The role of Nd^{3+} in the population inversion between $^1G_4$ and $^3H_6$ states of Tm^{3+} in Yb:Nd:Tm:YLF crystal [1]

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In this paper, we present the energy transfer rates of YLF:Yb:Tm:Nd system, identifying the most important processes that lead to the thulium blue upconversion emission under excitation around 792 nm. The calculation of the rate equations system based on numerical method using Runge-Kutta method was employed for analyzing the population inversion between $^1G_4$ and $^3H_4$ states of Tm^{3+}. Population inversion was achieved only in Yb:Nd:Tm doped YLF crystal, which exhibits a pumping rate threshold of 620 s^{-1}. The Nd^{3+} absorption near 792 nm is very important because the excitation is rapidly transferred to Yb^{3+}, that also interacts with Tm^{3+}.

Key words: Tm^{3+} blue emission upconversion. Numerical simulation.

1 Introduction

Thulium-doped materials generate blue laser emission through the nonlinear conversion of radiation from the infrared into visible range (GOSNELL et al., 2003), after various cross-relaxation (CR) and excited state absorption (ESA) processes (CHADEYRON et al., 2002). 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 (MEIJERINK et al., 2002).

$LiYF_4$ (YLF) crystals doped with thulium (Tm^{3+}) and also co-doped with ytterbium (Yb^{3+}) (BASS et al., 1995; CASSANJES et al., 2002) 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 (JOUBERT, 1999; BASS et al., 2004; GOMES et al., 2004). It was demonstrated that the addition of Nd^{3+} as a second sensitizer for YLF:Yb:Tm crystals improves the upconversion mechanism that gives rise to the Tm^{3+} blue emission in 475 nm (BALDOCHI et al., 2005).

In this work, we compare the blue thulium emission obtained after pumping the YLF: Yb(20mol%):Tm(0.5mol%):Nd(1%) crystal at two different wavelengths: 792 nm or 960 nm.

2 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 60mm in length and 20mm in diameter was used. Samples were cut from this crystal (middle). Nd concentration was measured to be 1 mol%. The samples were cut and polished with 2 mm thickness.

The absorption spectra of the glasses were measured by using a spectrophotometer (Cary/OLIS17D) operating in the range of 300-2000 nm. For emission and lifetime measurements of the excited states of the Yb^{3+},Tm^{3+} and Nd^{3+} ions. The sample was excited by laser radiation generated by tunable optical parametric oscillator (OPO), which was pumped by the second harmonic of a *Q*-switched Nd-YAG laser (Brilliant B from Quantel) of 4 ns and 10 HZ; and observed by a 0.25 m Kratos monochromator, EGG Bos car Processor, EMI S-20 PMT and InSb 77K infrared detector (Judson).

All the fluorescence decay times were measured at 300 K. In order to isolate these luminescence signals, band pass filters with ~80 % transmission at 1200 and 2000 nm (each with a half width of 15 nm and an extinction coefficient of $\sim 10^{-5}$) was used.

3 Results and discussions

YLF:Yb:Tm:Nd crystal has two main absorptions in the near infrared at ~960 nm (Yb^{3+}) and near 792 nm due to Nd^{3+} and Tm^{3+} ions, which

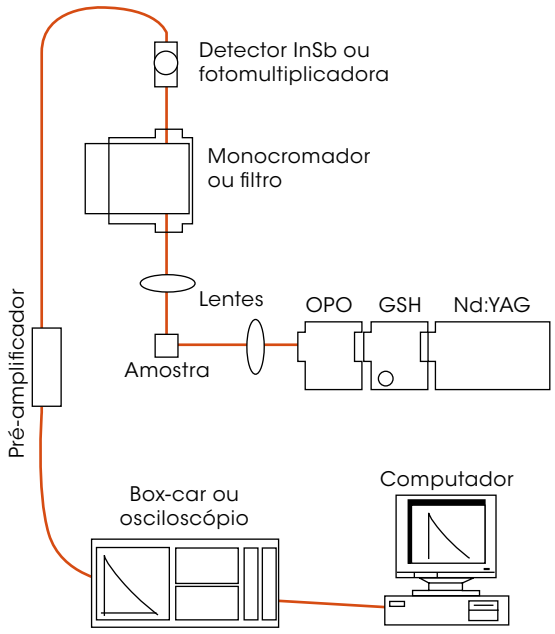

Figure 1: Schematic diagram of the experimental setup
Source: The authors.

