 300.6280, 190.7220, 160.2750, 160.4670.

1. INTRODUCTION

Recently, interest in upconversion emission in rare-earth-doped materials has increased because of the search for all-solid compact laser devices operating in the visible region and the availability of powerful near-infrared (near-IR) laser diodes. The potential applications include detection of IR radiation by conversion of the IR signal into the visible range and upconversion lasers.^{1–3} Among rare-earth-doped glass materials, erbium-doped glasses are promising host materials because of their important optical properties, which make them suitable for applications in photonics such as lasers, optical amplifiers, and frequency upconverters. Er^{3+} -doped waveguide laser and upconversion laser operations have been achieved at room temperature.^{1,2} In the near-IR spectral region, Er^{3+} has a favorable energy-level structure with the two transitions $^4I_{15/2} \rightarrow ^4I_{11/2}$ (at ≈ 980 nm) and $^4I_{15/2} \rightarrow ^4I_{9/2}$ (at ≈ 800 nm), which can be efficiently excited with high-power semiconductor lasers, yielding blue, green, and red emission. An efficient upconversion laser at 540 nm pumped with a laser diode at 800 nm has been

obtained with a higher efficiency than the one achieved by harmonic generation techniques.⁴

The upconversion efficiency is generally considered to be low in oxide glasses because of a large multiphonon relaxation rate caused by the high-energy phonons. However, oxide glasses are more appropriate for practical applications because of their high chemical durability and thermal stability. In the past, IR-to-visible upconversion has been demonstrated in several oxide glasses.^{5,6} Among oxide glasses, lead-germanate-based glasses combine high mechanical strength, high chemical durability, and temperature stability with good transmission in the IR region⁷ up to $5.5\ \mu\text{m}$, which make them promising materials for technological applications such as new lasing materials, upconverting phosphors, and optical waveguides.^{8–12} These glasses have smaller maximum vibrational frequencies than those shown by silicate, phosphate, and borate glasses.^{7,8} The reduced phonon energy increases the quantum efficiency of luminescence from excited states of rare-earth ions and the upconversion efficiency. IR-to-visible upconversion in Er^{3+} -doped

lead-germanate glasses under continuous-wave excitation has been reported by Pan *et al.*¹³ More recently, IR-to-visible upconversion in Nd³⁺-doped lead-niobium-germanate glasses and bismuth-lead-germanate glasses^{14,15} and orange-blue frequency upconversion in a Pr³⁺-doped lead-niobium-germanate glass have been reported by the authors and others.^{16,17}

In this work, in addition to characterizing the optical properties of Er³⁺ ions in lead-niobium-germanate glass (60GeO₂-25PbO-15Nb₂O₅), we report a dynamic study of the IR-to-visible frequency upconversion. The study includes one-photon (OP) absorption and emission spectroscopy and lifetime measurements for the visible and IR fluorescence, and IR-to-green and IR-to-red upconversion processes for concentrations ranging from 0.5% to 3% of Er₂O₃. The time evolution of the upconverted green emission from the ⁴S_{3/2} level indicates that energy-transfer upconversion (ETU) and excited-state absorption (ESA) processes are responsible for the upconverted emission. The increase of the weak red emission corresponding to the ⁴F_{9/2} → ⁴I_{15/2} transition with increasing Er³⁺ concentration, together with its temporal behavior, suggests that for Er₂O₃ concentrations higher than 1 wt.%, the upconverted red emission is the result of multiphonon relaxation from the ⁴S_{3/2} level and ETU processes.

2. EXPERIMENTAL TECHNIQUES

Batches of 20 g of glass have been prepared by mixing high-purity reagents GeO₂ (Alfa 99.999), PbO (Alfa 99.9995), and Nb₂O₅ (Alfa 99.999); the glass of composition 60GeO₂-25PbO-15Nb₂O₅ (GPN) was doped with 0.5-, 1-, 2-, and 3-wt.% Er₂O₃ (Alfa 99.999). This mixture was melted in a platinum crucible placed in a vertical tubular furnace at temperature between 1100 °C and 1300 °C for 1 h and then poured onto a preheated brass plate, followed by 1-h annealing at 450 °C and a further cooling at 1.5 °C/min down to room temperature. Finally, the samples were cut and polished for optical measurements.

Conventional absorption spectra were performed with a Cary 5 spectrophotometer. The steady-state emission measurements were made with an argon laser and a Ti-sapphire ring laser (0.4-cm⁻¹ linewidth) in the 760–940-nm spectral range as exciting light. The fluorescence was analyzed with a 0.25-m monochromator, and the signal was detected by a Hamamatsu R928 photomultiplier and finally amplified by a standard lock-in technique.

Lifetime measurements were obtained by exciting the samples with a dye laser pumped by a pulsed nitrogen laser and a Ti-sapphire laser pumped by a pulsed frequency-doubled Nd:YAG laser (9-ns pulse width) and by detecting the emission with Hamamatsu R928 and R5509-72 photomultipliers. Data were processed by a Tektronix oscilloscope.

