Investigation of the up-conversion processes in Er$^{3+}$:LiYF$_4$ crystals

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Abstract

In this work, we investigated the up-conversion processes in two LiYF$_4$ (YLF) crystals doped with 1 and 50 mol% of Er$^{3+}$. The up-conversion processes include the excited state absorption of pumping radiation process (ESA) and the energy-transfer up-conversion process (ETU). The luminescence lifetime was measured from decay curve of the $^4$S$_{3/2} \rightarrow ^4$I$_{15/2}$ (556nm) transition using pulsed laser excitations tuned between 967 and 999nm 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 ions in Er(50%):YLF crystal. For this investigation, we used the Inokuti-Hirayama model that is due an energy transfer between ions without involving the excitation migration through donors.

Introduction

Nowadays, the spectroscopical properties of rare-earth doped crystals have been world widely investigated due to the great benefit of new infrared lasers operating at 3μm range [1,2] for medical and odontological applications [3]. Particularly, 2.75μm Er-laser has been extensively used in researches on biological tissue laser radiation interaction [4], 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 of pumping radiation (ESA) 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 (ns) and ETU occurs in a time longer than the ESA process (μs) [5,6].

Experimental Setup

The available samples were two LiYF$_4$ (YLF) single crystals doped with 1 and 50% of Er$^{3+}$. The crystals were grown by Czochralski technique in the Crystals Growth Laboratory of 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 (0.25m) and detected with a photomultiplier (EMI S-20). The photomultiplier had a response time of 20ns and the signal was analyzed using an oscilloscope interfaced with a microcomputer.

Figure 1: Schematic representation of the time resolved spectroscopy system.
Results and Discussions

ESA and ETU discrimination

Firstly, the up-conversion processes were investigated in the Er(1%):YLF crystal by pumping the $^4I_{15/2} \rightarrow ^4I_{11/2}$ transition at 982nm with 17mJ per pulse. All the possible luminescence in the visible range that occur due to up-conversion processes are shown in the figure 2(a). In the figure 2(b), it is shown the strongest luminescence due to the $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition at 556nm. In this figure, one can see that the excitation time is instantaneous, hence the Er(1%) 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 figure 2(c) by observing the luminescence of $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition at 556nm in Er(50%):YLF crystal. The ESA process follows the excitation time ($ns$), while the ETU process has a slow time constant ($\mu s$).

For a better understanding of the up-conversion processes in the Er(50%) crystal, we varied the excitation wavelength from 965nm to 999nm (the maximum limit of the OPO laser emission). The results for 973nm and 983nm excitations are shown in figures 3(a) and (b), as an example.
The up-conversion processes are totally dependent on the excitation wavelength, as it is seen in figure 3(a) and (b). Both processes can be separated calculating the integrated area for each process as indicated in figure 4(a).

For the ESA process, the rise constant is similar to the pumping duration (~20ns) 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 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 figure 4(b) for comparison.

The ESA process is the only one present in the excitation range from 965nm to 980nm. However, both processes can be present for excitation in the range of 980nm to 1000nm.

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

The luminescence decay time of 556nm emission has two components as can be seen in figure 5. The decay of $^4S_{3/2}$ luminescence in high doped crystal is dominated by the cross-relation process involving two Er 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 the ESA process only. The Inokuti-Hirayama model was used to fit the decay and the expression by multipolar interaction [7] is given:

\[ \phi(t) = \sum_{\Delta t \Delta s} \exp \left[ -\frac{t}{\tau_0} - \left( \frac{c_A}{c_0} \right)^{\frac{1}{3}} \left( \frac{t}{\tau_0} \right)^s \right] \]

where \( \Gamma(x) \) is the Euler gamma function, \( \tau_0 \) is the intrinsic lifetime (\( \tau_0 = 590 \mu s \) for \( ^4S_{3/2} \)), \( c_A = 1.41 \times 10^{22} \) de acceptor concentration, \( c_0 \) is a critical concentration defined by \( c_0 = 4 \pi R_c^3 / 3 \) and \( s \) is the multipolar interaction parameter (\( s = 6 \) for \( d-d \) and \( s = 8 \) for \( d-q \)).

The figure 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 radii (\( R_c \)) using the expressions above for \( c_A \) and \( c_0 \). For \( d-d \) interaction it was obtained \( R_c^{d-d} = (10.1 \pm 0.2) \AA \) and \( R_c^{d-q} = (3.4 \pm 0.1) \AA \) for \( d-q \) interaction.

![Figure 5: Luminescence decay curve with the best fit obtained using the Inokuti-Hirayama expression for \( d-d \) and \( d-q \) interactions.](image)

**Conclusions**

The up-conversion processes in low and high doped Er\(^{3+} \):YLF crystals (1 and 50%) 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%):YLF crystal only the ESA process is present, while in the Er(50%):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 nm 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 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 is interesting that the decay curve of 556 nm emission was well fitted by a model that does not involves migration through Er ions as was expected for highly concentrated system (50%).

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