Study of Blue Thulium Emission on Nd:Yb:Tm Doped YLF Crystal Pumped at 792 nm and 965 nm

Lilia Coronato Courrol

CEETEPS/Fatec-SP, Departamento de Ensino Geral, Praça Coronel Fernando Prestes, 30, 01124-060, São Paulo, Brazil

e-mail: lcourrol@fatecsp.br

Izilda Marcia Ranieri, Luiz Vicente Gomes Tarelho, Sônia Lícia Baldochi, Niklaus Ursus Wetter, Laércio Gomes, Nilson Dias Vieira Júnior

CNEN/IPEN-SP, Centro de Lasers e Aplicações

Abstract

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 and 965 nm. Analysis of the 450 and 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 the anti-Stokes emission. Advantages and disadvantages of the pumping wavelength are described.

Introduction

Thulium-doped materials generate blue laser emission through the nonlinear conversion of radiation from the infrared into visible range [1], after various cross-relaxation (CR) and excited state absorption (ESA) processes [2]. Particularly, blue laser is 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]

$YLiF_4$ (YLF) crystals doped with thulium (Tm^{3+}) and also co-doped with ytterbium (Yb^{3+}) [4] [5] 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 [6, 7, 8]. It was demonstrating that the addition of Nd^{3+} 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 [9].

In this work we compare the blue thulium emission obtained pumping the YLF:Yb(20mol%):Tm(0.5mol%):Nd(xmol%) (with x=0.44, 0.63 and 1.08mol%) crystals at two different wavelengths: 797 nm or 965 nm.

Experimental Setup

The rare earth fluorides were prepared from pure oxide powders (Alpha-Johnson Matthey, 99.99%) by hydrofluorination 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 YLF:Yb:Tm:Nd crystal with 60 mm in length and 20 mm 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 or a GaAlAs laser diode (Optopower A020) at 965 nm, and observed by a 0.5 m Spex monochromator, Stanford chopper, PAR 7220 -EG&G lockin, Hammamatsu S-20 PMT and Germanium detector.

Results and Discussions

Figure 2 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.

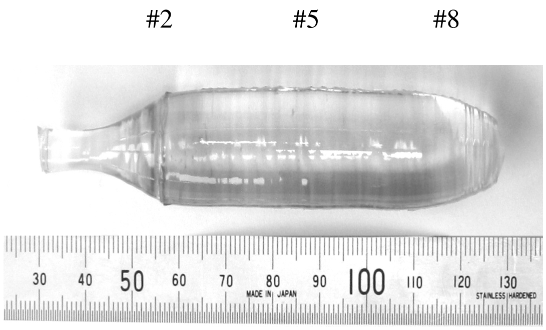

Figure 1. The crystal of YLF:Yb:Tm:Nd grown by the Czochralski method.

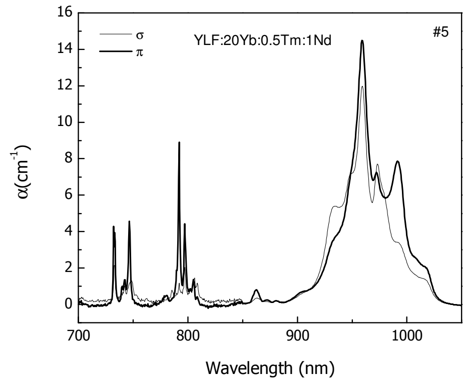

Figure 2. Polarized absorption spectra of YLF:Yb:Tm:Nd crystal.

When YLF samples containing Tm^{3+} co-doped with Yb^{3+} and Nd^{3+}, are excited at 792 nm, a strong blue emission is observed, **figure 3**. Blue emission band at 475 nm, due to the transition $^1G_4$ T^3H_6, appears more intense than red emission at ~650 nm.

We observe also for excitation at 792 nm that a little 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 4,** indicating that the presence of Nd ions is important on the population of $^1G_4$ Tm level.

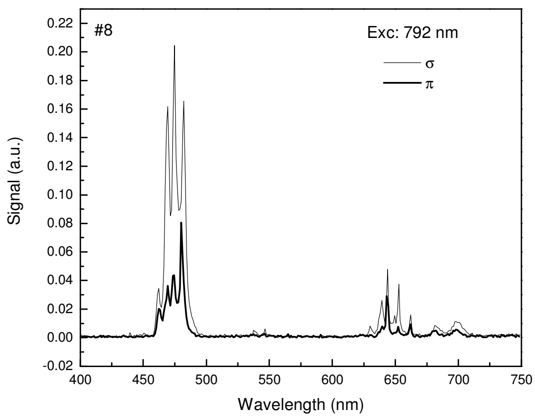

Figure 3. Polarized emission spectra of YLF:Yb:Tm:Nd excited at 792 nm.

