Investigation of the up-conversion processes in Er^{3+}:$LiYF_4$ crystals [1 2]

Fábio Henrique Jagosich
Doutor em Tecnologia Nuclear [Materiais] – Ipen.
jagosich@ipen.br, São Paulo – SP [Brasil]

Luiz Vicente Gomes Tarelho
Doutor em Tecnologia Nuclear [Materiais] – Ipen;
Pesquisador-colaborador – Cnen/Ipen.
ltarelho@ipen.br, São Paulo – SP [Brasil]

Laércio Gomes
Doutor em Tecnologia Nuclear [Materiais] – Ipen;
Pesquisador-colaborador – Cnen/Ipen.
lgomes@ipen.br, São Paulo – SP [Brasil]

Izilda Márcia Ranieri
Doutora em Tecnologia Nuclear [Materiais] – Ipen;
Pesquisadora-colaboradora – Cnen/Ipen.
iranieri@ipen.br, São Paulo – SP [Brasil]

In this work, we investigated the up-conversion processes in $LiYF_4$ (YLF) crystals doped with 1 mol% of Er^{3+} and containing 50 mol% of Er^{3+}. The up-conversion processes include the excited state absorption (ESA) of pumping radiation process and the energy-transfer up-conversion (ETU) process. The luminescence lifetime was measured from decay curve of the $^4S_{3/2} \rightarrow {}^4I_{15/2}$ (556 nanometers [nm]) transition using pulsed laser excitations tuned between 967 and 999 nm from an optical parametric oscillator pumped by the second harmonic of a Q-switched Nd:YAG laser. We also studied the dipole-dipole and dipole-quadrupole interactions that occur among Er^{3+} ions in Er (50 mol%):YLF crystal. For this investigation, we used the Inokuti-Hirayama model that is due to an energy transfer between ions without involving the excitation migration through donors.

Key words: Energy-transfer up-conversion. Excited state absorption. Laser emission. Laser exitation.

1 Introduction

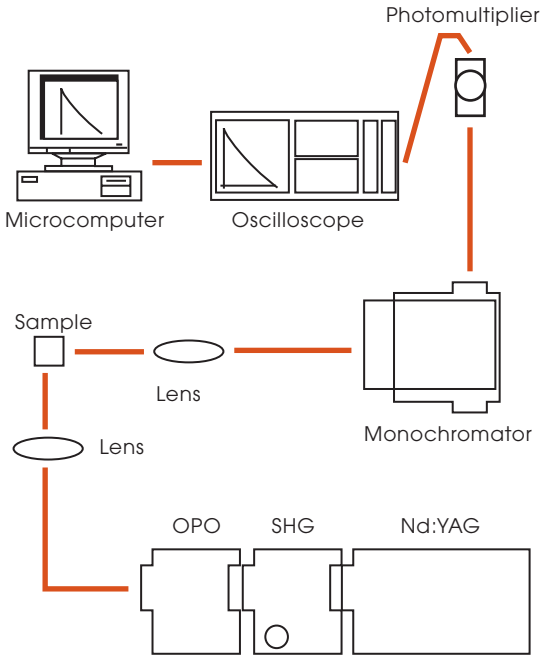
Nowadays, the spectroscopic properties of rare-earth doped crystals have been world widely investigated due to the great benefit of new infrared lasers operating at 3 micrometers (μm) range (LOTEM et al., 1988; MOULTON; ADAMKIEWICZ; WRIGHT, 1992) for medical and odontological applications (HECHT, 1993). Particularly, 2.75 μm Er-laser has been extensively used in researches on biological tissue laser radiation interaction (STRUVE; HUBER, 1991), mainly due to the laser emission being resonant with the water absorption, making it attracted to bone cutting and teeth drilling.

However, the laser energy of this system is decreased by up-conversion processes. Two of these processes are: the excited state absorption (ESA) of pumping radiation and the energy-transfer up-conversion (ETU). The ESA process is the absorption of two photons by the same ion and the ETU process is the energy transfer between two different ions. However, they can be distinguished, i.e., the ESA has an instantaneous excitation time (nanoseconds [ns]) and ETU occurs in a time longer than the ESA process microseconds (μs) (AUZEL, 1992; SCHEPS, 1996).

