Enhancement of blue thulium emission on Nd:Yb:Tm doped YLF crystals

Lilia C. Courrol*, Izilda M. Ranieri, Ricardo E. Samad, Sônia L. Baldochi, Laércio Gomes, Anderson Z. de Freitas, Nilson D. Vieira Junior

CEETEPS/FATEC-SP, Departamento de Ensino Geral, São Paulo, SP –Brazil, Praça Coronel Fernando Prestes, 30 – Bom Retiro CEP 01124-060
Centro de Lasers e Aplicações, IPEN/CNEN-SP, São Paulo, SP -Brazil

In this paper we present the spectroscopic properties of YLF:Yb:Tm:Nd system identifying the most important processes that lead to the thulium blue up conversion emission, under excitation around 792 nm. Analysis of the 475 nm emission 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 an enhancement in up conversion.

Keywords: YLF, Thulium, Blue, Laser, Up conversion, Energy transfer.

1. INTRODUCTION

Thulium-doped materials generate blue laser radiation through the nonlinear conversion of radiation from the infrared into visible range [1, 2]. Particularly, blue laser are important in the compact disc industry, optical storage systems, color displays and in new medical and dentistry applications and in atmospheric and physics research[3, 4, 5, 6]. The dynamics of up-conversion[7] is explained by taking into account various cross-relaxation (CR) and excited state absorption (ESA) processes. The emissions at 480 nm and 450 nm can be observed after pumping thulium ions with two or three red or infrared photons. It is well-known that the use of ytterbium as a sensitizer enhances the efficiency of the process in one or two orders of magnitude [8].

Results on glasses demonstrated an enhancement of over two orders of magnitude of the up converted emission at 480 nm when neodymium (Nd^{3+}) were cooped with thulium ions in tellurite glass, and a 40-fold enhancement of the blue emission in a fluorozirconate glass [9]. Additionally, bright blue up conversion emission through sensitization of thulium ions in lead and cadmium germanate glass triply doped with Nd–Tm–Yb under excitation around 800 nm demonstrated that for the same excitation power, the triply -cooped sample generated ten times more 475 nm blue up conversion fluorescence than the Yb^{3+}-sensitized Tm^{3+}-doped samples[10].

$YLiF_4$ (YLF) crystals doped with thulium (Tm^{3+}) and also co-doped with ytterbium (Yb^{3+})[11,12] are well-known as active media that generate stimulated radiation on a number of lines over a wide spectral range from 450 nm to 2350 nm, upon selective laser, laser diode, and flash lamp pumping [13,14,15, 16].

In this work we proposed to study the effect of Nd used as a second sensitizer to pump Tm ions in an The YLF:Yb(20mol%):Tm(0.5mol%):Nd(1mol%) crystal using a 792 nm excitation.

2. MATERIALS AND METHODS

The rare earth fluorides were prepared from pure oxide powders (Alpha-Johnson Matthey, 99.99%) by hydro fluorination at high temperature in HF atmosphere. The powder was contained in a cylindrical platinum boat, which was inserted in a sealed platinum tube. The $LiF-LnF_3$ (Ln=Y, Yb, Nd, and Tm) mixture was melted using an open platinum

boat in the same atmosphere, with a composition of 1.02 LiF: 1 LnF$_3$. LiF powder (Alpha-Johnson Matthey, 99.9%) was zone-refined before it was added to the mixture.

The studied crystal was grown by the Czochralski method using diameter automatic control, with growing rate of 1.30 mm/h and rotation rate of 15 rpm for the <100>-oriented boule. During the process, the atmosphere inside the Czochralski furnace was composed by Ar (1.4 bar) and CF$_4$ (0.2 bar). The crystal characterization has been made by the optical absorption to determine the segregation coefficients; differential thermal analysis (DTA) to verify any change on the crystal melting point; infrared absorption to detect any contamination on the crystal; powder x-ray diffraction to determine lattice parameters; and, spectroscopic characterization to study the blue emission mechanisms on this crystal.

Powder X-ray diffraction (XRD) measurements for the lattice parameter determinations were carried out on a Bruker AXS diffractometer; model D8 Advance, operated at 40 kV and 30 mA, in the 2θ range of 18-66º. The lattice constants were obtained by minimum square fittings. DTA curves were obtained in TGA-DTA equipment, model 2960, TA Instruments. The samples weighing around 50 mg were placed in open platinum crucibles without a reference material and the measurements were performed under a flux of purified helium, with a heating rate of 10^{0}C/min.