can be used for solid state laser system pumped by diode laser. The most intense absorption is near 960 nm due to high concentration of Ytterbium in the sample. Besides that, Neodymium absorption at ~792 nm is approximately 8 times more intense than Thulium absorption (at) due to the highest absorption cross section of Nd^{3+} in the π polarization.

When YLF sample containing Tm^{3+} co-doped with Yb^{3+} and Nd^{3+}, excited at 792 nm, a strong blue emission is observed with maximum at 475 nm, due to the transition $^1G_4 \rightarrow {}^3H_6$. It is more intense than the red emission at ~ 650 nm. Figure 2 shows the 1.06μm emission, in which the fast component is due to Nd ($^4F_{3/2}$) → Yb transfer (process b). Figure 3 shows the 1.06μm emission from Yb^{3+} indirectly excited by Tm → Yb transfer (process d).

We observe also that the Nd(1 mol%) effect in the Yb:Nd:Tm:YLF crystal causes an enhancement of the Tm^{3+} blue emission due to the Nd($^4F_{3/2}$) → Tm($^3H_4$) (process h, seen in Figure 3), which indicates that Nd ions significantly contribute to the population of $^1G_4$ excited level.

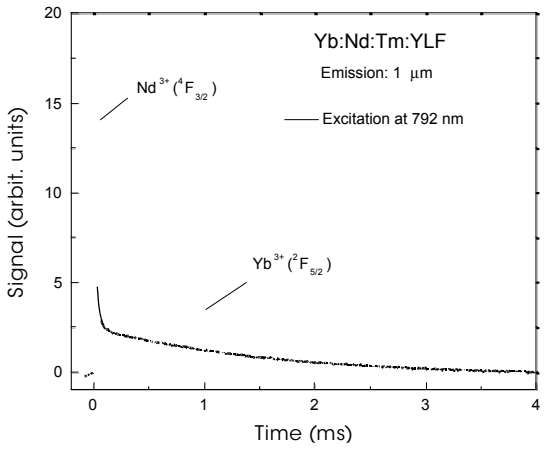

Figure 2: Emission decay curve (1.06μm) excited by pulsed laser at 792 nm in Yb:Tm:Nd:YLF crystal
Source: The authors.

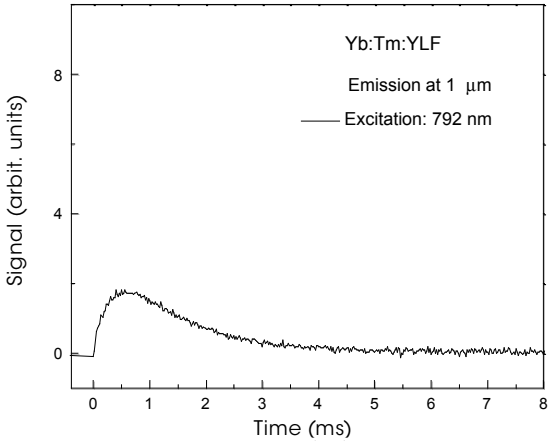

Figure 3: Emission decay curve (1.06μm) excited by pulsed laser at 792 nm in Yb:Tm:YLF crystal
Source: The authors.

3.1 Rate equations system

Figure 4 shows a simplified energy level scheme of the (Yb^{3+}, Tm^{3+}, Nd^{3+}) system considered for continuous laser pumping at 797nm.

