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Study of color centers produced in thulium doped YLF crystals irradiated by electron beam and femtosecond laser pulses

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Abstract

In this work, we report the influence of the presence of photochromic and color centers in the photobleaching of thulium ions blue emission in YLF ($YLiF_4$) crystals doped with 1 mol% Tm (3+). The samples were irradiated at room temperature both with electron beam and high intensity ultrashort pulses from a Ti:Sapphire CPA laser system. In both irradiations the production of photochromic and color centers was observed via the absorption bands in the UV and visible ranges. Pure LiF and pure and oxygen doped YLF crystals were used to identify the color centers produced and their optical properties. From a phenomenological model it was possible to study the interaction between color centers and thulium ions, and their effect in photobleaching and photodarkening behaviors. Finally, the blue up laser level population was computed using a rate equation analysis.

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Keywords: Laser; Crystal; Thulium; Fluorescence; Up-conversion; Energy transfer; Color centers; Waveguide

1. Introduction

Nowadays laser research is widely focused in the development of compact sources in the visible spectrum. Particularly, blue lasers are important in the compact disc industry, optical storage systems, color displays [1] and in new medical and dermatological applications [2], besides playing an important role in atmospheric and physics research [3]. Solid state lasers are attractive for most applications because they are rugged, relatively simple and easy to use.

Thulium-doped materials like YLF (Yttrium Lithium Fluoride – $YLiF_4$), YAG and ZBLAN [4] generate blue laser emission through nonlinear up-conversion of radiation from the infrared to the visible range. The dynamics of up-conversion is explained by taking into account various cross-relaxation (CR) and excited state absorption (ESA) processes. The transitions $^1G_4 \rightarrow {}^3H_6$ and $^1D_2 \rightarrow {}^3F_4$ are responsible for the 480 nm and 450 nm emissions, respectively, after pumping thulium ions with two or three red or infrared photons [5].

YLF crystals doped with thulium, and also co-doped with ytterbium, 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, under laser or flash lamp pumping. By micro-pulling-down (μPD) technique [6] it is possible to obtain YLF fibers that are conveniently used on the construction and operation of compact visible up-conversion lasers [7].

To obtain a blue up-conversion solid state laser few options are available. As an example, co-doping fluoride

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crystals with Yb^{3+} and Tm^{3+} results in blue emission at 480 nm under 980 nm pumping [8]. However, in addition to the disadvantages that 980 nm laser diode has, the efficiency of this up-conversion process is low because it is a three-step process. Recently, conversion of 680 nm into 450 nm blue light in Tm^{3+} co-doped materials has been reported [9], offering the most promising way to realize a compact blue up-conversion laser.

Up-conversion processes occur under high intensity pumping conditions. In these conditions photobleaching and photodarkening are also commonly observed [10]. These effects are detrimental for thulium based blue lasers pumped by high intensity diode lasers. Understanding why these effects arise is important to eliminate them. One of the hypotheses is that the high intensity pumping creates color centers (lattice vacancies or defects trapping electrons or holes) that absorb part of the blue emission, degrading the laser action [11]. This type of effect has to our knowledge, not previously been described in YLF crystals.

Up to now color centers in YLF were created mainly by ionizing radiation beams [7,12]. In this work we report the production of color centers by focusing high-intensity ultrashort laser pulses into YLF and LiF (lithium fluoride) crystals. LiF has a very simple crystal lattice that allows us to understand linear and nonlinear optical processes that lead to color center formation [13]. Here we try to explain the color center creation by laser sources and their role in the degradation of thulium ions blue emission. From a phenomenological model, we studied the interaction between the created defects and thulium ions, and their influence in photobleaching and photodarkening behavior.

2. Materials and methods

In this work we have studied pure LiF crystals, pure YLF crystals, YLF crystals doped with 1 mol% and 15 mol% Tm (3+), and YLF doped with 100 μmol of O^{2-}. Pure YLF and LiF samples were grown by zone refine method, and doped samples were grown by Czochralski technique under Argon atmosphere. The samples were oriented, cut and polished to 2 mm thickness.