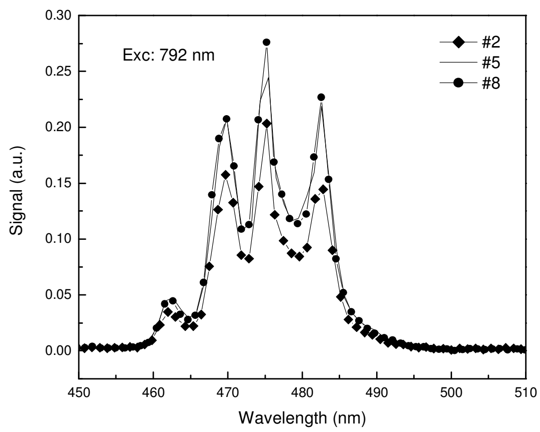

Figure 4. Variation of Tm blue emission intensity in the three YLF:Yb:Tm:Nd samples containing different Nd concentrations.

Figures 5 and **6** show the results obtained exciting sample (#8) at 965 nm. We can observe some differences with regard to 797 nm excitation. The first one is the presence of the thulium emission band at 450 nm due to the $^1D_2T^3F_4$ transition. This emission is very interesting for the construction of an up conversion laser since does not terminate in the ground state. The thulium $^1D_2$ level can be populated via a cross relaxation process between Tm: $^1G_4$ level a Tm: $^3F_4$ level. The emission originates from the transition ^1D_2T $^3H_6$ around 360 nm can be also observed (**figure 7**). The second remarkable difference between two excitations is the polarization dependence. Emission obtained for σ polarization is most intense than π polarization for 797 nm excitation while for 965 nm excitation π polarization is most intense than σ polarization. Finally we observe for 797 nm excitation that emission has a second order dependence with pumping power while for 965 nm excitation a third order dependence was observed (**figure 7**). We can also observe similarities: both excitations 797 nm or 965 nm result in very strong blue luminescence and the blue emission intensity depends on Neodymium concentration for both cases (figure 6).

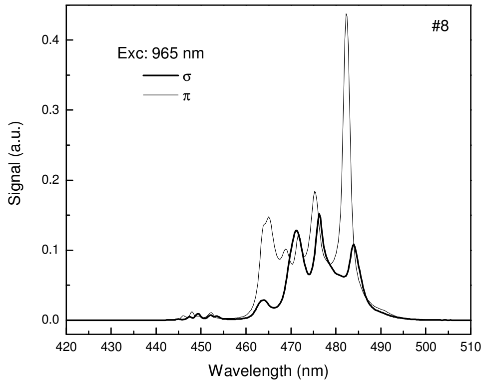

Figure 5. Polarized emission spectra of YLF:Yb:Tm:Nd sample excited at 965 nm.

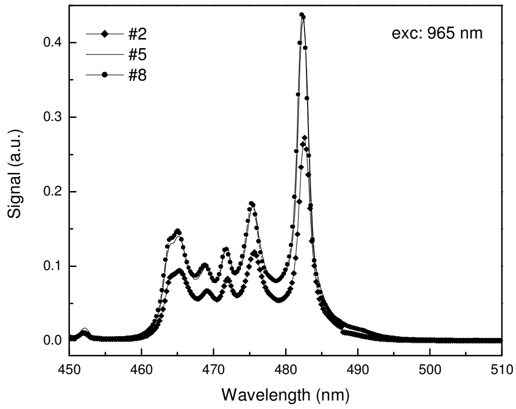

Figure 6. Variation of Tm blue emission intensity in the three samples YLF:Yb:Tm:Nd containing different Nd concentrations.

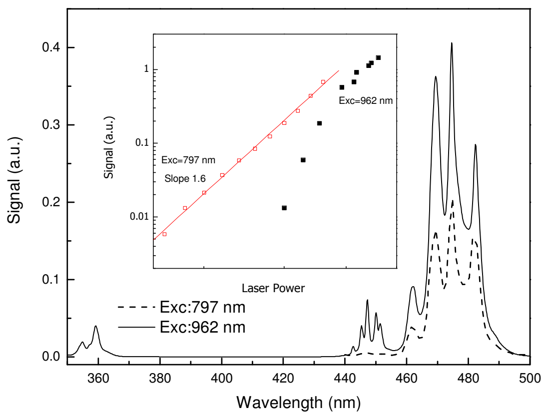

Figure 7. Comparisons between the excitations at 797 nm and 965 nm and blue thulium emission intensity at 476 nm as a function of diode laser pump power (inside figure).