The YLF: Yb:Tm:Nd crystal with 60mm in length and 20mm in diameter is shown in **Figure 1**. Three samples were cut from this crystal from the beginning (#2), half (#5) and end (#8). Nd concentrations in each sample are 0.44, 0.63 and 1.08 mol%, respectively. 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 7220 -EG&G lock in, Hammamatsu S-20 PMT and Germanium detector.

For the lifetime measurements, the samples were pumped by a Ti:Sapphire laser at 830 nm (Coherent Odim), with 50 fs, 230 μJ and 500Hz.The signal was analyzed with a 0.5 m Spex monochromator, Hammamatsu PMT S-20 or S-1 and processed by a Lecroy WaveRunner 6051 oscilloscope.
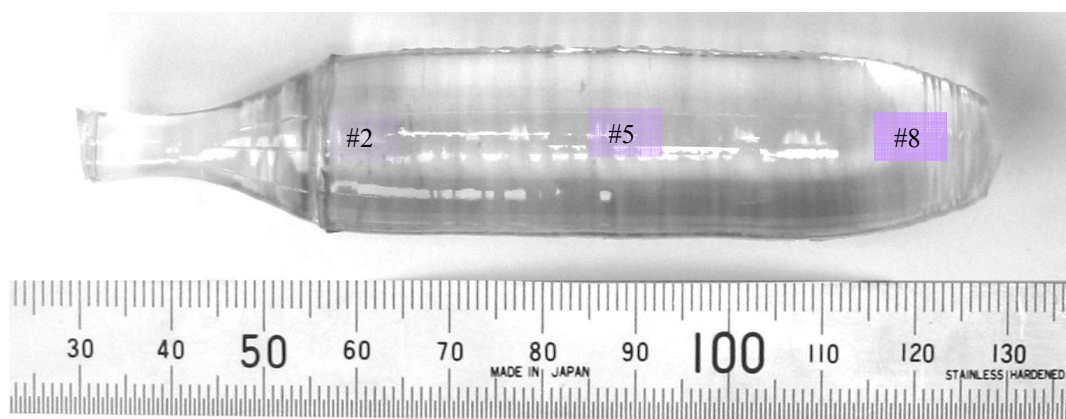

Figure 1. The crystal of YLF:Yb:Tm:Nd grown by the Czochralski method.

The infrared spectrum, showed a small OH$^-$ contamination, due to the formation of Me(OH)$_2$ complexes (Me= divalent metals) resulting from a residual water moisture on the growing atmosphere (**Figure 2**).
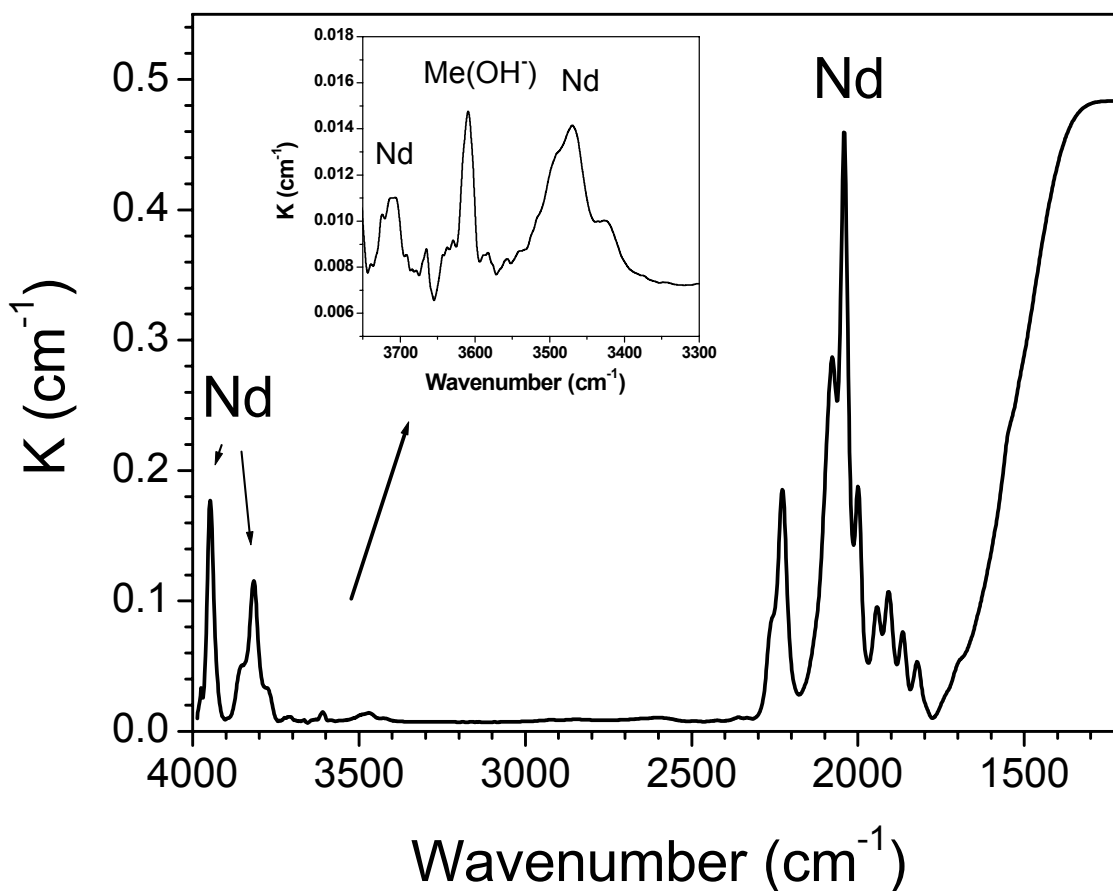
Figure 2- Absorption coefficient in the infrared of an YLF:Yb:Tm:Nd sample with 20mm thick.

