Enhancement of blue upconversion mechanism in $YLiF_4$:Yb:Tm:Nd crystals

Lilia Coronato Courrol
Faculdade de Tecnologia de São Paulo–Laboratório de Espectroscopia Óptica CEETEPS, São Paulo, Brazil

Izilda Marcia Ranieri, Luís Vicente Gomes Tarelho, Sônia Lícia Baldochi, Laércio Gomes, and Nilson Dias Vieira Júnior
Instituto de Pesquisas Energéticas e Nucleares–Centro de Lasers e Aplicações, CNEN, São Paulo, Brazil

(Received 30 March 2005; accepted 20 October 2005; published online 5 December 2005)

In this paper we present a comparison between $YLiF_4$:Yb:Tm and $YLiF_4$:Yb:Tm:Nd systems identifying the most important processes that lead to a 20 times enhancement of thulium blue upconversion emission, under excitation around 792 nm, for the double sensitized system. Analysis of the 483 nm and 1030 nm emissions for the samples with different concentrations of Nd^{3+} ions showed that energy transfer between Nd^{3+} and Yb^{3+} is the main mechanism and responsible for the enhancement in upconversion. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2137462]

I. INTRODUCTION

The development of compact blue lasers based on thulium (Tm^{3+}) upconversion processes is nowadays widely studied mainly due to the potential of high performance OEM applications, such as biomedical and analytical instrumentation, display systems, photoprinting.[1,2]

In upconversion processes the infrared excitation is converted into shorter wavelength into the ultraviolet (UV) and visible ranges.[3] In thulium doped media, the efficiency of this process is very low, but it was noticed that the mechanism could be made one or two orders of magnitude more efficient by using ytterbium (Yb^{3+})[4] or neodymium (Nd^{3+})[5] as sensitizer ions.

In this paper, we compare the thulium sensitization by Yb and Yb/Nd in the $YLiF_4$ (YLF) host.

In YLF, the neodymium upper laser level presents a very long storage time, a natural birefringence, and a relatively weak thermal lensing. These characteristics make the YLF:Nd crystal a very important laser medium.[6] Recently, single doped YLF fibers were produced showing a very interesting new way to the develop compact low-loss and low-cost laser systems.[7]

We present here the spectroscopic characterization of the new YLF:Yb:Tm:Nd crystal, under pumping at 792 nm. This pump, in the Nd absorption band, results in a blue upconversion emission that can be used to make a YLF fiber laser.

II. MATERIALS AND METHODS

In this work we used YLF crystals grown by the Czhochraski method in different compositions: YLF:1%Tm; 10%Yb;1%Tm; and 20%Yb^{3+},0.5%Tm^{3+},x%Nd^{3+}. Three samples were cut from this last crystal from the beginning (#2), half (#5), and end (#8) that have a little Nd concentration change due to segregation coefficient. The samples were cut and polished with 2 mm thickness.

For the absorption measurements a spectrometer Cary 17D-Olis was used. For emission measurements, the samples were excited by a SDL diode laser at 792 nm, and observed by a 0.5 m Spex monochromator, Stanford chopper, PAR-EG&G lockin, Hammamatsu s-20 PMT and Germanium detector.

III. RESULTS

Figure 1 shows the absorption spectra of these two samples. Figure 2 shows the polarized spectra of the sample. When YLF samples containing Tm^{3+} co-doped with Yb^{3+} or Yb^{3+} and Nd^{3+}, are excited at 792 nm, a strong blue emission is observed. It is important to mention that the same excitation of YLF:1%Tm do not result in any detectable blue emissions.