The absorption spectra of the samples at room temperature in the range 200–1000 nm were measured using a Varian Spectrometer Cary 17 D.

Time resolved luminescence spectroscopy was employed to measure the luminescence decays induced by resonant laser excitations in order to determine the mechanism involved in the energy transfer up-conversion processes that produce the blue emission. The excitation system consists of a tunable optical parametric oscillator (OPO) from OPOTEK pumped by the second harmonic of a Q-switched Quantel Nd-YAG laser. This laser system delivers pulses of 10 mJ with duration of 4 ns and repetition rate of 10 Hz, and can be tuned from 0.68 to 2.0 μm. Laser pump at 707 nm was used to excite the $^3F_3$ level of Tm^{3+}. The time dependence luminescence of the acceptor was detected by a 0.25 m Kratos monochromator and a S-20 photomultiplier and analyzed using a signal-processing box-car averager (PAR 4402) or a digital 200 MHz Tektronix TDS 410 oscilloscope. The relative errors in the emission and lifetime measurements are estimated to be <10%.

To irradiate the samples, a Ti:Sapphire CPA system (Coherent Mira-Seed pumping a Quantronix Odin) was used, producing 1 kHz train of pulses, at 830 nm, with 640 μJ and 60 fs of duration (FWHM), in a $M^2 = 1.6$ beam. The beam was focused by a 200 mm lens, producing a converging beam with a waist of 25 μm. The samples were placed before the beam waist in such way that the color center creation threshold was achieved inside the crystals.

Similar samples were irradiated with electron beam at room temperature (18 s, 2.8 KGy/s, 0.7 mA, 1.5 MeV) for comparison.

3. Results

3.1. Defects production

LiF and YLF crystals were irradiated or by electron beam or by a high intensity laser pulses to produce defects in the material. Effects of the both kinds of irradiations were studied and compared. Fig. 1 shows the absorption spectra obtained immediately after the electron (5 MRad at room temperature during 18 s) and femtosecond laser irradiated (room temperature during 15 s) LiF crystals. In both cases the formation of the basic color center (the F absorption band lays in the UV region) is observed. F_3^+ and F_2 centers (two electrons bound to three and two neighboring anion vacancies, respectively) are responsible for the almost overlapping absorption band generally called M band, around 448 nm (F_3^+) and 440 nm (F_2). Besides, these two main absorption bands, other types of aggregate defects have been detected: the 520 nm and

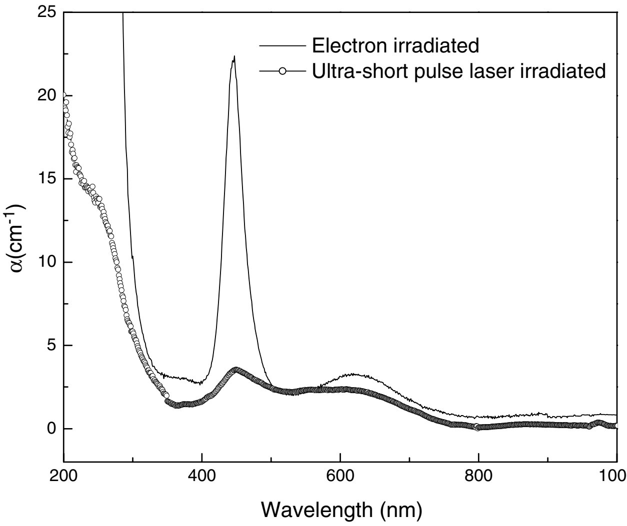

Fig. 1. Absorption spectra of color centers created in LiF crystals by electron irradiation and by 640 μJ, 60 fs laser pulses.

545 nm bands, attributed to N_1 and N_2 transitions of four associated F centers (N center), and the 632 nm band due to F_2^+ center (ionized F_2 center). The comparison between the two kinds of irradiations shows that the formation of neutral aggregate defects is strongly reduced under ultrashort laser irradiation with respect to electron irradiation.