3. RESULTS

A. Absorption and Emission Properties

The room-temperature absorption spectra were obtained for all samples in the 300–1700-nm spectral range. As

an example, Fig. 1 shows the absorption coefficient as a function of the wavelength for the sample doped with 2% of Er₂O₃ ($3.44 \times 10^{20} \text{ cm}^{-3}$). The inhomogeneously broadened bands are assigned to the transitions from the ⁴I_{15/2} ground state to the excited states of Er³⁺ ions. The spectra obtained for the other samples are similar, except for the band intensities, which are dependent on the Er³⁺ concentration. The integrated absorption coefficient for different absorption bands shows a linear dependence on the concentration, which indicates that the relative concentrations of Er³⁺ ions are in agreement with the nominal values.

Data from the spectrum in Fig. 1, together with the values of the refractive index ($n = 1.998$) and the Er³⁺ concentration ($3.44 \times 10^{20} \text{ cm}^{-3}$), have been used to calculate the radiative transition rates by means of the Judd–Ofelt theory.^{18,19} The absorption bands measured are all dominated by electric dipole transitions except the transition ⁴I_{15/2} → ⁴I_{13/2}, which contains electric dipole and magnetic dipole contributions. The magnetic dipole contribution f_{md} can be obtained from the equation $f_{\text{md}} = nf'$, where n is the refractive index of the studied glass and f' is a calculated quantity based on the energy-level parameters for lanthanide aquo ions.²⁰ The electric dipole oscillator strength for this transition is then obtained by subtracting the calculated magnetic dipole contribution from the experimental oscillator strength. If one employs a least-squares fitting of calculated and experimental oscillator strengths, the Judd–Ofelt parameters obtained for this glass are $\Omega_2 = 6.64 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 1.52 \times 10^{-20} \text{ cm}^2$, and $\Omega_6 = 0.97 \times 10^{-20} \text{ cm}^2$, with a root-mean-square deviation equal to 2.62×10^{-7} . These values are in agreement with those previously reported in binary lead-germanate glasses⁹ and in lead-tellurium-germanate-based glasses.²¹

The radiative transition probabilities for all excited levels of Er³⁺ can be calculated by using the Judd–Ofelt parameters. The radiative transition probability from the initial manifold $|(SL)J\rangle$ to the terminal manifold $|(S'L')J'\rangle$ is given by²²

$$A[(S, L)J; (S', L')J'] = \frac{64\pi^4 e^2}{3h\lambda^3(2J+1)} \left[n \frac{(n^2+2)^2}{9} S_{\text{ed}} + n^3 S_{\text{md}} \right], \quad (1)$$

Fig. 1. Room-temperature absorption spectrum for the sample doped with 2% of Er₂O₃.

Table 1. Predicted Radiative Transition Rates, Lifetimes, and Branching Ratios of Er³⁺ in GPN Glass

Transitions	Energies (cm ⁻¹)	A _{rad} (s ⁻¹)	τ _{rad} (ms)	β (%)
⁴ I _{13/2} → ⁴ I _{15/2}	6587	195.7 (ed) 79.6 (md)	3.63	100
⁴ I _{11/2} → ⁴ I _{15/2}	10209	285.2	3	85.6
⁴ I _{13/2}	3622	30(ed) 17.8 (md)		14.4
⁴ I _{9/2} → ⁴ I _{15/2}	12430	251	3	76.9
⁴ I _{13/2}	5843	73		22.3
⁴ I _{11/2}	2221	2.5 (md)		0.8
⁴ F _{9/2} → ⁴ I _{15/2}	15243	2673.8	0.338	90.6
⁴ I _{13/2}	8656	144.7		4.9
⁴ I _{11/2}	5034	123.4		4.18
⁴ I _{9/2}	2813	8.4		0.28
⁴ S _{3/2} → ⁴ I _{15/2}	18324	1949.7	0.344	67.1
⁴ I _{13/2}	11737	786.02		27
⁴ I _{11/2}	8115	63.2		2.17
⁴ I _{9/2}	5893	105.8		3.64
⁴ F _{9/2}	3080	0.94		0.03
² H _{11/2} → ⁴ I _{15/2}	19106	17796.04	—	—
⁴ F _{7/2} → ⁴ I _{15/2}	20430	5103.1	—	—
² H _{9/2} → ⁴ I _{15/2}	24518	2406	0.135	32.7
⁴ I _{13/2}	17931	3525.9		47.8
⁴ I _{11/2}	14309	1296.7		17.6
⁴ I _{9/2}	12088	61.5		0.83
⁴ F _{9/2}	9275	77.6		1.05

where the local field correction is $n[(n^2 + 2)^2/9]$ for electric dipole transitions and n^3 for magnetic dipole transitions. The magnetic dipole transitions have the selection rule $\Delta S = \Delta L = 0, \Delta J = 0, \pm 1$ (but not $0 \leftarrow$ or $0 \rightarrow 0$).²³ Therefore only three transitions need to be considered. These magnetic dipole transition rates were calculated by using the values for LaF₃ and were corrected for the refractive-index difference.²⁰

The radiative lifetime is related to radiative transition probabilities by

$$\tau_R = \left\{ \sum_{S', L', J'} A[(S, L)J; (S', L')J'] \right\}^{-1}. \quad (2)$$

The fluorescence branching ratio can be obtained from the transition probabilities by using

$$\beta[(S, L)J; (S', L')J'] = \frac{A[(S, L)J; (S', L')J']}{\sum_{S', L', J'} A[(S, L)J; (S', L')J']}. \quad (3)$$

The radiative transition probabilities, the branching ratios, and the radiative lifetimes of Er³⁺ in GPN glass are displayed in Table 1.