According to the energy levels diagram of Figure 4, the following rate equations were derived for Yb:Nd:Tm:YLF system under continuous laser pumping at 792 nm. The n_1 and n_2 are the Yb^{3+} population, n_3, n_4, n_5 and n_6 refers to the

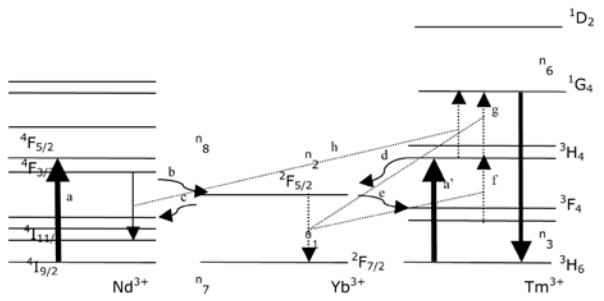

Figure 4: Energy levels scheme and energy transfer mechanisms of Yb/Tm/Nd system. Continuous line (up) 797 nm excitation, dashed line (up) 965 nm excitation. Dash dot line (down) blue thulium emissions. Dot lines (up and down) Yb emission and cross relaxation processes

Source: The authors.

Tm^{3+} and n_7, n_8, are the Nd^{3+} populations, in which $n_1+n_2= 20\ mol\%$, $n_3+n_4+n_5$, $n_6=0.5\ mol\%$ and $n_7+n_8= 1mol\%$.

$$R_P = \acute{o}_{\mathfrak{Z}} \frac{I_P}{h\nu_P}$$

is the pumping rate (s^{-1}), I_p is the intensity of pumping given in W/cm^2 and $h\nu_p$ is the photon energy of pumping radiation. Cross-section absorption $\sigma_{35} = 7.3 \times 10^{-21}\ cm^2$ for Tm, and $\sigma_{78} = 5.7 \times 10^{-20}\ cm^2$ for Nd, respectively.

Rate equation of the system, energy transfer rates and lifetimes values used in the calculation are listed in the Table 1.

Figures 5a and 5b exhibit the Tm (n_5 and n_6) population dependence on the pumping rate (intensity) obtained from the numerical simulation of the described rate equations. These results are in agreement with the experimental dependence observed for these Tm^{3+} levels in Yb:Nd:Tm:YLF crystals excited with diode laser at 792 nm.

Figure 6 shows the population difference (n_6-n_3) of Tm^{3+} obtained by means of numerical simulation of rate equations system for the 792 nm pumping of Tm and Nd ions. Populations of each excited level involved were taken after the system getting the equilibrium. We observed that

Table 1: Rate equation of the system and spectroscopic parameters

$$\frac{dn_1}{dt} = \frac{n_2}{\tau_2} + gn_2n_5 + en_3n_3 - dn_1n_5 + fn_2n_4 - bn_1n_8 + cn_2n_7$$

$$\frac{dn_2}{dt} = \frac{n_2}{\tau_2} + dn_1n_5 - gn_2n_5 - en_2n_3 - fn_2n_4 + bn_1n_8 - cn_2n_7$$

$$\frac{dn_3}{dt} = - R_pn_3 + \frac{n_4}{\tau_4} + \frac{\beta_{53}}{\tau_5}n_5 + \frac{\beta_{63}}{\tau_6}n_6 + dn_1n_5 - en_2n_3$$

$$\frac{dn_4}{dt} = - \frac{n_4}{\tau_4} + \frac{\beta_{54}}{\tau_5}n_5 + \frac{\beta_{64}}{\tau_6}n_6 - fn_2n_4 + en_2n_3$$

$$\frac{dn_5}{dt} = - R_pn_3 + \frac{n_5}{\tau_5} + \frac{\beta_{65}}{\tau_6}n_6 - dn_1n_5 - gn_2n_5 - hn_5n_8 + fn_2n_4$$

$$\frac{dn_6}{dt} = - \frac{n_6}{\tau_6} + hn_5n_8 + gn_2n_5$$

$$\frac{dn_7}{dt} = - 7.8\ R_pn_7 + \frac{n_8}{\tau_8} + bn_1n_8 + hn_5n_8$$

$$\frac{dn_8}{dt} = 7.8\ R_pn_7 - \frac{n_8}{\tau_8} - bn_1n_8 - hn_5n_8$$

Energy transfer rates (from best fitting) (given in s^{-1}):
b = 98246
c = 241
d = 238
e = 2000
f = 14510
g = 960
h = 14912

Lifetimes values used in the calculation:
$\tau 2$ = 2 ms
$\tau 4$ = 15 ms
$\tau 5$ = 1 ms
$\tau 6$ = 0.75 ms
$\tau 8$ = 0.57 ms
Source: The authors.