Fig. 2a shows the YLF samples irradiated by electron beam. The lack of coloration in the pure YLF crystal shows that the color centers formed during the electron beam irradiation are not stable. Fig. 2b shows tracks of color centers created in LiF crystals by the femtosecond laser (green emission of F_3^+ centers when excited by white light). Fig. 2c shows the laser irradiated pure YLF crystal. In this case the YLF was moved transversely to the beam for 3 mm, to produce planes of stable color centers.

Fig. 3 shows the absorption spectra of femtosecond laser irradiated LiF, YLF and YLF:O samples measured after several days of storage at room temperature. Comparing the LiF spectra with the one shown in Fig. 1, measured just after the irradiation, we observe that non stabilized F_2^+ centers are reduced to F_2 or F centers explaining the increase in the absorption bands around 250 and 450 nm. Correspondent absorption bands calculated by Mollwo-Ivey [14] relations for absorption bands in YLF [15] can be observed in the spectra: $F \cong 296$ nm, $F_2 \cong 473$ nm, $F_3 \cong 343$ nm, $F_3^+ \cong 512$ nm (proposed) and $F_2^+ \cong 650$ nm (proposed). We can see that the YLF:O samples present more defects than the YLF ones. In YLF:O, the secondary oxygen defects produced with irradiation (O^{2-} and O^-), must be responsible for the blue shift of the F_2^+ color center absorption band.

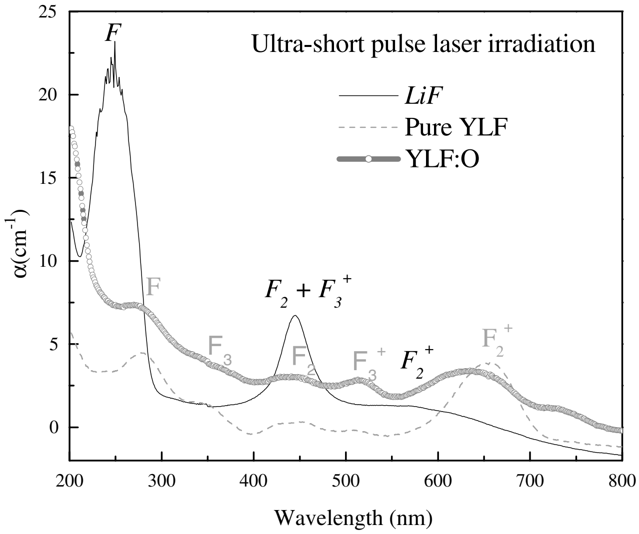

Fig. 3. Absorption spectra of LiF, YLF and YLF:O samples irradiated by ultrashort laser pulses. The spectra were measured after several days of storage at room temperature.

The absorption spectra of the 15 mol% YLF:Tm sample before and after electron irradiation is shown in Fig. 4. YLF:Tm shows a mix of color centers, photochromic centers [16] and ionized Tm centers. Color centers adjacent to a trivalent impurity cation (photochromic centers) must be responsible for the absorption bands at 320 nm and 531 nm in the YLF:Tm crystal. Ionized Tm^{2+} ions are also produced in this case, what is evidenced by the broad absorption from 350 to 900 nm due to the 4f–5d transitions [17]. The comparison between the femtosecond laser and electron beam irradiations, in this case, shows that the formation of photochromic centers defects is decreased under ultrashort laser irradiation with respect to electron irradiation.