B. Infrared-to-Visible Upconversion

Visible upconversion has been observed for all samples at room temperature under continuous-wave (cw) and pulsed-laser excitation in resonance with the ⁴I_{9/2} level.

The upconverted emission spectra obtained under cw excitation were measured by using a Ti-sapphire ring laser. Cutoff filters were used to remove the pumping radiation. As an example, Fig. 2 shows the room-temperature upconverted emission spectrum of Er³⁺-doped GPN glass obtained under cw near-IR excitation at 803 nm for the sample doped with 0.5% of Er₂O₃. The observed emissions correspond to transitions ²H_{11/2} → ⁴I_{15/2} (529 nm), ⁴S_{3/2} → ⁴I_{15/2} (548 nm), and ⁴F_{9/2} → ⁴I_{15/2} (653 nm). The ²H_{11/2} → ⁴I_{15/2} emission can be observed at room temperature because the ²H_{11/2} level is populated from ⁴S_{3/2} by means of a fast thermal equilibrium between the levels. As can be observed, the most intense emission corresponds to the green emission from level ⁴S_{3/2}. The weak red emission from the ⁴F_{9/2} level is due to the population of this level from the ⁴S_{3/2} through multiphonon relaxation. The energy gap between the two levels is 3010 cm⁻¹, and the maximum phonon energy is 810 cm⁻¹. The phonon order involved in this process is approximately 4, which indicates that relaxation occurs with a moderate rate. The upconverted emission spectra are similar to those found under excitation in the ⁴F_{7/2} level at 488 nm exception made of the intensity of the red emission. Whereas in the emission spectra obtained under OP excitation the ratio between the red and green emission intensities remains constant for all concentrations, in the case of the upconverted emission there is an increase in the red emission intensity relative to the green emission with increased Er³⁺ concentration.

To investigate the excitation mechanisms for populating the ²H_{11/2}, ⁴S_{3/2}, and ⁴F_{9/2} levels after IR excitation, we have obtained the evolution of the upconverted emission intensities for different pumping powers. Upconversion intensities were recorded at 529, 548, and 653 nm for different pump powers. The upconversion emission intensity (*I*_{em}) depends on the incident pump power (*P*_{pump}) according to the relation *I*_{em} ∝ (*P*_{pump})^{*n*}, where *n* is the number of photons involved in the pumping mechanism. Figure 3 shows a logarithmic plot of the integrated emission intensity of the upconverted fluorescence at 529, 548, and 653 nm as a function of the pump laser intensity. The dependence of the intensity on the pump power is quadratic, which indicates a two-photon (TP) upconver-

Fig. 2. Upconversion emission spectrum obtained under excitation at 803 nm for the sample doped with 0.5% of Er₂O₃.

Fig. 3. Logarithmic plot of the integrated intensities of the upconverted emission from $^2H_{11/2}$ (529 nm), $^4S_{3/2}$ (548 nm), and $^4F_{9/2}$ (653 nm) levels obtained under excitation at 803 nm.

Fig. 4. Experimental emission decays curves of the (a) green and (b) red emissions obtained under excitation at 484 nm and 803 nm for the samples doped with 0.5% and 3% concentrations, respectively. Data correspond to room temperature.

sion process to populate the $^2H_{11/2}$, $^4S_{3/2}$, and $^4F_{9/2}$ levels. This in turn may be associated with ESA and/or ETU.^{24,25}

To further investigate the nature of the upconversion processes in these glasses, we performed decay time measurements by exciting the samples in resonance with the $^4I_{9/2}$ level, with a Ti-sapphire laser pumped by a frequency-doubled pulsed Nd:YAG laser. The decays and the lifetimes of the $^4S_{3/2}$ and $^4F_{9/2}$ levels were also obtained for all samples under OP excitation with a dye laser. As an example, Fig. 4(a) shows the experimental decays of the green emission at room temperature by exciting at 484 and 803 nm for the sample doped with 0.5% of Er_2O_3 . These decays are nearly single exponentials for all concentrations. As can be observed, the de-

cay curve of the upconverted emission shows a lifetime longer than that of level $^4S_{3/2}$ under direct excitation. This behavior is observed for all concentrations. The temporal evolution of the red upconverted emission shows a different behavior. For the sample doped with 1% of Er_2O_3 , the decay curves obtained under IR excitation show a lifetime similar to that of level $^4F_{9/2}$ under OP excitation. However, for concentrations higher than 1%, the lifetimes are longer than those obtained under OP excitation and longer than those of the $^4S_{3/2}$ level. As an example, Fig. 4(b) shows the experimental decay curves obtained under excitation at 484 and 803 nm for the sample doped with 3% of Er_2O_3 . In the case of the red emission, the decays obtained under OP excitation are single exponentials at all concentrations, whereas in the case of the upconverted emission, the decays of the samples doped with 2% and 3% are not single exponentials. For the sample doped with 0.5% of Er_2O_3 , the decay obtained under IR excitation is too weak to be accurately measured.

