Upconversion effect on fluorescence quantum efficiency and heat generation in Nd^{3+}-doped materials

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Abstract: The thermal lens technique was carried out to experimentally determine the influence of the energy transfer upconversion (ETU) processes on fluorescence quantum efficiency (η) in Nd^{3+}-doped materials. The samples with high Nd^{3+} concentration present a considerable reduction in η with the increasing excitation power due to the efficient ETU processes. Besides, the energy migration was identified as the mechanism responsible for the upconversion losses. In addition, it was verified that the critical inversion density is not concentration independent, as previously stated, but it decreases with the Nd concentration. Our results point out the approach based on TL technique as a valuable alternative because of its sensitivity allowing the measurements to be performed in a pump power regime that avoids damages in the investigated material.

OCIS codes: (140.6810) Thermal effects; (160.3380) Laser materials; (160.4760) Optical properties; (190.7220) Upconversion

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1. Introduction

Intense diode pumping of active materials doped with Nd^{3+} is a common approach to produce efficient, reliable, and compact high-power laser systems. The high efficiency of diode pumping can develop large population inversion densities in the $^4F_{3/2}$ upper level that can be lased at either ~1.06 or ~1.3 μm. The upper-state fluorescence quantum efficiency (η) is an important parameter for engineering such lasers since it affects the achievable energy storage density for a given pumping scheme and ultimately determines the output energy of the laser. The intense-pumping regime brings new effects into prominence, which may change the system parameters, required for optimum performance. Some of these effects are upconversion losses [1-11].

The most common excitation processes that populate the energy states higher than $^4F_{3/2}$ level are energy-transfer upconversion (ETU) and pump excited-state absorption. It is well know that ETU is normally the dominant mechanism [10,11]. This process involves the interaction of two excited Nd^{3+} ions in the $^4F_{3/2}$ metastable laser level, such that one ion returns to the $^4I_{11/2}$ and/or $^4I_{13/2}$ while the other is promoted to the higher-lying excited state ($^4G_{7/2}$, $^2K_{13/2}$, $^4G_{9/2}$, $^2D_{3/2}$, $^4G_{11/2}$ and $^2K_{15/2}$). These states decay by fast multiphonon relaxation back to the $^4F_{3/2}$ level, generating heat, and can, therefore, be treated as a single state for our purpose. In this way, the ETU processes related to these transitions are necessary for the description of the nonradiative losses of the $^4F_{3/2}$ level, since they lead to a reduction in the available gain and to heating of the host lattice. Therefore, an accurate knowledge of the ETU rate is important for appropriate design of intensely pumped systems.

The aim of this work is the determination of upconversion parameter (γ) and its effect on η of Nd-doped materials using the thermal lens (TL) technique.

2. Theoretical background and experiment

The dynamics of $^4F_{3/2}$ level considering the ETU mechanisms can be described by:

$$\frac{dN_e}{dt} = \frac{\sigma I}{h\nu_{ex}} N_g - \frac{N_e}{\tau} - \gamma N_e^2 \qquad (1)$$

where N_e, N_g, and $N_t \approx N_e + N_g$ are the excited metastable state ($^4F_{3/2}$), ground state ($^4I_{9/2}$), and total population, respectively. σ is the absorption cross-section at the pump photon energy $h\nu_{ex}$, I is the pump intensity, and γ(cm^3/s) is the upconversion parameter. In the low pump regime ($\gamma N_e << \tau^{-1}$) the fluorescence decay is basically exponential with the measured decay rate (τ^{-1}) given mainly by the sum of radiative (τ_{rad}^{-1}), multiphonon, and cross relaxation

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decay rates. The ETU mechanisms causes an additional decay rate $W_{up} = \gamma N_e$. Since W_{up} increases with N_e, it results in nonexponential fluorescence decay.

In the absence of ETU, i.e., in the regime of very low pump power, the fluorescence quantum efficiency of a given level is given by $\eta_o = \tau/\tau_{rad}$ (the ratio between its radiative and total rates). As the pump rate increases and consequently N_e, ETU becomes significant and the total decay rate can be written as $W_t = \tau^{-1} + \gamma N_e$. In this case η is given by [3]:

$$\eta = \frac{\eta_o}{1 + \beta n_e} \tag{2}$$

where $n_e = N_e/N_t$ is the fraction of ions in the excited state $^4F_{3/2,}$ and $\beta = \gamma\tau N_t$ is a dimensionless parameter related to the strength of ETU processes. It should be noticed that τ and consequently η_o are strongly dependent on N_t due to concentration quenching. In Nd^{3+} doped materials, quenching is related to energy transfers $^4F_{3/2}$,$^4I_{9/2} \rightarrow {}^4I_{15/2}$, $^4I_{15/2}$ and $^4F_{3/2}$,$^4I_{9/2} \rightarrow {}^4I_{9/2}$, $^4F_{3/2}$. [6].