The blue emission observed in these spectra can be understood referring to the energy levels diagram shown in Fig. 3. When the co-doped Yb/Tm sample is excited at 792 nm

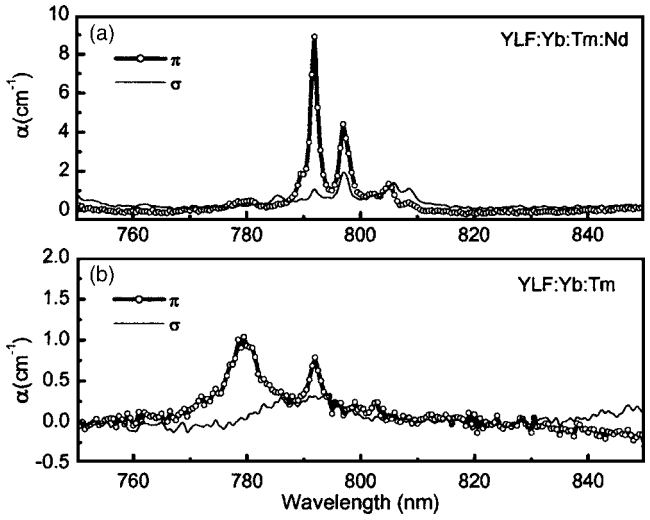

FIG. 1. Polarized absorption spectra of YLF:Yb:Tm:Nd (a) and YLF:Yb:Tm (b) samples.

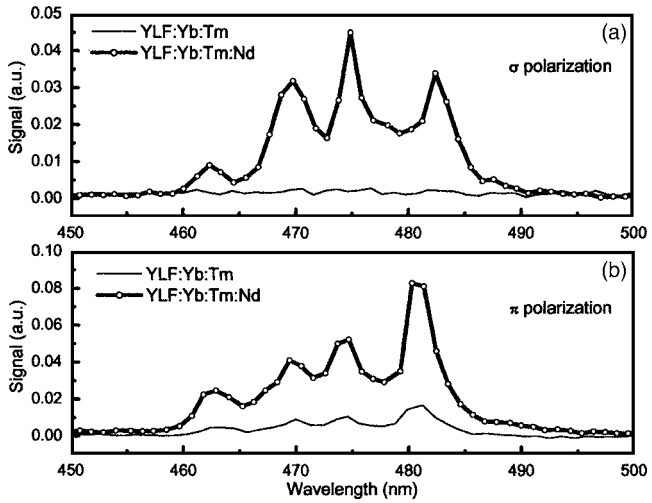

FIG. 2. Polarized emission spectra of YLF:Yb:Tm:Nd (a) and YLF:Yb:Tm (b) samples excited at 792 nm.

the following processes $\underline{a'}$, $\underline{c}$, $\underline{d}$, and $\underline{f}$ occur and populate the $Tm^{3+1}G_4$ level that emits blue. These processes are:

(a') Ground state absorption of Tm (σ_{aTm});
(c) Energy transfer Tm-Yb:

$$Tm(^3F_4) + Yb(^2F_{7/2}) \rightarrow Tm(^3H_6) + Yb(^2F_{5/2});$$

(d) Cross-relaxation Yb×Tm:

$$Yb(^2F_{5/2}) + Tm(^3F_4) \rightarrow Yb(^2F_{7/2}) + Tm(^1G_4);$$

(f) Back transfer Yb-Tm:

$$Yb(^2F_{5/2}) + Tm(^3H_6) \rightarrow Tm(^3H_5) + Yb(^2F_{7/2}).$$

The same processes are complemented by the processes $\underline{a}$, $\underline{b}$, $\underline{e}$, $\underline{g}$, $\underline{h}$, and $\underline{i}$ with the addition of Nd as co-dopant in YLF:Yb:Tm:

(a) Ground state absorption of Nd (σ_{aNd});
(b) Cross relaxation Nd×Yb,

$$Nd(^4F_{3/2}) + Yb(^2F_{7/2}) \rightarrow Nd(^4I_{11/2}) + Yb(^2F_{5/2});$$

(e) Cross relaxation Nd×Tm:

$$Nd(^4F_{3/2}) + Tm(^3F_4) \rightarrow Nd(^4I_{11/2}) + Tm(^1G_4);$$

(g) Back transfer Yb-Nd

$$Yb(^2F_{5/2}) + Nd(^4I_{9/2}) \rightarrow Yb(^2F_{7/2}) + Nd(^4I_{15/2});$$

(h) Energy transfer Nd-Tm:

$$Nd(^4F_{5/2}) + Tm(^3H_6) \rightarrow Nd(^4I_{9/2}) + Tm(^3F_4);$$

(i) Energy transfer Tm-Nd:

$$Tm(^3F_4) + Nd(^4I_{9/2}) \rightarrow Tm(^3H_6) + Nd(^4F_{5/2}).$$

TABLE I. Energy transfer parameters for the YLF:Yb:Tm:Nd crystal. The uncertainty in the cross section and lifetime values are 5% and 10% in energy transfer microparameter values.

Parameters	Values
$\sigma_{abs(\pi)}$ (Nd) (792 nm)	5.7×10^{-20} cm^2
$\sigma_{em(\pi)}$ (Nd) (1047 nm)	6.0×10^{-19} cm^2
σ_{em} (Nd) (960 nm)	2.1×10^{-21} cm^2
σ_{abs} (Yb) (960 nm)	2.1×10^{-21} cm^2
$\sigma_{absb(\pi)}$ (Tm) (792 nm)	7.3×10^{-21} cm^2
σ_{em} (Tm) (475 nm)	3.5×10^{-21} cm^2
$\tau(^2F_{7/2})$	2 ms
$\tau(^3F_4)$	15 ms
$\tau(^3H_5)$	1 ms
$\tau(^3H_4)$	2.1 ms
$\tau(^1G_4)$	750 μs
$\tau(^4F_{3/2})$	570 μs
$\underline{f}$	($C_{YbTm}=13.7\times10^{-40}$ cm^6/s; $Rc=12.0$ Å)
$\underline{c}$	($C_{TmYb}=9.1\times10^{-40}$ cm^6/s; $Rc=11.2$ Å)
$\underline{b}$	($C_{NdYb}=5.5\times10^{-40}$ cm^6/s; $Rc=9.8$ Å)

Table I shows the energy transfers parameters obtained by overlap-integral between sensitizer emission cross sections and receptor absorption cross section bands.[8] The energy transfer processes $\underline{f}$, $\underline{c}$, and $\underline{g}$ are more important that the back transfer mechanism $\underline{e}$ since this last one involves absorption of phonons least probable that creation of phonons.

The energy transfer rate between Tm-Yb in the sample containing 10%Yb:1%Tm is 660 s^{-1} and in the sample containing 20%Yb:1%Tm is 1020 s^{-1}.[4] The energy transfer efficiencies are 47% and 57% in the samples containing 10% Yb and 20% Yb, respectively. It was observed that back transfer Tm-Yb is also an important mechanism, and that Tm-Yb energy transfer grows with Yb concentration.

We observe that a small Nd concentration variation in the YLF:Yb:Tm:Nd samples results in an enhancement of the Tm blue emission as it can be seen in Fig. 4. The Nd concentration variation reflects too in an enhancement in the Yb emission band in the infrared as can be seen in Fig. 5. This indicates that the process $\underline{b}$ has high efficiency.

The blue emission comes from the $Tm^{3+1}G_4$ levels and increases with the pumping intensity with a slope of 1.6 in