4. DISCUSSION

As we have seen in Section 3, $^2H_{11/2}$, $^4S_{3/2}$, and $^4F_{9/2}$ levels are responsible at room temperature for the observed luminescence in these glasses. The pumping power dependence of the upconverted emissions from these levels indicates that a TP upconversion process is responsible for the green and red emissions. This process may be associated with ESA involving single ions and/or ETU involving two excited ions.^{24,25}

Figure 5 shows the possible upconversion mechanisms to account for the green and red emissions under 803-nm excitation. The ($^2H_{11/2}$, $^4S_{3/2}$) levels can be populated by ESA and/or ETU. In the first case, in a first step the absorption of one IR pump photon excites the electrons to the $^4I_{9/2}$ level, then multiphonon relaxation to the $^4I_{11/2}$ level occurs, subsequently ESA of a second 803-nm pump

Fig. 5. Energy-level diagram of Er^{3+} ion in GPN glass and possible upconversion mechanisms.

photon promotes the electrons to the $^4F_{3/2,5/2}$ levels, and, finally, by nonradiative relaxation, $^2H_{11/2}$ and $^4S_{3/2}$ levels are reached. Part of the excitation energy in the $^4I_{11/2}$ level relaxes further, radiatively and nonradiatively to the $^4I_{13/2}$ level. Under this excitation condition, ESA from $^4I_{13/2}$ to $^2H_{11/2}$ can occur. Another possibility is an energy transfer from the $^4I_{11/2}$ level, in which two Er^{3+} ions in the $^4I_{11/2}$ level interact, and one ion gains energy and reaches the $^4F_{7/2}$ level whereas the other loses energy and goes to the ground state.

The time evolution of the upconversion luminescence after an excitation pulse provides a useful tool in discerning which is the operative mechanism. The radiative ESA process occurs during the excitation pulse width and leads to an immediate decay of the upconversion luminescence after excitation. Upconversion by energy transfer leads to a decay curve for the upconversion emission that shows a rise time after the laser pulse, followed by a decay and a lifetime longer than the one after direct excitation. The rise and decay times are determined by both the intermediate and upper excited-state lifetimes. This distinction is possible when the pulse width is much

Fig. 6. Temporal behavior of the upconverted $^4S_{3/2}$ luminescence for the samples doped with (a) 0.5% and (b) 2% concentration at room temperature after pulsed infrared excitation at 803 nm (open circles) and fitted to Eq. (6a) (solid curves). The insets show the same curves in semilogarithmic representation for the sake of clarity.

Table 2. Lifetimes of the $^4S_{3/2}$ Level Obtained under One-Photon Excitation at 484 nm and Infrared Excitation at 803 nm at Room Temperature

%Er ₂ O ₃	$\lambda_{\text{exc}} = 484 \text{ nm}$	$\lambda_{\text{exc}} = 803 \text{ nm}$
0.5	24.1 μs	35.3 μs
1	21.7 μs	36.4 μs
2	17.2 μs	33.1 μs
3	12.5 μs	28.2 μs

Fig. 7. Upconversion emission spectra of Er^{3+} -doped GPN glass with different Er_2O_3 concentrations: (a) 0.5%, (b) 1%, (c) 2%, and (d) 3%, obtained under excitation at 803 nm. The intensities of emission are normalized to the 548-nm band.

shorter than the time constant of the relevant energy-transfer step.²⁶ Figure 6 shows the time evolution of the upconverted $^4S_{3/2}$ emission in GPN glass at room temperature for two different Er^{3+} concentrations obtained after an IR excitation pulse of 9 ns. The insets show the same decays but in a semilogarithmic plot. The decays show a rise and a nearly exponential decay with a lifetime longer than that of the $^4S_{3/2}$ level under OP excitation, even for the sample doped with 0.5%. Table 2 presents the lifetime values of this level for all concentrations obtained under direct and IR excitation. This time dependence of the upconverted luminescence indicates the presence of an ETU process to populate the $^4S_{3/2}$ level, although the presence of an ESA mechanism cannot be disregarded. In Fig. 6, we can see that the intensity does not start at zero at $t = 0$. There is an initial population that must be due to an ESA process.

In the case of the red emission identified as the $^4F_{9/2} \rightarrow ^4I_{15/2}$ transition, the population of this level at low concentrations is due to multiphonon relaxation from the $^4S_{3/2}$ level. The concentration dependence of the upconversion red emission suggests the presence of an additional channel of population of $^4F_{9/2}$ level. As we mentioned in Section 3, in the case of the upconverted emission there is an increase in the red emission intensity relative to the green emission with increased Er^{3+} concentration. Figure 7 shows the upconversion emission spectra for all concentrations normalized to the 548-nm band. In addition, the experimental decays of the red emission obtained after IR excitation show a lengthening of the $^4F_{9/2}$ lifetime compared with the $^4S_{3/2}$ level as Er_2O_3 concentration increases.