This crystal presented smaller lattice parameters as compared with that of YLF crystals, due to the substitution of 20 mol% of Y by Yb, which has a shorter atomic radius (1,019 and 0,985 Å respectively) (Table I). It is noticeable a slight enhancement of the lattice parameters mainly due to the bigger concentration of Neodymium on the bottom of the crystal, as no variations of the concentrations of thulium and ytterbium along the crystal were detected by optical absorption.

Sample	Lattice parameters (Å)
2.1.1.1. YLF:Yb:Tm:Nd	a= 5,126 (1)
(top)	c= 10,622 (3)
YLF:Yb:Tm:Nd	a= 5,130 (1)
(bottom)	c= 10,628 (5)
YLF	a = 5,167 (1)
	c = 10,729 (2)

Table I- Lattice parameters determined from x-ray diffraction analysis, using Si as an internal pattern.

3. RESULTS

Figure 3 shows the absorption spectra of YLF:Yb:Tm:Nd samples in both polarizations σ and π. Obviously the higher absorption band intensity corresponds to Yb absorption band at ~960 nm in both polarizations due to high concentration of Ytterbium in the sample. However at π polarization absorption band at ~792 nm is also very intense and corresponds to neodymium absorption that have high absorption cross section.
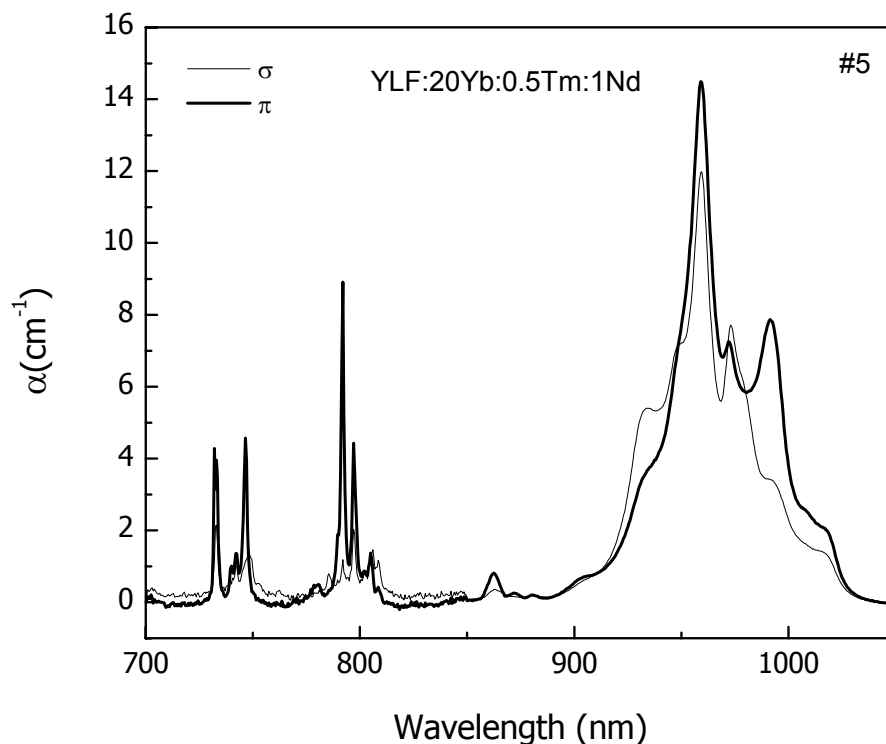