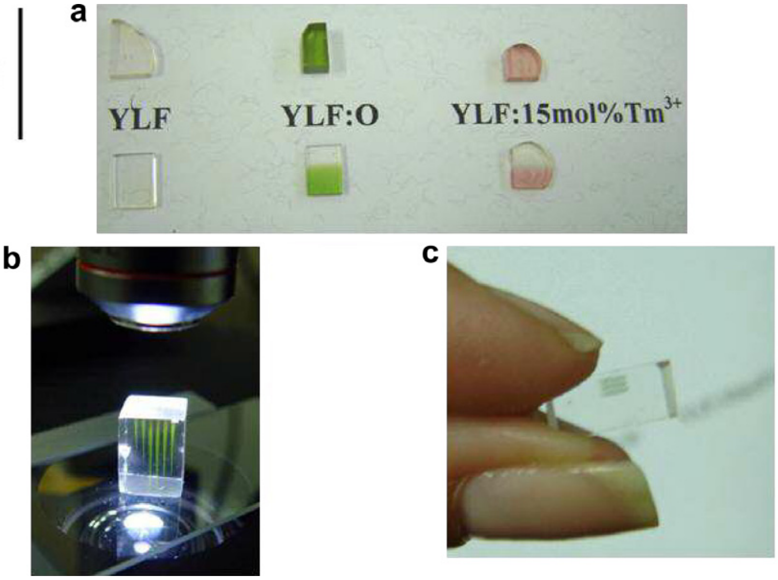

Fig. 2. (a) Pure YLF, YLF:O and YLF:Tm crystals irradiated by electron beam; the samples in the lower part of the photography were partially covered by lead masks preventing electron beam interaction and color centers formation. (b) LiF crystal irradiated by ultrashort laser pulses; under white light excitation, green emission characteristic of the F_3^+ color created during the irradiation is observed. (c) Color centers created in pure YLF crystal by ultrashort laser pulses.

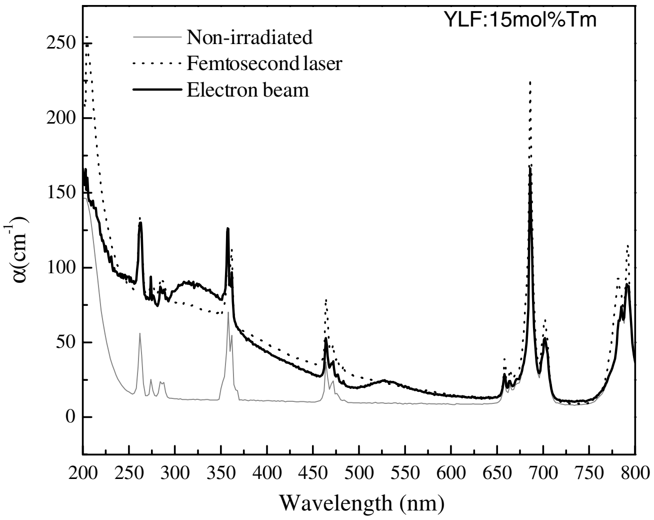

Fig. 4. Absorption spectra of YLF:15 mol%Tm before and after femtosecond pulse laser and electron irradiation.

In ultrashort high intensity regime, a strong non-linear multiphoton absorption generates free electrons [18]. An anion vacancy that traps an electron neutralizes the vacancy charge creating an F center. The migration of primary defects (F centers and vacancies) promotes the formation of complex defects. The difference of using a focused laser beam is that the density of primary defects formed is so much higher than the usual methods and therefore the probability of aggregation (mainly F_2^+ and F_3^+) is very much increased.

The threshold for color center formation in pure YLF crystals under ultrashort laser pulse irradiation was measured to be 1.9 TW/cm^2 [18]. However, the presence of thulium ions reduces this threshold since stepwise excitation of the thulium ion leads to photoionization and photochromic centers production.

3.2. Energy transfer between thulium ions and color centers

The energy transfer mechanism between thulium ions and color centers was studied by analyzing the population of $^1D_2$ level, that has a high absorption coefficient (lines around 350 nm in Fig. 4) in the presence and on absence of color centers. A 1 mm thickness YLF:1 mol% crystal irradiated by electrons was used in this study since the ionizing radiation produces a homogenous distribution of color centers in the sample.