2 Experimental setup

The available samples were two $LiYF_4$ (YLF) single crystals doped with 1 and 50 mol% of Er^{3+}. The crystals were grown by Czochralski technique in the Crystals Growth Laboratory of Instituto de Pesquisas Energéticas e Nucleares (Ipen).

The luminescence decay curves of the Er^{3+} ions were obtained using a pulsed laser excitation from a tunable optical parametric oscillator pumped by the second harmonic of a Q-switched Nd:YAG laser from Quantel. The laser pumping was focused in the sample and the emission was focused using a CaF_2 lens into the analyzer monochromator (0.25 meters [m]) and detected with a photomultiplier (EMI S-20). The photomultiplier had a response time of 20 ns and the signal was analyzed using an oscilloscope interfaced with a microcomputer.

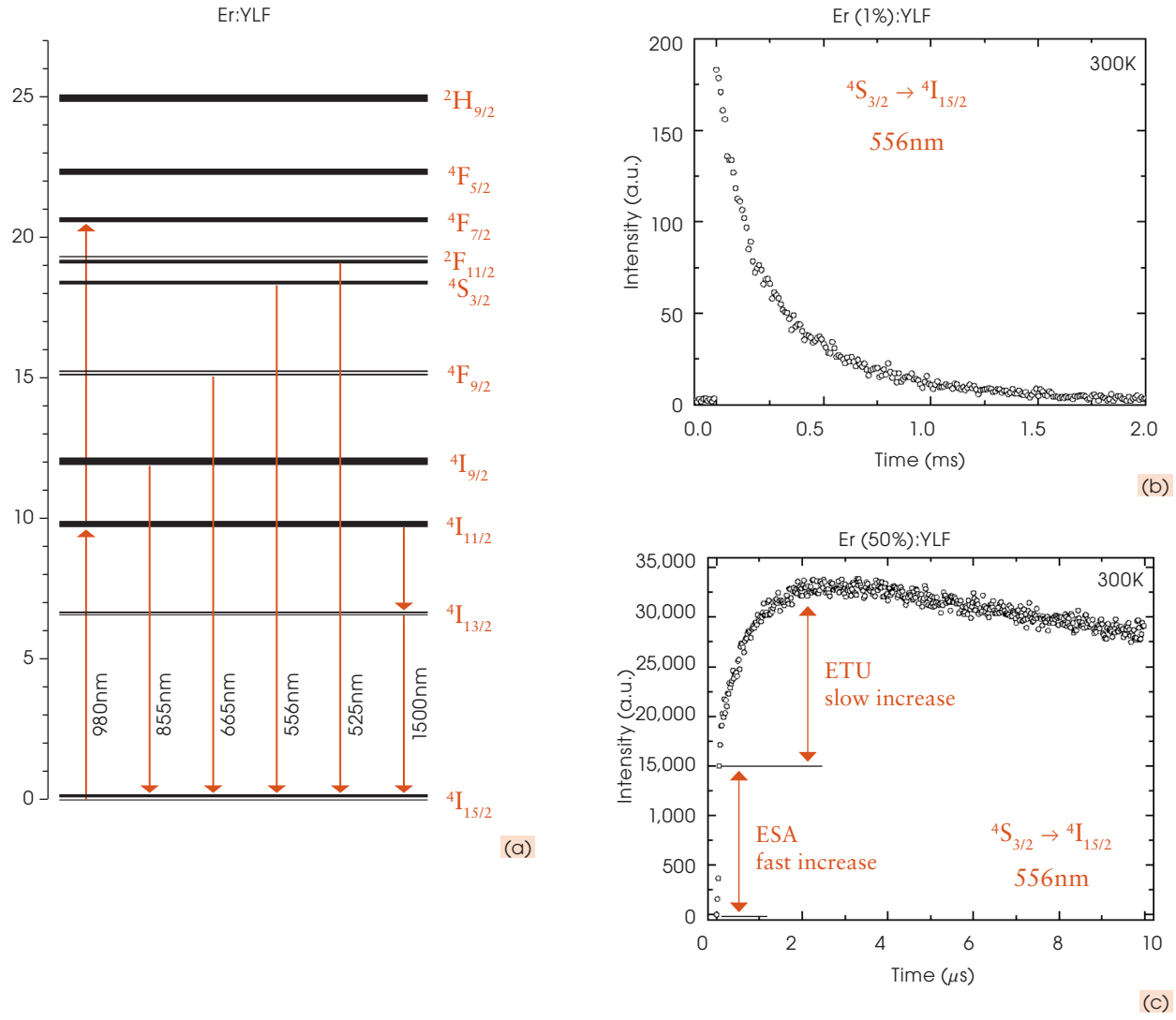


Graphic 1: Schematic representation of the time resolved spectroscopy system

Source: The authors.