Figure 3. Polarized absorption spectra of YLF:Yb:Tm:Nd (a) and YLF:Yb:Tm (b) samples.

When YLF samples containing Tm^{3+} co-doped with Yb^{3+} and Nd^{3+}, are excited at 792nm, a strong blue emission is observed, **figure 4**. Blue emission band at 475 nm appears more intense than red emission at ~650 nm.
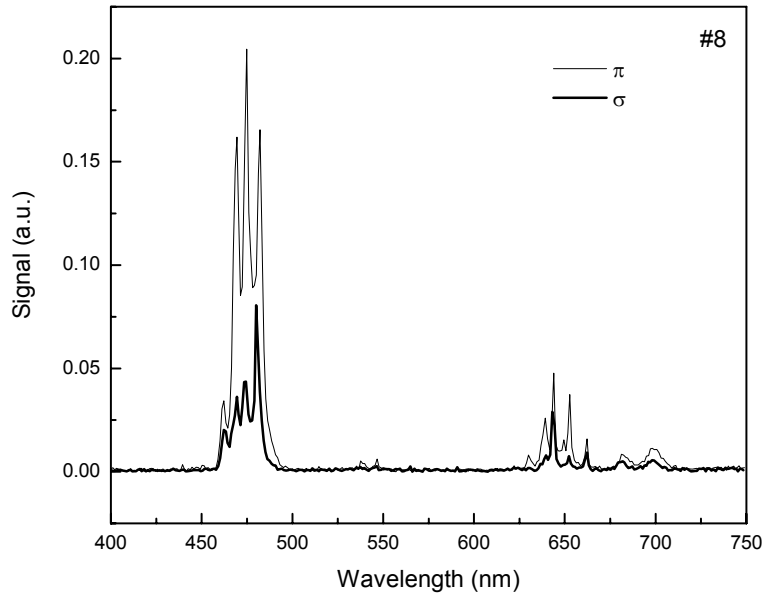
Figure 4. Polarized emission spectra of YLF:Yb:Tm:Nd (a) and YLF:Yb:Tm (b) samples excited at 792 nm.

We observe also that a small Nd concentration variation in the YLF:Yb:Tm:Nd samples results in an enhancement of the Tm blue emission as we can be seen in the **figure 5,** indicating that Nd ions have great importance on the population of $^1G_4$ Tm level.
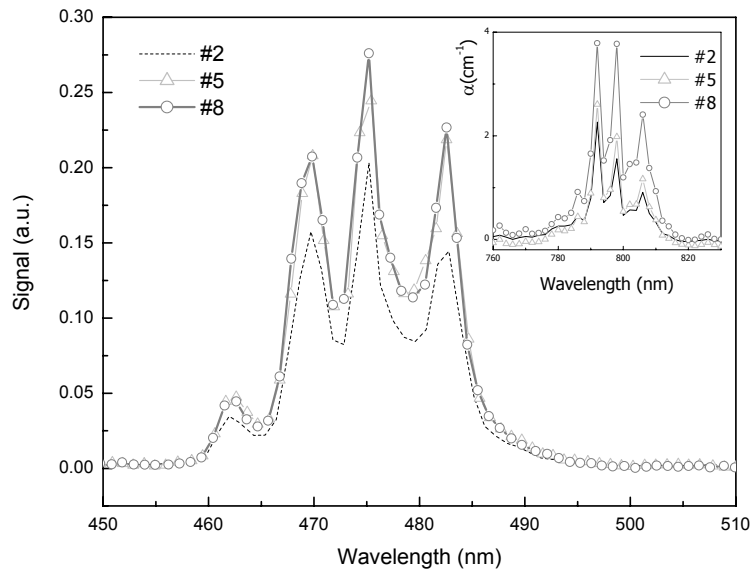

Figure 5. Variation of Tm blue emission intensity in the three samples YLF:Yb:Tm:Nd containing different Nd concentrations. The inside figure shows the absorption coefficient of the three different samples of YLF:Yb:Tm:Nd crystal.