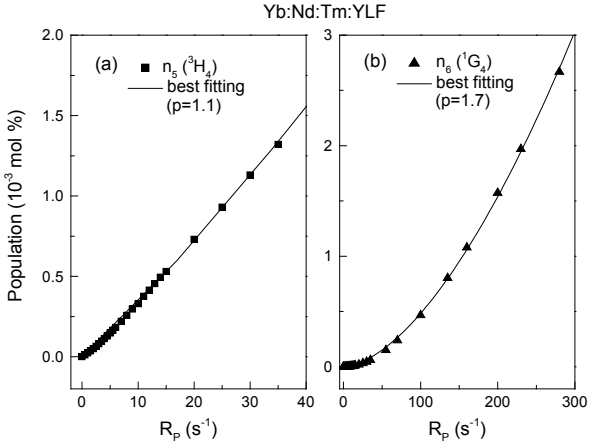

Figure 5: Energy excitation dependence of (a) $^3H_4$ and (b) $^1G_4$ levels

Source: The authors.

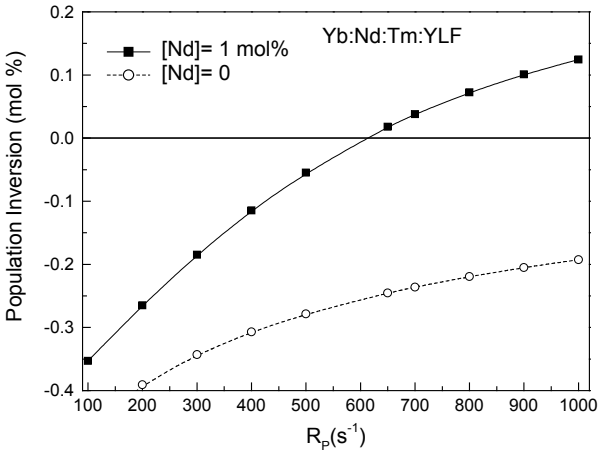

Figure 6: Variation of Tm^{3+} blue emission intensity as a function of the pumping rate in the samples of Yb:Tm:Nd:YLF: and Yb:Tm:YLF (dashed line)
Source: The authors.

the presence of Nd (1 mol%) promotes population inversion for a pumping rate since 620 s^{-1}. On the other hand, the Yb:Tm:YLF system does not show population inversion as it can be seen by the dashed curve exhibited in the Figure 6.

From this investigation using time resolved spectroscopy, we can infer that the most effective way of populating $^1G_4$ excited state of Tm^{3+} after 792 nm excitation occurs according to the following sequence:

i) (a) Ground state absorption of Nd and Tm (a') at 792 nm;
ii) Neodymium deactivation (10 μs): $Nd(^4F_{3/2}) \rightarrow Yb(^2F_{5/2})$ (process b);
iii) Three sequential cross relaxation processes: 1) $Yb(^2F_{5/2}) \rightarrow Tm\ (^3F_4)$ (process e); 2) $Yb(^2F_{5/2}) \rightarrow Tm\ (^3H_4)$ (process f) and 3) $Yb(^2F_{5/2}) \rightarrow Tm\ (^1G_4)$ (process g).

Conclusions

In this work, we used a time resolved spectroscopic technique together with the selective pulsed laser excitation to discriminate the energy transfer parameter or rates for each process involving Nd:Yb), Yb:Tm) and Nd:Tm). Rate equations of the system were numerically solved and the populations of the involved levels were obtained, which allowed the obtaining of the population inversion for the $^1G_4 \rightarrow {}^3H_6$ emission of Tm^{3+} in Yb:Nd:Tm:YLF crystal. A comparison with the results also obtained for Yb:Tm:YLF showed that Nd (1 mol%) played an important role in the population inversion, which shows that this triply-doped system can be used for the development of laser emitting in the blue region operating in continuous pumping regime at 792 nm.

Note

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