The luminescence lifetime measured for the $^1D_2$ level for the irradiated YLF:1%Tm crystal is shown in Fig. 5. Comparing irradiated with non irradiated crystals we observed a change in the lifetime shape, probably due to energy transfer between Tm ions and color centers produced in the samples. In this case, the measured decay lifetime τ_{tot} of $^1D_2$ level is given by:

$$\tau_{tot}^{-1} = W_r + W_{nr} + W_{other}, \tag{1}$$

where W_r and W_{nr} are the radiative (equal to spontaneous emission probability, A_{rad}) and non-radiative decay rates, respectively. Non-radiative processes include transitions by multiphonon emission and by energy transfer arising from Tm^{3+}–Tm^{3+} ions interaction. Non-radiative decay from the $^1D_2$ level can be neglected due to the large energy gap of 6799 cm^{-1} ($^1D_2 \rightarrow {}^1G_4$) [19]. Under these considerations the Eq. (1) can be reduced to:

$$\tau_{tot}^{-1} = A_{rad} + W_{other}. \tag{2}$$

The term W_{other} is the energy transfer rate from Tm^{3+} to impurities, like color centers or photochromic centers, present in the sample which is proportional to the acceptor and donor concentrations, and can be expressed by:

$$W_{other} = \gamma' n_{Tm}, \tag{3}$$

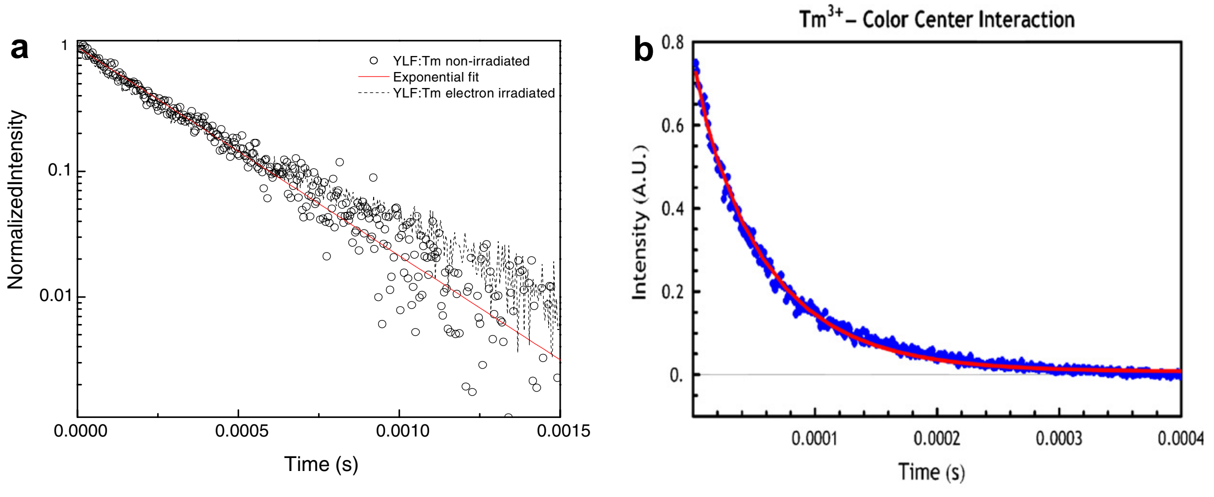

Fig. 5. (a) $^1D_2$ level decay time obtained for YLF:1 mol%Tm excited at 707 nm at room temperature, before (circles and exponential fit – solid line) and after (dashed line) electron irradiation. (b) Inokuti-Hirayama fit curve (solid line) for $^1D_2$ level decay time (points) in the irradiated YLF:1 mol%Tm crystal.

where n_{Tm} is the Tm concentration and γ' is the rate of energy transfer between thulium ions (donor) and defects (acceptor).