Measured lifetimes for the emissions at 475 nm ($^1G_4$ Tm), 800 nm ($^4F_{3/2}$ Nd) and 963 nm ($^2F_{5/2}$ Yb) are shown in the **figure 6.** The blue thulium emission band shows a no exponential temporal decay for the studied samples of ~750 µs. The decays at 800 nm and 963 nm are purely exponential and preceded by a rise time since the emitting levels are indirectly excited.
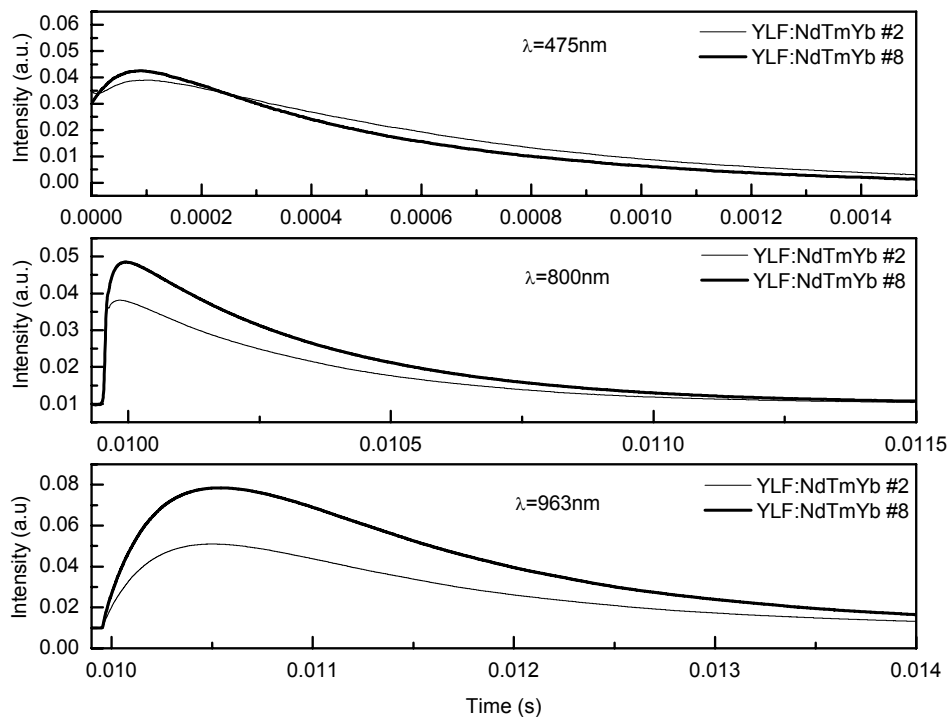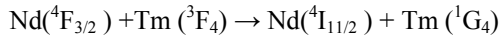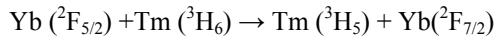

Figure 6. Fluorescence decay curves of #2 and #8 YLF:Yb:Tm:Nd crystals for the emissions at 475 nm, 800 nm and 963 nm, obtained with excitation at 830 nm.

The energy levels diagram for the Nd:Yb:Tm system is shown in the **figure 7**. When the co-doped Yb/Tm/Nd sample is excited ate 792nm the following mechanisms can coexist[17]:
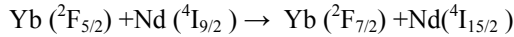
a) Ground state absorption of Nd (σ_{aNd});

a') Ground state absorption of Tm (σ_{aTm});

b) Cross relaxation Nd x Yb:

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

c) Energy transfer Tm-Yb:

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

d) Cross-relaxation Yb x Tm:

Yb($^2F_{5/2}$) +Tm ($^3F_4$) → Yb ($^2F_{7/2}$) + Tm ($^1G_4$)
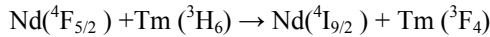
e) Cross relaxation Nd x Tm:

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

f) Back transfer Yb-Tm:

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

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:

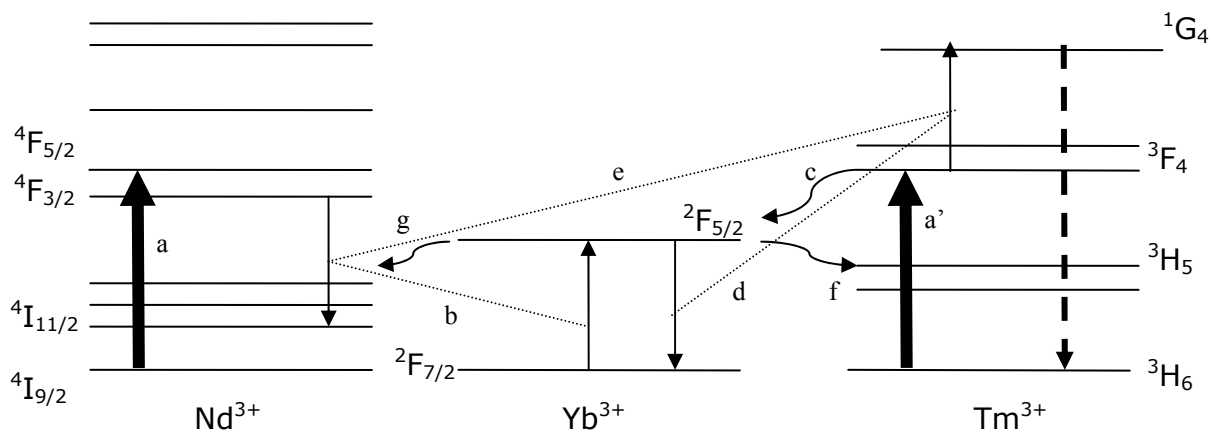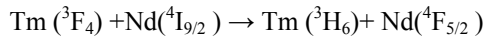$Tm(^3F_4) + Nd(^4I_{9/2}) \rightarrow Tm(^3H_6) + Nd(^4F_{5/2})$

Figure 7. Energy levels scheme and the energy transfer mechanism of Yb/Tm/Nd system.

Table II shows the energy transfers parameters obtained by overlap-integral between sensitizators emissions cross sections and receptors absorptions cross sections bands[18]. The energy transfer processes *f* , *c* and *g* are more important that the back transfer mechanism *e* since this last one involves absorption of phonons least probable that creation of phonons.

When 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 ~475 nm can be used for generate stimulated emission using ground state depletion or pump-resonant excitation methods; the cross-relaxation Nd x Tm leads to a grown in the $^1G_4$ population; 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; the enhancement in blue emission is proportional to the enhancement in Nd absorption.

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)	$3.5\ 10^{-21}\ cm^2$
τ ($^2F_{7/2}$)	2 ms
τ ($^3F_4$)	15 ms
τ ($^3H_5$)	1 ms
τ ($^3H_4$)	2.1 ms
τ ($^1G_4$)	750 μs
τ ($^4F_{3/2}$)	570 μs
$\underline{f}$	($C_{YbTm} =13.7\ 10^{-40} cm^6/s$; $Rc=12.0$ Å)
$\underline{c}$	($C_{TmYb} =9.1\ 10^{-40} cm^6/s$; $Rc=11.2$ Å)
$\underline{b}$	($C_{NdYb} =5.5\ 10^{-40} cm^6/s$; $Rc=9.8$ Å)

Table II. Energy transfer parameters for YLF:Yb:Tm:Nd crystal. The uncertaininess in the cross section and lifetime values are 5% and 10% in energy transfer micro parameters values.

4. CONCLUSIONS

In this paper it was demonstrate that good quality YLF:Yb:Tm:Nd crystals can be obtained, and that the addition of Nd as a second sensitizer for YLF:Yb:Tm crystals improve the up conversion mechanism that gives rise to the Tm blue emission in 475 nm. As the enhancement in Tm blue emission and the Yb emission in the infrared are proportional to the increase in Nd absorption, it can be conclude that there is an efficient mechanism of energy transfer from Nd to Yb and from Yb to Tm. However the concentration of Nd in the crystal must be around 0.8 mol% to prevent back transfer form Yb to Nd, which is detrimental to the blue emission of Tm.

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