The time evolution of the red emission obtained under excitation at 803 nm for two Er^{3+} concentrations is shown in Fig. 8. As can be observed, in this case no rise time is observed and the semilogarithmic plot shows a clear double-exponential decay. A fit to a double exponential for the decay curve of the sample doped with 2% reveals a 70% component with a lifetime $\tau_s = 15 \mu\text{s}$ and a 30% component with a lifetime $\tau_l = 76 \mu\text{s}$. For the sample doped with 3%, the fit shows a 65% component with $\tau_s = 16 \mu\text{s}$ and a 35% component with $\tau_l = 88 \mu\text{s}$. The

Fig. 8. Temporal behavior of the upconverted ${}^4F_{9/2}$ luminescence for the samples doped with (a) 2% and (b) 3% concentration at room temperature after pulsed infrared excitation at 803 nm (open circles) and fitted to Eq. (10) (solid curves). The insets show the same curves in semilogarithmic representation for the sake of clarity.

Table 3. Lifetimes of the ${}^4F_{9/2}$ Level Obtained under One-Photon Excitation at 484 nm and Infrared Excitation at 803 nm at Room Temperature^a

% Er_2O_3	$\lambda_{\text{exc}} = 484 \text{ nm}$ 653 nm (${}^4F_{9/2}$)	$\lambda_{\text{exc}} = 803$ 653 nm (${}^4F_{9/2}$)	$\lambda_{\text{exc}} = 803$ 978 nm (${}^4I_{11/2}$)
0.5	25.1 μs	—	92.6 μs
1	20.1 μs	20.1 μs	91.8 μs
2	15.1 μs	$\tau_s = 15 \mu\text{s}$, $\tau_l = 76 \mu\text{s}$	88.9 μs
3	11.8 μs	$\tau_s = 16 \mu\text{s}$, $\tau_l = 88 \mu\text{s}$	81.5 μs

^aLifetimes of the ${}^4I_{11/2}$ level are also included.

fraction of the slow component increases with Er_2O_3 concentration. Table 3 shows the lifetime values of the ${}^4F_{9/2}$ level obtained under OP excitation at 484 and 803 nm as well as the lifetime values of the ${}^4I_{11/2}$ level. It can be noted that the short lifetime of the decays of the upconverted emission is close to the ${}^4F_{9/2}$ lifetime, whereas the lifetime of the long decay is close to the one of level ${}^4I_{11/2}$. On the other hand, for the sample doped with 1-wt.% Er_2O_3 , the lifetime is similar to the one obtained under OP excitation at 484 nm. This behavior indicates that for Er_2O_3 concentrations higher than 1 wt.%, the upconverted red emission cannot be the result of multiphonon relaxation from level ${}^4S_{3/2}$ by itself; rather, additional ETU processes are involved. Different ETU processes have been proposed to account for the increase in the red emission relative to the green emission when increasing Er^{3+} concentration.^{13,27–29} Energy transfer could take place by means of transitions (${}^4I_{9/2} \rightarrow {}^4I_{13/2}$) ($\Delta E = 5843 \text{ cm}^{-1}$) and (${}^4I_{11/2} \rightarrow {}^4F_{9/2}$) ($\Delta E = 5004 \text{ cm}^{-1}$) (henceforth referred to as I) and/or (${}^4I_{11/2} \rightarrow {}^4I_{15/2}$) ($\Delta E = 10,209 \text{ cm}^{-1}$) and (${}^4I_{13/2} \rightarrow {}^4F_{9/2}$) ($\Delta E = 8656 \text{ cm}^{-1}$) (henceforth referred to as II). Another process to populate the ${}^4F_{9/2}$ level exists (henceforth referred to as III) in which two Er^{3+} ions interact, one of them in the ${}^4I_{11/2}$ level and the other in the ${}^4F_{7/2}$ level, both going to level ${}^4F_{9/2}$ (see Fig. 5). This process is nearly resonant with an energy mismatch of 182 cm^{-1} . The lifetime of a higher-energy level excited by ETU reflects those of the intermediate levels from which upward excitation takes place. Taking into account that the long decay time of the red emission is close to the lifetime of the ${}^4I_{11/2}$ level (the lifetime of level ${}^4I_{13/2}$ is 3.7 ms), the last process seems to be the most likely candidate to explain the increase in the red emission with increasing Er_2O_3 concentration. However, as we shall see in the following, this is not the case for the present host matrix. To this end, let us consider the rate equations that describe the upconversion dynamics for each of the aforementioned ETUs under pulsed excitation. In the following, we will use the notation n_1, n_2, n_3, n_4, n_5 , and n_6 to represent the populations of the ${}^4I_{15/2}, {}^4I_{13/2}, {}^4I_{11/2}$ (${}^4I_{9/2}$), ${}^4F_{9/2}$, ${}^4S_{3/2}$, and ${}^4F_{3/2}$ (${}^4F_{5/2}$) levels, respectively. The rate equations that include all the possible ETU mechanisms for IR upconversion described above are given by

$$\dot{n}_1(t) = \frac{n_2}{\tau_2} + \frac{n_3}{\tau_3} + \frac{n_4}{\tau_4} + \frac{n_5}{\tau_5} + W_t n_3^2 + \gamma_{\text{II}} n_2 n_3, \quad (4a)$$