In the decay curve obtained for the $^1D_2$ level for the non-irradiated YLF:1 mol%Tm crystal shown in Fig. 5a, the lifetime exhibits a exponential decay, and in the electron irradiated sample the decay and cannot be fitted by a single exponential decay. By assuming that the donor decay is due to the average interaction with the entire acceptor ion located inside of an interaction volume V and calculating the limit $V \to \infty$, it is possible to use the Inokuti-Hirayama [20] solution to fit the $^1D_2$ luminescence decay in the presence of defects $\phi(t)$, given by:

$$\phi(t) = \exp\left[-\frac{t}{\tau} - \frac{C_A}{C_0}\Gamma\left(1-\frac{3}{S}\right)\left(\frac{t}{\tau}\right)^{3/s}\right] \qquad (4)$$

$$C_0^{-1} = \frac{4\pi R^3}{3},$$

where C_A is the acceptor concentration, R is the critical radius (the distance at which an isolated donor acceptor pair has the same transfer rate as the spontaneous decay rate of the donor τ) and τ is the thulium lifetime in the absence of defects, s is the multipolar interaction parameter and C_0 is critical concentration.

Fitting Eq. (4) to the experimental data shown in Fig. 5b, $\gamma' = 30.7\ \mathrm{s}^{-1}$ was obtained for the YLF:1 mol% Tm, with a transfer efficiency of 11%.

3.3. Rate equations

By pumping thulium doped YLF at 707 nm, electronic population is excited from the ground state $^3H_6$ to $^3F_2 + {}^3F_3$ levels (Fig. 6). A fraction of the excited state population decays non-radiatively to the $^3H_4$ level, from where the absorption of another photon then raises the Tm^{3+} ion to the $^1D_2$ level. The transition $^1D_2 \to {}^3F_4$ generates blue emission around 453 nm. In Fig. 7 the emission spectrum measured after pumping YLF:1%Tm at 707 nm is shown. This wavelength was obtained tuning the OPO laser to obtain the highest intensity in blue emission. A base time of 100 μs was selecting to measure this spectrum. Under pumping at 707 nm, the emission at 483 nm emission was not observed.

Let us now consider a simplified system in which there are possible up-conversion processes and excited state absorption of pumping radiation at 707 nm. The ions are excited from the ground level 1 ($^3H_6$) to the upper level 2 ($^3F_2$, $^3F_3 + {}^3H_4$) by the pumping radiation. A second pump photon promotes the system to level 4 ($^1D_2$). The ions in level 4 and 3 ($^1G_4$) can either directly decay to the ground state 1 or to their inferior level. The populations of these levels are then described by:

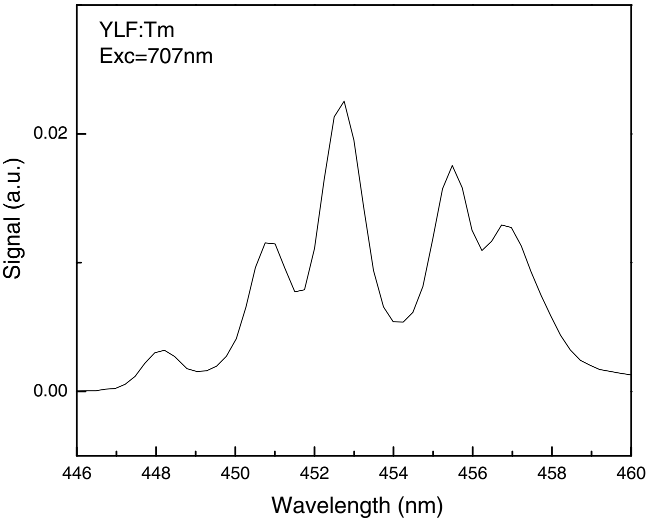

Fig. 7. YLF:1 mol%Tm blue thulium emission (σ + π) spectra obtained under pumping at 707 nm at room temperature.

