INVESTIGATION OF THE UP CONVERSION PROCESSES IN Ho - DOPED YLF CRYSTAL BY F_2^- COLOR CENTER LASER EXCITATION

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Abstract

An intense emission centered in 650 nm was observed in $YLiF_4$ crystals doped with Holmium, when excited by a LiF:F_2^- laser, at room temperature. This emission is due to the $^5F_5 \rightarrow {}^5I_8$ Holmium (3+) transition, and it corresponds to a two or three photon absorption process. In this work we present a discussion of all processes including a non-resonant up conversion, that are responsible for this red emission.

1. Introduction

New solid state lasers systems pumped by high-power lasers are now currently produced[1]. Fluoride crystals doped with rare-earth ions are very useful for a very large number of applications, as exemplified by the 2.07 micron (Ho:YLF) that is very convenient as medical tools[2]. High-power lasers also provide high intensity sources for the study of nonlinear effects. One of them is the up conversion process discussed in this paper, where the infrared pumping radiation can be converted into visible fluorescence[3]. We identified an anti-Stokes emission caused by a nonlinear effect, produced by high intensity pumping. A LiF:F_2^- color center laser, emitting in the region of 1153 nm, was utilized as pumping source [4]. This wavelength corresponds the fundamental absorption $^5I_8 \rightarrow {}^5I_6$ of the Ho^{3+} ions. An excited state absorption, populates the $^5F_5$ level of the Ho involving a phonon assisted absorption. The transition $^5F_5 \rightarrow {}^5I_8$ originates an emission around 658 nm. This process was studied in samples of $YLiF_4$ (YLF) doped with of 2, 5, 7 and 100 mol% of Ho^{3+}.

2. Experimental Setup

The Ho:YLF samples were grown in our crystal growth laboratory. The Yttrium and the rare-earth fluorides were synthesized from ultra-pure oxides, using the process of high temperature hydro fluorination, in an atmosphere of fluoridric acid (HF) and argon gas. The YLF was purified using the technique of zone refining at the melting temperature ,under a continuous flux of HF. The crystals were grown using the Czochralski technique under argon gas atmosphere, and the Ho ions were introduced in various concentrations 2, 5, 7 and 100 mol%, during the growth. The crystals were grown in the [100] crystallographic direction. Finally, the crystal suffered a thermal treatment under argon atmosphere, to eliminate internal stress.

The excitation and emission spectra of the samples, were obtained using a system composed by a home made LiF:F_2^- laser, a half-meter Spex monocromator, and a S-20 cathode photomultiplicator. The signal was time resolved and processed by a PAR Boxcar Averager.

The schematic diagram of the pumping system is shown in the figure 1. This system is constituted mainly by: a LiF:F_2^- color center laser (CCL) (5) pumped by a Nd:YLF laser (1-4). In this scheme, the Nd–laser crystal is Q-switched by an LiF:F_2^- crystal, which operates in coupled cavity regime. For each Nd–laser pulse at 1047 nm, the LiF:F_2^- can delivery 1 to 4 pulses with the following characteristics: 50 ns width (20 ns of separation) and 1 mJ of energy.

The total pulse width utilized was 200 μs at 10 Hz of repetition rate. The laser output wavelength of LiF:F_2^- CCL was tuned in the maximum of $^5I_8 \rightarrow {}^5I_6$ Ho transition at 1153 nm.

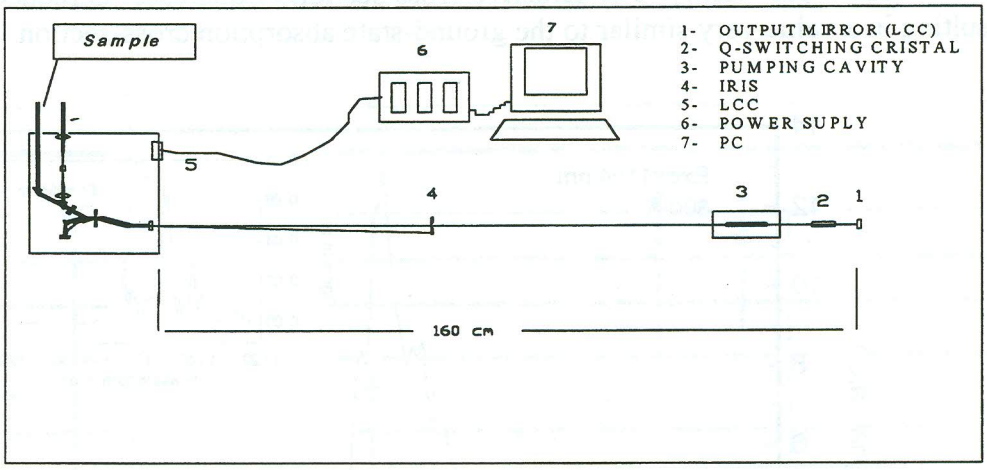


Figure 1. Schematic diagram of the pumping system constituted by a laser of YLF:Nd (1-4) and a LiF:F_2^- lasers (CCL) (5).