3 Results and discussions: ESA and ETU discrimination

Firstly, the up-conversion processes were investigated in the Er (1 mol%): YLF crystal by pumping the $^4I_{15/2} \rightarrow {}^4I_{11/2}$ transition at 982 nm with 17 millijoules (mJ) per pulse. All the possible luminescence in the visible range that occur due to up-conversion processes are shown in the Graphic 2a. In the Graphic 2b, it is shown the strongest



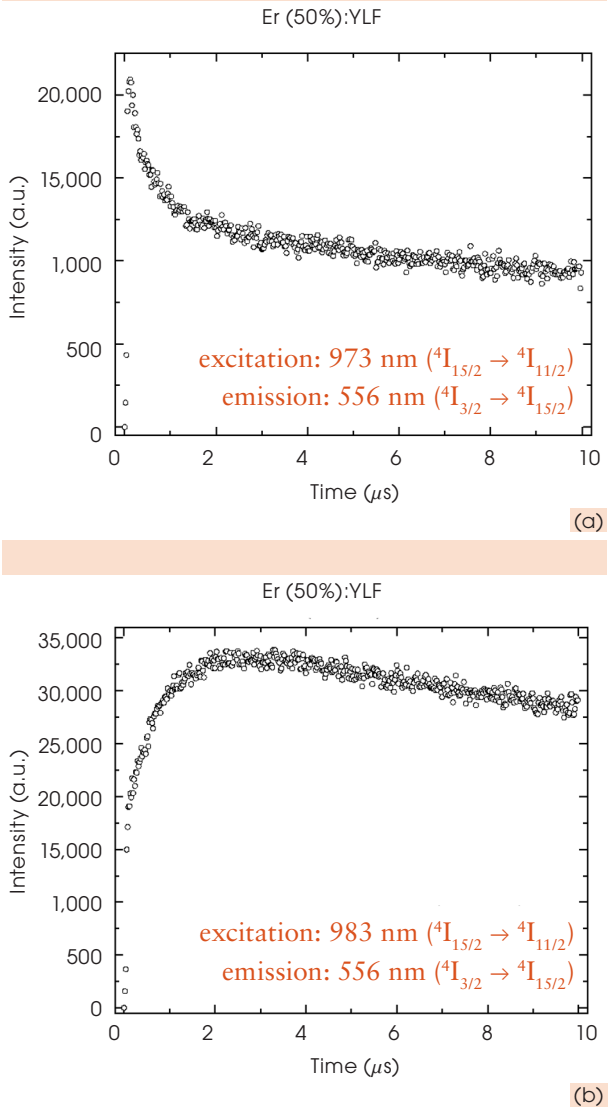
Graphic 2: (a) Diagram of the energy levels of Er^{3+} showing all the up-conversion luminescence processes involved; (b) Luminescence decay curve of the 556 nm emission for the Er (1 mol%) that occurs by ESA process; (c) Luminescence decay curve of the 556 nm emission in the Er (50 mol%) obtained by ESA and ETU

Source: The authors.

luminescence due to the $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition at 556 nm. In this illustration, one can see that the excitation time is instantaneous, hence the Er (1 mol%) presents just the ESA process. This observation confirmed that ESA is more probable to occur in low concentrated systems.