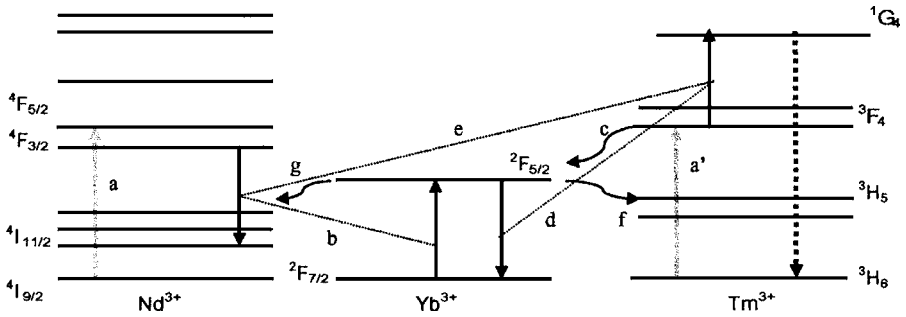

FIG. 3. Energy levels scheme and the energy transfer mechanism of the Yb/Tm/Nd system.

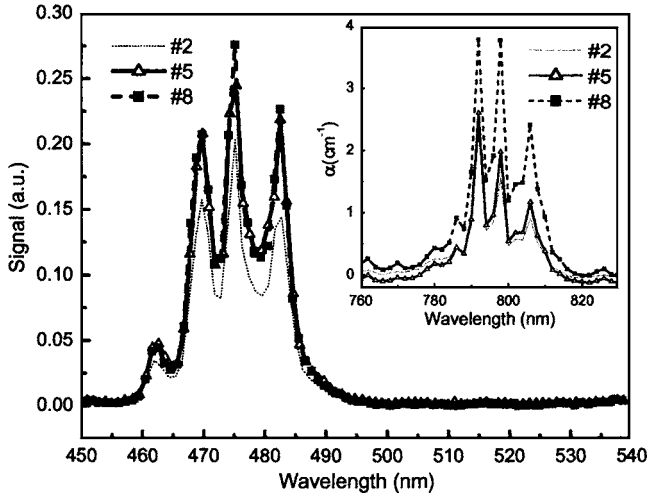

FIG. 4. Variation of Tm blue emission intensity in the three samples YLF:Yb:Tm:Nd containing different Nd concentrations. The inside figure shows the absorption coefficient of the three different samples of the YLF:Yb:Tm:Nd crystal.

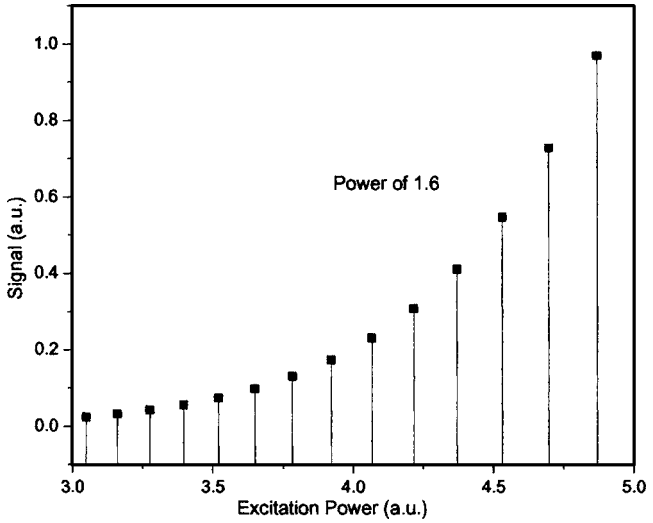

FIG. 6. Dependence of the blue emission signal with the pumping intensity.

both the Yb:Tm and Yb:Tm:Nd samples (Fig. 6 and Ref. 4), confirming that the upconversion process from the $^3F_4$ state to the $^1G_4$ state is a two photon process.

IV. CONCLUSIONS

Comparing the two different YLF compositions Yb/Tm and Yb/Tm/Nd we can conclude that:

(1) Both composition are efficient and generate blue emission by a two photon process mechanism arising from the 792 nm excitation;
(2) The YLF:Yb:Tm:Nd sample has a higher absorption coefficient at 792 nm than the YLF:Yb:Tm sample, and consequently a higher absorption cross section;
(3) Since Tm ions are directly pumped by 792 nm wavelength, the ground state can be depleted, and therefore, the transition $^1G_4 \rightarrow {}^3H_6$, at ~483 nm can be used for generating stimulated emission using ground state depletion or pump-resonant excitation methods;
(4) The cross-relaxation Nd×Tm leads to a growth in the $^1G_4$ population;
(5) A very important energy transfer mechanism between Nd and Yb ions was notice considering that no Nd emission is observed in infrared region, this fact also impeaches the Tm $^3F_4$ population decreases due to Tm-Nd interaction.