$$\dot{n}_2(t) = -\frac{n_2}{\tau_2} + \gamma_{\text{I}} n_3^2 - \gamma_{\text{II}} n_2 n_3, \quad (4b)$$

$$\dot{n}_3(t) = -\frac{n_3}{\tau_3} - 2W_t n_3^2 - 2\gamma_{\text{I}} n_3^2 - \gamma_{\text{II}} n_2 n_3 - \gamma_{\text{III}} n_3 n_5, \quad (4c)$$

$$\dot{n}_4(t) = -\frac{n_4}{\tau_4} + W_{54} n_5 + \gamma_{\text{I}} n_3^2 + \gamma_{\text{II}} n_2 n_3 + 2\gamma_{\text{III}} n_3 n_5, \quad (4d)$$

$$\dot{n}_5(t) = -\frac{n_5}{\tau_5} - W_{54}n_5 + W_t n_3^2 + W_{65}n_6 - \gamma_{\text{III}}n_3n_5, \quad (4e)$$

$$\dot{n}_6(t) = -W_{65}n_6. \quad (4f)$$

In these expressions, W_t is the ETU coefficient for the process that populates $^4S_{3/2}$; γ_I , γ_{II} , and γ_{III} are the coefficients for the different ETU mechanisms that could populate the $^4F_{9/2}$ level; W_{54} is the multiphonon decay rate from $^4S_{3/2}$ to $^4F_{9/2}$; and τ_i are the radiative transition probabilities from level i to $^4I_{15/2}$. W_{65} represents the decay rate from $^4F_{3/2}(^4F_{5/2})$ to $^4S_{3/2}$. In writing down Eqs. (4), we involve some approximations. First, the terms describing the ESA processes are not included. The reason is that these processes occur on a timescale much shorter (the duration of the pulse) than the time scale of the green and red decays. This implies that by the time the first data points are acquired, the ESA processes have already taken place. Therefore the effect of these processes, on the time scale of interest (μs), can be replaced, to an excellent approximation, by initial populations of $^4F_{3/2}(^4F_{5/2})$ and $^4S_{3/2}$. Another approximation consists in assuming that the nonradiative transitions $^4I_{9/2} \rightarrow ^4I_{11/2}$, $^4I_{11/2} \rightarrow ^4I_{13/2}$, and $(^4F_{7/2} \rightarrow ^2H_{11/2}, ^4S_{3/2})$ occur instantaneously. This approximation is supported by the experimental fact that the radiative emissions from $^4I_{11/2}$, $^4I_{13/2}$, and $^4S_{3/2}$ exhibit no rise time under direct pumping of the $^4I_{9/2}$, $^4I_{11/2}$, and $^4F_{7/2}$ levels, respectively. For this same reason, the ETU process $(^4I_{9/2}, ^4I_{11/2}) \rightarrow (^4I_{13/2}, ^4F_{9/2})$ can be cast in the form $\gamma_I n_3^2$ to an excellent approximation.

It is easy to realize that the coupled system (4) does not admit a closed solution in terms of elementary functions. However, it is easy to find analytical approximations to this solution under some reasonable approximations. In particular, assuming that

$$\frac{n_3}{\tau_3} \gg 2W_t n_3^2 + 2\gamma_I n_3^2 + \gamma_{\text{II}} n_2 n_3 + \gamma_{\text{III}} n_3 n_5, \quad (5)$$

i.e., the radiative component is much larger than any other term that depopulates $^4I_{11/2}$, the rate equations (4) can be solved in a closed form. This approximation is usually well justified, and, in our particular case, it is experimentally observed that n_3 follows an exponential decay with a rate constant similar to τ_3 , which implies that relation (5) constitutes an excellent approximation. As we are mainly interested in identifying the mechanism that contributes the most to the red upconversion, we will solve Eqs. (4) separately for each of the possible ETU mechanisms described above, instead of giving the full solution to Eqs. (4) (which is rather cumbersome). To investigate the effect of the first proposed mechanism (see I in Fig. 5), we set γ_{II} and γ_{III} equal to zero. Under these conditions, the time evolution of the green and red emissions is given by

$$n_5(t) = -n'_{60} \exp(-W_{65}t) + n'_{30} \exp(-2t/\tau_3) + (n_{50} + n'_{60} - n'_{30}) \exp(-t/\tau_5), \quad (6a)$$

$$\begin{aligned} n_4(t) = & C_I \exp(-t/\tau_4) \\ & + n'_{60} W_{54} \frac{\tau_4}{W_{65}\tau_4 - 1} \exp(-W_{65}t) + (n_{50} \\ & + n'_{60} - n'_{30}) W_{54} \frac{\tau_4 \tau'_5}{\tau'_5 - \tau_4} \exp(-t/\tau'_5) \\ & + (n'_{30} W_{54} \\ & + n'_{30} \gamma_I) \frac{\tau_3 \tau_4}{\tau_3 - 2\tau_4} \exp(-2t/\tau_4), \end{aligned} \quad (6b)$$