3. Results

The YLF crystals with various concentrations of Ho^{3+} , were excited with the CCL system. In all the samples an intense anti-Stokes emission in the red, around 658 nm was observed. This emission corresponds the $^5F_5 \rightarrow {}^5I_8$ transition, as shown by the spectrum of figure 2. The inset of figure 2 shows the excitation spectrum of the red emission showing a structure composed by convolution of three multiplets structures involved. .That measurements was obtained by tuning the CCL wavelength. The crystal with 7 mol% of Holmium presents a greater luminescence intensity comparing to the others. In this sample, the measured lifetime of $^5F_5$ level was 810 μs. Its becomes faster for the sample with 100 mol% of Holmium (160 μs), as can be seen in Figure 3. In this figure one can see also the dependence of the lifetime integration (area) with the concentration variation, showing a nonlinear behavior. The emission lifetime was verified be independent of the pumping intensity.

The observed Ho anti-Stokes fluorescence, originated from the $^5F_5$ level, exhibits an intensity (I) behavior showing a nonlinear dependence with the pumping power (P) as is shown in Figure 4. The data were fit by an $I \propto P^n$ law, with the order of the process (n) equal to 2.42.

The present result indicated the occurrence of a two and three-photon absorption processes that generate the anti-Stokes emission from the level $^5F_5$. Others expected emissions at 960 nm and 1438 nm from this level, were not observed due to the small branching ratios (0.18 and 0.11, respectively), expected and the limitation of the signal detection of our experimental set-up. No indication of emission from the $^5S_2$ and $^3F_3$ levels was obtained.

Those observations lead us to propose three possible processes leading to the up conversion fluorescence as indicated in figure 5:

1-$^5I_8 + 2\,h\upsilon \rightarrow {}^5F_5 + \Delta E$ (1 ion process)

2-($^5I_6$, $^5I_6$) $\rightarrow$ ($^5I_8$, $^5F_5$) $+\Delta E$ (2 ions process)

3-($^5I_7$, $^5I_7$, $^5I_7$) $\rightarrow$ ($^5I_8$, $^5I_8$, $^5F_5$) (3 ions process)

The process 1 is a non-resonant two-photon absorption involving a four-phonon emission ($^5I_6$ emission sideband). The value 1.5 x10^{-19} cm^2 was expected for the zero-phonon excited state absorption cross-section for the $^5I_6 \rightarrow {}^5F_5$ transition. Once this transition is phonon-assisted, the correct value for the excited-state absorption cross-section must be corrected by the phonon emission probability. The effective cross-section in this case, is reduced by a factor of 3, resulting in a value very similar to the ground-state absorption cross-section.

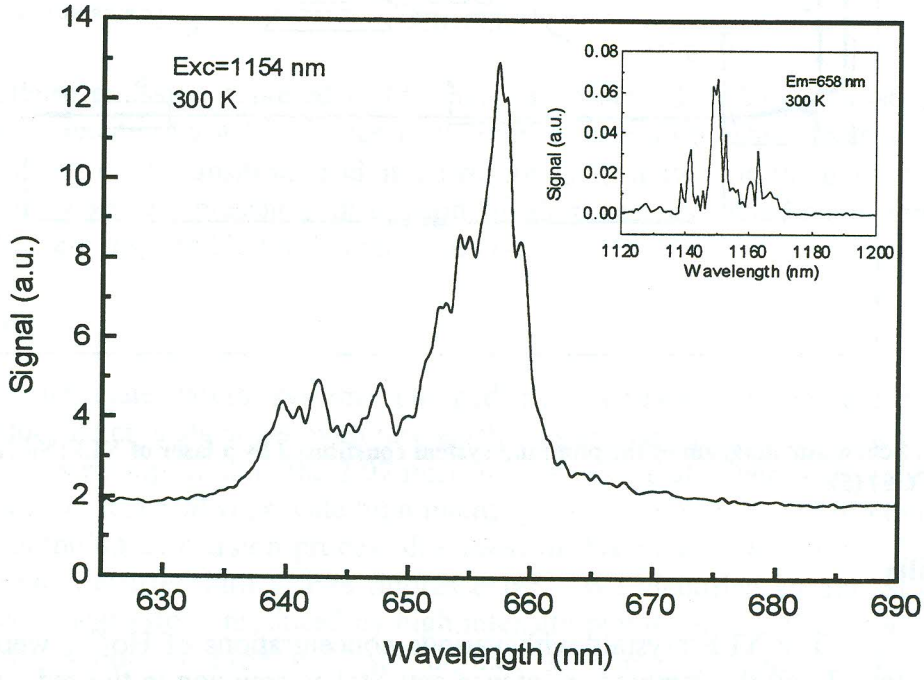
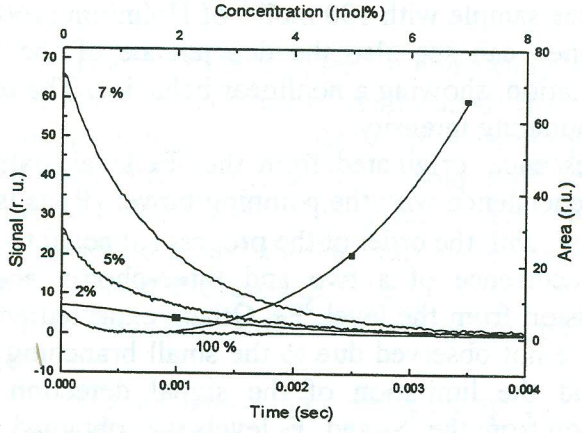


Figure 2. The emission spectrum of Ho^{3+} ($^5F_5 \rightarrow {}^5I_8$) in YLF excited by LiF:$F_2^-$ laser. The excitation spectrum is shown by the inset.