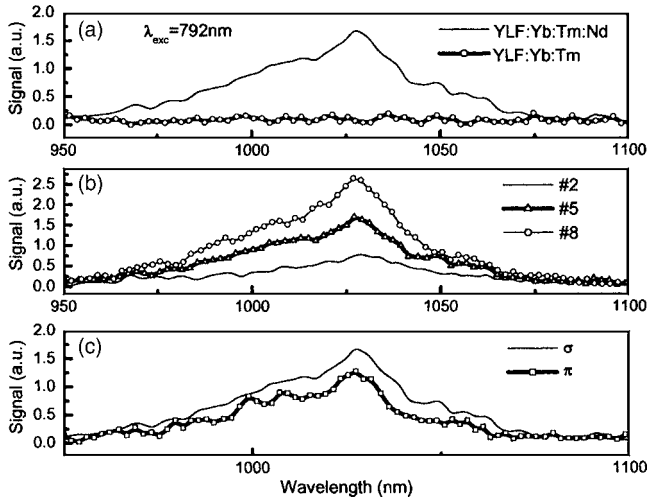

FIG. 5. (a) Variation of the infrared Yb emission band of the YLF:Yb:Tm and YLF:Yb:Tm:Nd, (b) in the three different YLF:Yb:Tm:Nd samples, and (c) variation with polarization.

The enhancement in blue emission is proportional to the enhancement in Nd absorption.

In conclusion, an enhancement in ~483 nm Tm^{3+} emission of almost 20 times was observed in the samples YLF:Yb:Tm:Nd compared to the YLF:Yb:Tm sample. This system could be interesting for development of compact laser systems using doped YLF fibers with about 5 mm in length and 300 μm in diameter, under a diode laser pump.

[1]W. P. Risk, T. R. Gosnell, and A. V. Nurmikko, *Compact Blue-Green Lasers, Cambridge Studies in Modern Optics* (Cambridge University Press, Cambridge, 2003).
[2]Lee Laser, DPSS 473-nm Microchip Blue Laser, Photonics Mini Magazine (2003).
[3]A. Wnuk, M. Kaczkan, Z. Frukacz, I. Pracka, G. Chadeyron, M.-F. Joubert, and M. Malinowski, J. Alloys Compd. **341**, 353 (2002).
[4]X. X. Zhang, P. Hong, M. Bass, and B. H. T. Chai, Phys. Rev. B **51**, 9298, (1995).
[5]N. Rakov, G. S. Maciel, M. L. Sundheimer, L. de S. Menezes, A. S. L. Gomes, Y. Messaddeq, F. C. Cassanjes, G. Poirier, and S. J. L. Ribeiro, J. Appl. Phys. **92**, 6337 (2002).
[6]E. P. Maldonado, I. M. Ranieri, S. P. Morato, and N. D. Vieira, Jr.. in *Trends, Optics and Photonics Series, TOPS, Advanced Solid State Laser*, edited by C. R. Pollock and W. R. Bosenberg (Optical Society of America, Washington, D.C., 1997), Vol. 10, pp. 444–447.
[7]A. M. E. Santo, I. M. Ranieri, G. E. S. Brito, B. M. Epelbaum, S. P. Morato, N. D. Vieira, Jr., and S. L. Baldochi, J. Cryst. Growth **275**, 528 (2005).
[8]T. Förster, Ann. Phys. **2**, 55 (1948); D. L. Dexter, J. Chem. Phys. **21**, 836 (1953).