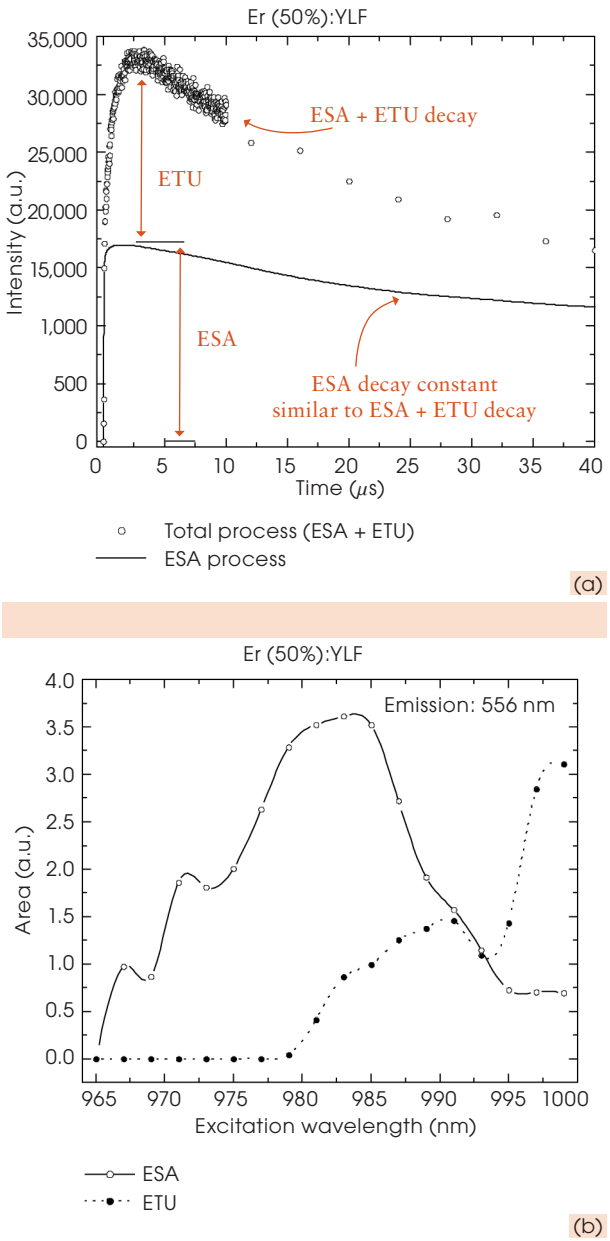
On the other hand, ETU and ESA processes occur in high concentrated crystals as it is shown in Graphic 2c by observing the luminescence of $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition at 556 nm in Er (50 mol%): YLF crystal. The ESA process follows the excitation time (ns), while the ETU process has a slow time constant (μs).

For a better understanding of the up-conversion processes in the Er (50 mol%) crystal, we varied the excitation wavelength from 965 to 999 nm (the maximum limit of the OPO laser emission). The results for 973 and 983 nm excitations are shown in Graphics 3a and 3b, as an example.



Graphic 3: Luminescence decay curves due to up-conversion processes in the Er (50 mol%): YLF with excitations at 973 (3a) and 983 nm (3b)

Source: The authors.



Graphic 4: a) Decay curve where it is shown the method for the separation between the two up-conversion processes of 556 nm luminescence; b) Contributions from ESA and ETU obtained from the areas below the luminescence decay curve

Source: The authors.

The up-conversion processes are totally dependent on the excitation wavelength, as it is seen in Graphics 3a and 3b. Both processes can be separated calculating the integrated area for each process as indicated in Graphic 4a.

For the ESA process, the rise constant is similar to the pumping duration (~20 ns) and the decay constant should be the same as observed for the total process (ESA + ETU). For the ETU process, the rise constant is slower and the area was estimated by the difference between the total integrated area of the curve and one obtained from ESA process. The acquisition of the data was done in two scales (μs and milliseconds [ms]) with 500 points each, hence the point density in the first region is higher than the second one (ms).

One can obtain the ESA and ETU excitation spectra from the integrated areas in arbitrary units, as it is shown in Graphic 4b for the sake of a comparison.

The ESA process is the only one present in the excitation range from 965 to 980 nm. However, both processes can be present for excitation in the range of 980 to 1,000 nm.