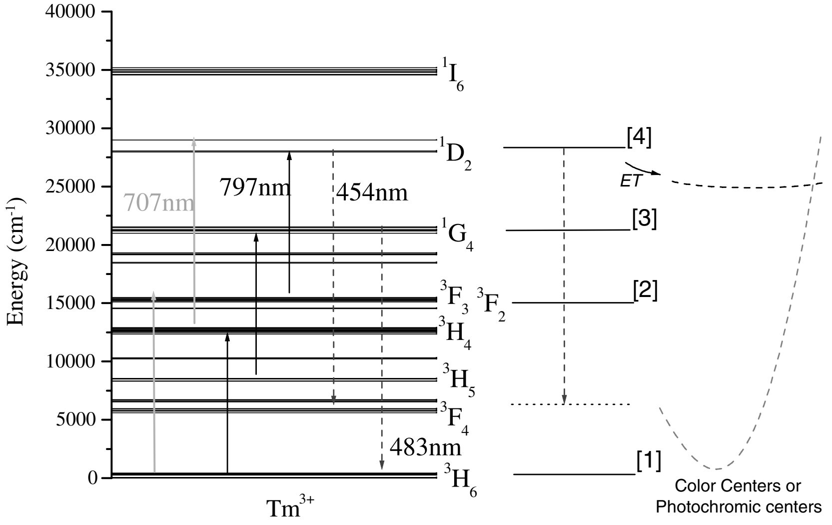

Fig. 6. In the figure, two upconversion processes are schematized, one of them a two photon process (pumping at 707 nm) and the other one a three photon process (pumping at 797 nm). An energy transfer mechanism between $^1D_2$ level [4] and color centers (broad band energy) is also represented.

Table 1
Spectroscopic parameters for YLF:1 mol%Tm

	YLF:1 mol% [19]
σ_a	0.05×10^{-20} cm^2 [19]
σ^*	1.48×10^{-20} cm^2
τ_2	2.1 ms [19]
τ_3	0.74 ms [19]
τ_4	0.076 ms
β_{43}	0.008 [19]
β_{42}	0.070 [19]
β_{32}	0.029 [19]
Concentration of the Tm ions	1.3×10^{20} ions/cm^3
γ^2	943.10 s^{-1}

$$
\begin{aligned}
\frac{\mathrm{d}n_1}{\mathrm{d}t} &= -n_1\sigma_a I_p + \frac{n_2}{\tau_2} + \frac{n_3}{\tau_3} + \frac{n_4}{\tau_4} \\
\frac{\mathrm{d}n_2}{\mathrm{d}t} &= \sigma_a I_p n_1 - \frac{n_2}{\tau_2} - \frac{n_3}{\tau_{32}} + \frac{n_4}{\tau_{42}} - n_2\sigma^* I_p \\
\frac{\mathrm{d}n_3}{\mathrm{d}t} &= -\frac{n_3}{\tau_3} + \frac{n_4}{\tau_{43}} \\
\frac{\mathrm{d}n_4}{\mathrm{d}t} &= -\frac{n_4}{\tau_4} + n_2\sigma^* I_p - \gamma n_4 \\
n_1 + n_2 &+ n_3 + n_4 = 1,
\end{aligned}
\tag{5}
$$

where n_1, n_2, n_3 and n_4 are the normalized population of levels 1, 2, 3 and 4, respectively. σ_a and σ^* are the ground state absorption (GSA) and the excited-state absorption (ESA) cross sections for pumping radiation at 707 nm. I_p is the pumping intensity and τ_2, τ_3 and τ_4 are the lifetimes of the levels 2, 3, and 4, respectively. The γ parameter here is the energy transfer parameter obtained from the fitted $^1D_2$ lifetime curve. The calculated and measured values of all parameters are shown in Table 1. σ^* was calculated applying MCumber [21] formula to the $^1D_2$–$^3H_4$ emission cross section.

At equilibrium, the system must obey the condition:

$$\frac{\mathrm{d}n_1}{\mathrm{d}t} = \frac{\mathrm{d}n_2}{\mathrm{d}t} = \frac{\mathrm{d}n_3}{\mathrm{d}t} = \frac{\mathrm{d}n_4}{\mathrm{d}t} = 0. \tag{6}$$