where

$$\begin{aligned} C_I = & n_{40} - n'_{60} \frac{\tau_4 W_{54}}{W_{65}\tau_4 - 1} - n'_{30} W_{54} \frac{\tau_3 \tau_4}{\tau_3 - 2\tau_4} - (n_{50} \\ & + n'_{60} - n'_{30}) W_{54} \frac{\tau_4 \tau'_5}{\tau'_5 - \tau_4} - n'_{30} \gamma_I \frac{\tau_3 \tau_4}{\tau_3 - 2\tau_4} \end{aligned}$$

and we have introduced the abbreviations

$$\begin{aligned} n'_{30} = & n_{30} \left(W_t \frac{\tau_3 \tau'_5}{\tau_3 - 2\tau'_5} \right)^{1/2}, \\ n'_{60} = & n_{60} \frac{W_{65} \tau'_5}{W_{65} \tau'_5 - 1}, \quad \frac{1}{\tau'_5} = \frac{1}{\tau_5} + W_{54} \end{aligned}$$

(the latter is the measured lifetime of the $^4S_{3/2}$ level).

Taking into account that $\tau_3/2 > \tau'_5$, τ_4 , W_{65}^{-1} , W_{54}^{-1} , the asymptotic behavior of the green and red emissions for $t \gg \tau_3/2$ is given by

$$n_5(t) \sim \exp(-2t/\tau_3), \quad (7a)$$

$$n_4(t) \sim \exp(-2t/\tau_3). \quad (7b)$$

Obviously, this model is consistent with the observed time evolution of the green emission but not with the long-time behavior of the red emission, which follows an exponential decay with a decay rate similar to τ_3 . Incidentally, the asymptotic behavior of the green emission comes from the ETU term $W_t [n_3(t)]^2$, in agreement with previous considerations made in this section.

Let us now analyze the third ETU mechanism proposed above (see III in Fig. 5), the almost-resonant one, which, for this reason, seems to be the best candidate to describe the red upconversion. To leading order in γ_{III} , the solution for the green emission is also given by Eq. (6a),³⁰ whereas the temporal evolution of the red population is given by³¹

$$\begin{aligned}
n_4(t) = & C_{\text{III}} \exp(-t/\tau_4) + W_{54} \left[n'_{60} \frac{\tau_4}{W_{65}\tau_4 - 1} \exp(-W_{65}t) \right. \\
& + n'_{30} \frac{\tau_3 \tau_4}{\tau_3 - 2\tau_4} \exp(-2t/\tau_3) + (n_{50} + n'_{60} \\
& \left. - n'_{30}) \frac{\tau_4 \tau'_5}{\tau'_5 - \tau_4} \exp(-t/\tau'_5) \right] \\
& + 2\gamma_{\text{III}} n_{30} n_{50} \left(\frac{\tau_3 \tau'_5 \tau_4}{\tau_3 \tau_5 - \tau_5 \tau_4 - \tau_3 \tau_4} \right) \\
& \times \exp \left[- \left(\frac{1}{\tau_3} + \frac{1}{\tau_5} \right) t \right], \quad (8)
\end{aligned}$$

where

$$\begin{aligned}
C_{\text{III}} = & n_{40} - W_{54} \left[n'_{60} \frac{\tau_4}{W_{65}\tau_4 - 1} + n'_{30} \frac{\tau_3 \tau_4}{\tau_3 - 2\tau_4} \right. \\
& \left. + (n_{50} + n'_{60} - n'_{30}) \frac{\tau_4 \tau'_5}{\tau'_5 - \tau_4} \right] \\
& - 2\gamma_{\text{III}} n_{30} n_{50} \frac{\tau_3 \tau'_5 \tau_4}{\tau_3 \tau_5 - \tau_5 \tau_4 - \tau_3 \tau_4}.
\end{aligned}$$

Again, the asymptotic behavior of the red emission is given by

$$n_4(t) \sim \exp(-2t/\tau_3), \quad (9)$$

which is not consistent with the observed behavior.

Finally, for mechanism II described above (see II in Fig. 5), the time dependence of the red emission is given by

$$\begin{aligned}
n_4(t) = & C_{\text{II}} \exp(-t/\tau_4) + W_{54} \left[n'_{60} \frac{\tau_4}{W_{65}\tau_4 - 1} \exp(-W_{65}t) \right. \\
& + n'_{30} \frac{\tau_3 \tau_4}{\tau_3 - 2\tau_4} \exp(-2t/\tau_3) + (n_{50} + n'_{60} \\
& \left. - n'_{30}) \frac{\tau_4 \tau'_5}{\tau'_5 - \tau_4} \exp(-t/\tau'_5) \right] \\
& + n_{30} n_{20} \gamma_{\text{II}} \frac{\tau_2 \tau_3 \tau_4}{\tau_2 \tau_3 - \tau_2 \tau_4 - \tau_3 \tau_4} \\
& \times \exp \left[- \left(\frac{1}{\tau_3} + \frac{1}{\tau_2} \right) t \right] \quad (10)
\end{aligned}$$

to leading order in γ_{II} , where

$$\begin{aligned}
C_{\text{II}} = & n_{40} - W_{54} \left[n'_{60} \frac{\tau_4}{W_{65}\tau_4 - 1} + n'_{30} \frac{\tau_3 \tau_4}{\tau_3 - 2\tau_4} + (n_{50} \right. \\
& \left. + n'_{60} - n'_{30}) \frac{\tau_4 \tau'_5}{\tau'_5 - \tau_4} \right] \\
& - \gamma_{\text{II}} n_{30} n_{20} \frac{\tau_2 \tau_3 \tau_4}{\tau_2 \tau_3 - \tau_2 \tau_4 - \tau_3 \tau_4}.
\end{aligned}$$

The asymptotic behavior is then given by

$$n_4(t) \sim \exp \left[- \left(\frac{1}{\tau_3} + \frac{1}{\tau_2} \right) t \right] \approx \exp(-t/\tau_3), \quad (11)$$

where we have made use of the fact that $\tau_2 \cong 3.7$ ms, whereas $\tau_3 \cong 90$ μ s.