The energy transfer mechanisms involved in the up conversion process resulting in the generation of the blue emission are presented in the Fig. 8. The following mechanisms can coexist with excitation at 797 nm: a)Ground state absorption of Nd; a')Ground state absorption of Tm; b) Cross relaxation between Nd and Yb: Nd($^4F_{3/2}$) +Yb ($^2F_{7/2}$) → Nd($^4I_{11/2}$) + Yb ($^2F_{5/2}$); c) Energy transfer from Tm to Yb: Tm ($^3F_4$) +Yb ($^2F_{7/2}$) → Tm ($^3H_6$) +Yb($^2F_{5/2}$); d) Cross-relaxation between Yb and Tm: Yb($^2F_{5/2}$) +Tm ($^3F_4$) → Yb ($^2F_{7/2}$) + Tm ($^1G_4$); e) Cross relaxation between Nd and Tm: Nd($^4F_{3/2}$) +Tm ($^3F_4$) → Nd($^4I_{11/2}$) + Tm ($^1G_4$); f) Back transfer from Yb to Tm: Yb ($^2F_{5/2}$) +Tm ($^3H_6$) → Tm ($^3H_5$) + Yb($^2F_{7/2}$); g) Back transfer from Yb to Nd: Yb ($^2F_{5/2}$) +Nd ($^4I_{3/2}$) → Yb ($^2F_{7/2}$) +Nd($^4I_{11/2}$); h) Energy transfer from Nd to Tm: Nd($^4F_{5/2}$) +Tm ($^3H_6$)→ Nd($^4I_{9/2}$) + Tm ($^3F_4$); and i) Energy transfer from Tm to Nd: Tm ($^3F_4$) +Nd($^4I_{9/2}$) → Tm ($^3H_6$)+ Nd($^4F_{5/2}$). With excitation at 965 nm, the cross relaxation process (h) between Yb and Tm: Yb($^2F_{5/2}$) +Tm ($^1G_4$) → Yb ($^2F_{7/2}$) + Tm ($^1D_2$), the energy transfer (i) between Tm and Nd ($^3F_4$) + Nd ($^4I_{9/2}$) → Tm ($^3H_6$) +Nd($^4F_{3/2}$) and the cross-relaxation process (j) between Nd and Tm Nd ($^4F_{3/2}$) + Tm ($^1G_4$) → Nd($^4I_{11/2}$) + Tm ($^1D_2$) populates $^1D_2$ level.

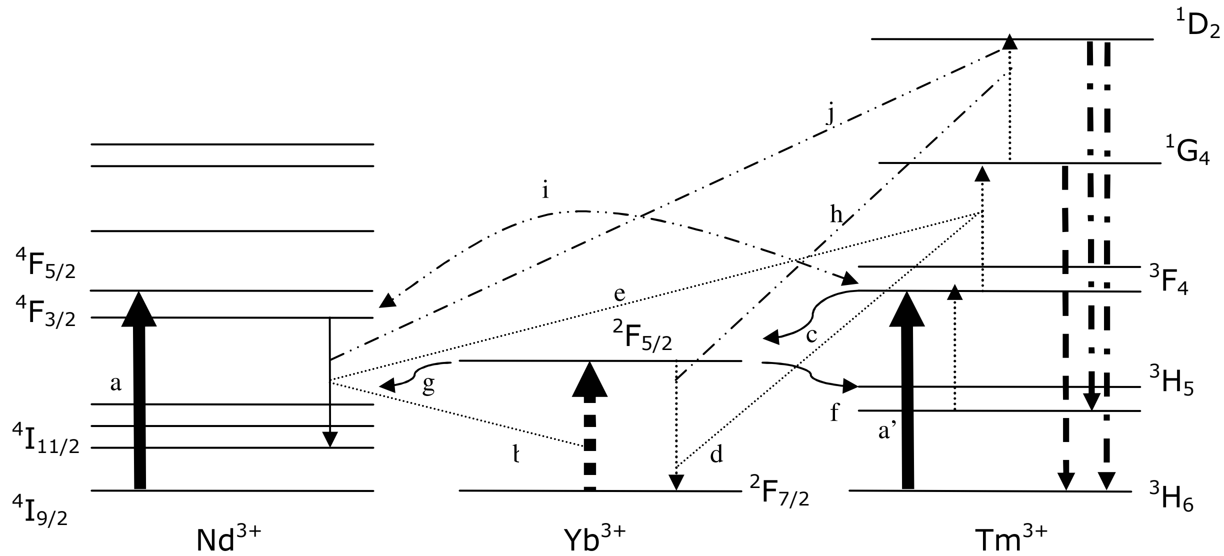

Figure 8. Energy levels scheme and energy transfer mechanisms of Yb/Tm/Nd system. Continuous line (up) 797 nm excitation, dashed line (up) 965 nm excitation. Dash dot line (down) blue thulium emissions. Dot lines (up and down) Yb emission and cross relaxation processes.

Conclusions

Strong blue thulium emission was observed exciting Yb:Tm:Nd doped YLF crystals at 797 nm or 965 nm. The blue emission is dependent of neodymium concentration in both excitations. The blue thulium emission at 476 nm has a second order dependence with diode laser pump power at 797 nm and a third order dependence with diode laser pump power at 965 nm. UV emission at 360 nm and blue emission at 450 nm can be observed pumping the crystal at 965 nm.

Acknowledgements

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