The equilibrium population for the level 4 is then given by:

$$n_4 = \frac{\sigma^* I_p^2 \tau^2 \tau^4 [n_0\sigma_a + n_0\sigma_a\beta_{32}]}{\theta + \phi}, \tag{7}$$

where $\phi = 1 + \sigma_a\tau_2 I_p + \sigma^*\tau_2 I_p + I_p^2\sigma_a\sigma^*\tau_2\tau_4 + \beta_{32} + \sigma_a\ \tau_2 I_p\beta_{32} + \sigma^*\tau_2 I_p\beta_{32} + I_p^2\sigma_a\sigma^*\beta_{32}\tau_4 - \sigma^*\tau_2 I\beta_{32}\tau_4\ \ \theta = I_p^2\sigma_a\sigma^*\beta_{32}\tau_4 + \tau_4\gamma + \sigma_a\tau_2\tau_4 I_p\gamma + \sigma^*\ \ \tau_2\tau_4 I_p\gamma + \sigma^*\sigma_a\tau_2\tau_3\tau_4\gamma I_p^2 + \tau_4\beta_{32}\gamma + \sigma_a\tau_2\tau_4 I_p\tau_4\ \beta_{32}\gamma$.

The population of $^1D_2$ level was analyzed with a pumping intensity simulation of cw diode pumping excitation. The results obtained are shown in Fig. 8. We can see that the presence of defects modifies the population dependence with pumping intensity. In the presence of defects, the $^1D_2$ population reaches saturation faster and at lower intensity then in the absence of these defects.

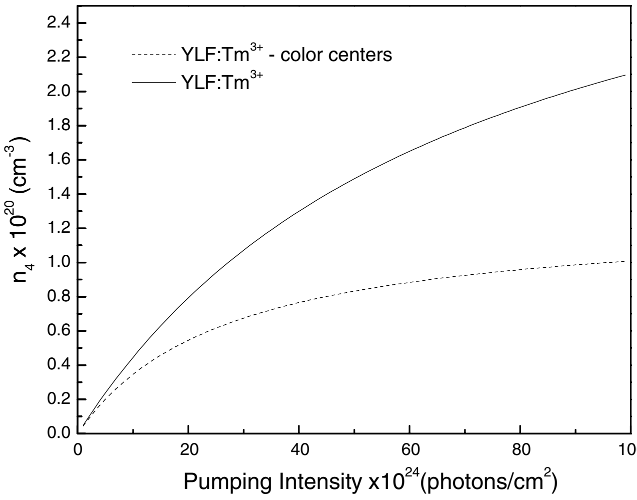

Fig. 8. $^1D_2$ population dependence with pumping intensity in YLF:1 mol%Tm, without (continuous line) and with (dashed line) energy transfer parameter.

4. Conclusions

This study demonstrated that a high intensity laser pumping can create defects in the form of color centers or photochromic centers, in pure, oxygen doped and thulium doped YLF crystals. These defects have absorption bands in the UV and visible ranges. The presence of the impurities reduces the threshold of color centers creation and stepwise excitation of the thulium ions leads to photoionization and photochromic centers production.

Using a phenomenological model we studied the interaction between the defects and thulium in 1% Tm doped YLF crystals, and its influence in photo-degradation of blue luminescence at 458 nm under 707 nm pumping. The interaction between thulium ions (donors) and color centers (acceptor) occurs via a non-radiative resonant energy transfer process. In this process ‘donor’, absorbs a photon and transfers this energy, non-radiatively, to the ‘acceptor’. For this case the decay profiles from donors can be fitted more appropriately by a stretched exponential function given by Inokuti Hirayama theory. We studied here an extreme case where high concentration of defects were produced by electron irradiation, and observed that the presence of defects induces a loss in $^1D_2$ thulium level population, and consequently an energy transfer mechanism with efficiency of 11%. In practical experiments of YLF crystals pumped by high intensity diode lasers, this energy transfer mechanism should be inefficient since concentration of defects surely should be small. Nevertheless, defects produced in YLF:Tm crystals irradiated with femtosecond laser induce permanent change in the refractive index into the material. This technique can be applied to fabricate photonic structures, such as optical waveguides. We believe that materials like glasses should have high order γ parameter and consequently important photodarkening processes.

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