4 Dipole-dipole (d-d) and dipole-quadrupole (d-q) interactions

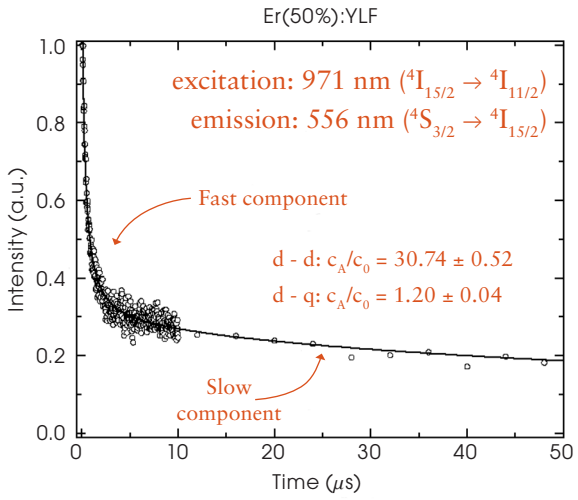
The luminescence decay time of 556 nm emission has two components and this can be seen in Graphic 5. The decay of $^4S_{3/2}$ luminescence in high doped crystal is dominated by the cross-relation process involving two Er^{3+} ions. The slow component is related to the d-d interaction and the fast component can be related to the d-q interaction.

For this investigation, we chose the excitation wavelength at 971 nm because it is present in the ESA process only. The Inokuti-Hirayama model (INOKUTI; HIRAYAMA, 1965), that was used to fit the decay and the expression by multipolar interaction, is given by:

$$\phi(t) = \sum_{s=6,8,10} \exp\left[-\frac{t}{\tau_D} - \left(\frac{c_A}{c_0}\right) \Gamma\left(1 - \frac{3}{s}\right) \left(\frac{t}{\tau_D}\right)^{\frac{3}{s}} \right]$$

where $\Gamma(x)$ is the Euler gamma function, τ_D is the intrinsic lifetime (τ_D = 590 μs for $^4S_{3/2}$), $c_A = 1.41 \times 10^{22} \times [Er]$ (cm^{-3}) is de acceptor concentration, c_0 is a critical concentration defined by $c_0^{-1} = 4\pi R_C^3/3$ and s is the multipolar interaction parameter (s = 6 for d-d and s = 8 for d-q).

Graphic 5 shows the luminescence decay curve showing the best fit obtained using the Inokuti-Hirayama expression with s = 6 and s = 8. The c_A / c_0 adjusted parameters were obtained, and with these parameters one can determine the critical radius (R_C) using the expressions above for c_A and c_0. For d-d interaction it was obtained $R_C^{d\text{-}d}$ = (10.1 ± 0.2)Å and $R_C^{d\text{-}d}$ = (3.4 ± 0.1)Å for d-q interaction.



Graphic 5: Luminescence decay curve with the best fit obtained using the Inokuti-Hirayama expression for d-d and d-q interactions

Source: The authors.

5 Final considerations

The up-conversion processes in low and high doped Er^{3+}:YLF crystals (1 and 50 mol%) were investigated using the luminescence decay curve of the $^4S_{3/2} \rightarrow {}^4I_{15/2}$ (556 nm) transition as a spectroscopic probe. In the Er (1 mol%):YLF crystal only the ESA process is present, while in the Er (50 mol%): YLF crystal we observed two up-conversion processes (ESA and ETU) where the ratio of each process is totally dependent on the laser excitation wavelength. We verified that the ESA process is more probable for the excitation wavelengths in the range of 965 to 980 nm. Nevertheless, lower wavelength can excite both processes (ESA and ETU).

Also the luminescence decay of 556 nm emission shows both components in high doped Er^{3+} crystal that are related to the d-d and d-q interactions. The luminescence decay curve was adjusted by Inokuti-Hirayama expression. The critical radius of d-d and d-q interactions could be obtained from the best fitting of the decay curve. It was interesting that the decay curve of 556 nm emission was well fitted by a model that did not involve migration through Er^{3+} ions as it was expected for highly concentrated system (50 mol%).

Notes

1 N. Ed.: Texto baseado em trabalho originalmente apresentado no XXV Encontro Nacional de Física da Matemática Condensada (ENFMC), realizado em Caxambu (MG), em 2002.

2 The authors thank Fundação de Amparo à Pesquisa do Estado de São Paulo (Fapesp) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for financial support of this work. One of the authors, Fábio Henrique Jagosich, thanks Fapesp for the fellowship.

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Recebido em: 29 mar. 2006 / aprovado em: 4 jun. 2006

Para referenciar este texto

JAGOSICH, F. H. et al. Investigation of the up-conversion processes in Er^{3+}:$LiYF_4$ crystals. *Exacta*, São Paulo, v. 4, n. 1, p. 129-134, jan./jun. 2006.