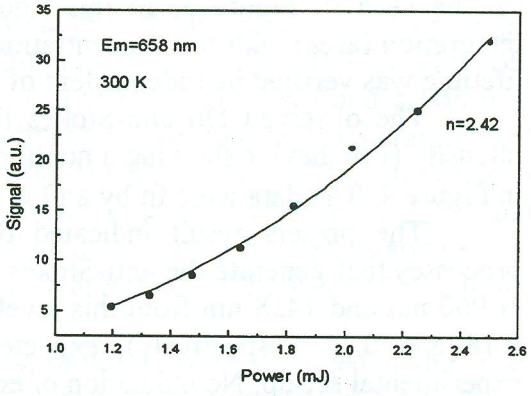


Figure 3. The luminescence lifetimes of Ho^{3+} ($^5F_5 \rightarrow {}^5I_8$) in YLF doped with 2, 5, 7 and 100 mol%, after pulsed CCL excitation (300 K). The scale at right indicates the time integrated luminescence versus Ho – concentration.

Figure 4. The dependence of Ho^{3+} ($^5F_5 \rightarrow {}^5I_8$) emission intensity on the incident pump power for YLF: Ho(7%).

The two others possible processes (2 and 3) are the Energy Transfer Up conversion (ETU)[5], where two nearestneighbors Ho ions interact[6]. In process 2 the first ion de-excites transferring its energy to the second which is promoted to the higher excited state, $^5F_5$ multiplet. This mechanism is represented by ($^5I_6$, $^5I_6$)→($^5I_8$, $^5F_5$) + ΔE. A three ions process is also possible (process 3) and is represented by: ($^5I_7$, $^5I_7$, $^5I_7$) → ($^5I_8$,$^5I_8$,$^5F_5$).

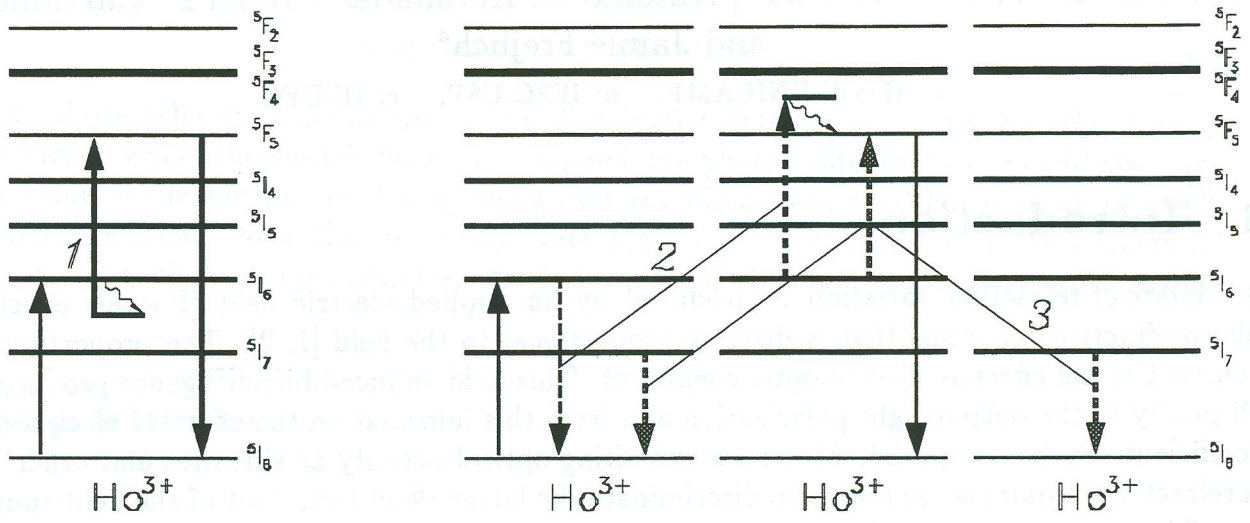


Figure 5. The two photon absorption process and the ETU processes (2,3).

4. Conclusion

Several non-resonant up-conversion processes were observed in YLF:Ho after the color center laser excitation at 1153 nm. This observation shows that the direct pumped $^5I_6$ multiplet, for lasing action at 2,1 or 2.9 microns in YLF:Ho crystal, is not the best solution, in view of the up conversion losses exhibited in this system, by the red emission.

References

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