Therefore this mechanism is consistent with the time dependence of both the red and green emissions, i.e., the long-time behavior of the green emission follows an exponential law with a decay rate half the decay rate of the $^4I_{11/2}$ level, whereas the red emission exhibits a long-time decay component with a decay rate similar to that of the $^4I_{11/2}$ level. It could seem surprising at first that the process with the largest energy mismatch (~ 1553 cm^{-1}) is more efficient populating the $^4F_{9/2}$ level than the process with the lowest energy mismatch (ETU III, with an energy mismatch of 182 cm^{-1}). However, taking into account that the characteristic energy of the phonons in the present matrix is 810 cm^{-1} , we think it fully justified to accept that a two-phonon assisted ETU can be quite efficient at room temperature. In any case, the mathematical evidence to support this fact is indisputable.

Once the mechanism responsible for the red upconversion has been identified, we proceed to analyze the experimental decay curves in the framework of this model. To this end, the experimental decay curves for the green emission have been fitted to expression (6a) and the experimental decay curves for the red emission have been fitted to Eq. (10). The fitted parameters obtained in this way have been used as initial guesses for a more rigorous regression analysis employing the numerical solution of system (4) with γ_{I} and γ_{III} set to zero. The results of such an analysis are depicted in Figs. 6 and 8. For the green emission, we get $W_{\text{I}} = 475$ s^{-1} and 665 s^{-1} for 0.5% and 2% Er_2O_3 wt. concentration, respectively. For the red emission, we get $\gamma_{\text{II}} = 375$ s^{-1} and 545 s^{-1} for 2% and 3% Er_2O_3 wt. concentration, respectively. We think it fair to say that this model does an excellent job in describing the experimental results at all concentrations.

5. CONCLUSIONS

Absorption and luminescence measurements have been performed in Er^{3+} -doped lead-niobium-germanate glass. The Judd–Ofelt intensity parameters and radiative transition rates have been calculated. Intense green emission due to the $(^2H_{11/2}, ^4S_{3/2}) \rightarrow ^4I_{15/2}$ transitions, together with a red emission corresponding to the $^4F_{9/2} \rightarrow ^4I_{15/2}$ transition, has been observed in all samples at room temperature under excitation at 803 nm in the $^4I_{9/2}$ level and attributed to a two-photon process. The time evolution of the green and red emissions can be described by a simple model in which after initial excitation to the $^4I_{9/2}$ level, very fast nonradiative decays to the $^4I_{11/2}$ and $^4I_{13/2}$ levels occur. The $^4S_{3/2}$ level from which green emission occurs is populated by an excited-state absorption process from $^4I_{13/2}$ and the energy-transfer upconversion process $(^4I_{11/2}, ^4I_{11/2}) \rightarrow (^4I_{15/2}, ^4S_{3/2})$. This last mechanism is responsible for the long-time behavior of the green emission. Also, there is a small contribution to the population of the $^4S_{3/2}$ level coming from the

($^4F_{3/2}$, $^4F_{5/2}$) level, which is populated by an excited-state absorption process originating in the $^4I_{11/2}$ level. The $^4F_{9/2}$ level from which the red emission occurs is populated by the process ($^4I_{11/2}$, $^4I_{13/2}$) $\rightarrow$ ($^4I_{15/2}$, $^4F_{9/2}$) and multiphonon relaxation from the $^4S_{3/2}$ level, even though this process is less important than the energy-transfer upconversion mechanism for Er_2O_3 concentrations higher than 1% wt.

ACKNOWLEDGMENTS

The authors thank A. Oleaga for his assistance in lifetime measurements. This work was supported by the Spanish Science and Technology Ministry (MCYT) (MAT2000-1135 and BFM2000-0352) and the Basque Country University (UPV13525/2001). One of us (A. J. Garcia-Adeva) wants to thank the Spanish MCYT for financial support under the "Ramón y Cajal" program.

*E-mail address: wupbacrr@bi.ehu.es.

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- In fact, $n_5(t)$ contains a term of the form $\exp[n_{30}\gamma_{\text{III}}\tau_3\exp(-t/\tau_3)]$, but this gives an exponentially small contribution to the temporal behavior of $n_4(t)$ that has been neglected. The same happens with process II analyzed below.
- It is possible to find analytical solutions to all orders in γ in terms of the incomplete gamma function (also for the model that will be analyzed next). However, the solutions are cumbersome and not as easy to interpret as the approximations presented here.