Quantum efficiencies can be measured by photothermal methods through the determination of the fraction of absorbed energy converted into heat (φ) [12-15], which is related to η through energy conservation by:

$$\varphi = 1 - \eta \frac{\langle \nu_{em} \rangle}{\nu_{ex}} , \tag{3}$$

since part of the absorbed excitation photon energy ($h\nu_{ex}$) is converted into heat and the remaining energy is converted into fluorescence, generating a photon with average energy $h\langle \nu_{em} \rangle$. Eq. (2) shows that as n_e is increased by the excitation power, η is reduced due to the factor $1+\beta.n_e$ associated with ETU. Therefore, by measuring the η dependence on the excitation power, it is possible to evaluate the influence of ETU on η and φ.

In the TL experiment, the sample is exposed to an excitation laser beam with a Gaussian intensity profile. A fraction of absorbed energy is converted into heat, generating a radial temperature profile $\Delta T(r,t)$. Since the refractive index of the sample changes with temperature, a refractive index gradient is produced, creating a lens-like optical element – the so-called TL. The presence of such TL is detected by its effect on the propagation of a probe beam passing through the sample. The temporal evolution of the on-axis probe beam intensity is measured in the far field using a circular aperture in front of a photodiode detector [12-16]. The TL signal is proportional to the phase difference, θ, of the probe beam between the beam center $r = 0$ and $r = \sqrt{2}\, w_e$, induced by the TL [16]. Here, r is the radial distance from the beam center in the sample. Since θ is proportional to the absorbed power of the excitation beam, P_{abs}, it is convenient to use the normalized parameter:

$$\Theta = -\frac{\theta}{P_{abs}} = \frac{\varphi}{K\lambda_p}\frac{ds}{dT} \tag{4}$$

in which λ_p is the probe beam wavelength, $K = \rho.c.D$ is the thermal conductivity, ρ is the density, c is the specific heat, D is the thermal diffusivity, and ds/dT is the temperature coefficient of the optical path length. More details can be found in references [12-16].

Considering the ETU effect on η, the expression for Θ becomes (see Eqs. 2-4):

$$\Theta = C\left[1 - \left(\frac{\eta_o}{1 + \beta n_e}\right)\frac{\langle \nu_{em} \rangle}{\nu_{ex}}\right] \tag{5}$$

where $C = (K\lambda_p)^{-1} ds/dT$. A closed expression for n_e can be obtained in steady state regime from Eq. (1). It is convenient to express the power dependence of n_e through the saturation

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parameter $S = I/I_s$, in which $I_s = h\nu_{ex}/\sigma\tau$ is the saturation intensity and I is the excitation intensity. Therefore, Eq. (5) allows the determination of the β parameter and thus of γ, by means of a fitting procedure of Θ as a function of the S parameter.

The TL measurements were performed in the dual beam mode-mismatched configuration. A He:Ne laser at 632.8nm was used as probe beam and a Ti:sapphire as excitation beam. The Ti:sapphire laser was tuned in resonance with the Nd^{3+} ($^4F_{5/2}$ + $^2H_{9/2}$) level (~800nm), which decay nonradiatively, pumping the $^4F_{3/2}$ metastable state. The TL measurements were recorded in the transient regime, where the parameters θ and $t_c = w_e^2/4D$ (TL formation characteristic time) were obtained from transients curves through theoretical fit using the TL equation. Details of experimental procedure can be found elsewhere [13,16]. The study was performed in a Nd:YLF crystal and three sets of glasses: Phosphate (Q-98), Fluoroindate (PGIZCa), and Fluorozirconate (ZBLAN) with different Nd concentrations. The glass composition of PGIZCa and ZBLAN glasses were described previously [12,13,15]. The phosphate glasses were manufactured by Kigre Inc.

3. Results and discussion

In the absence of ETU, Eq. (4) predicts that Θ should be independent of the excitation power, as observed in many experiments, including Nd^{3+} doped glasses [14]. In the high power regime, ETU causes a nonlinear increase of the TL signal (θ) with excitation power [3,8]. Consequently, Θ is no longer constant with S. Note that ETU leads to additional heat generation by means of multiphonon decays of the levels $^4G_{7/2}$, $^2K_{13/2}$, $^4G_{9/2}$, $^2G_{9/2}$, $^2D_{3/2}$, $^4G_{11/2}$, and $^2K_{15/2}$ for $^4F_{3/2}$. Fig. 1(a) shows a nonlinear enhancement of θ with S. This behavior is more evident in the plot of Θ versus S showed in Fig. 1(b). This increase of Θ with S can be attributed to the increase of φ, which in turn is caused by the decrease of η with excitation intensity due to ETU. These results can be easier understood in the low saturation regime ($S<<1$), where by Eqs. (1-2) $n_e \approx S(1-\beta S)$ and $\eta \approx \eta_o[1-\beta S+(\beta S)^2]$. Accordingly, for $\beta S<<1$, η decreases linearly and φ increases linearly with S. As the doping concentration increases, the parabolic behavior becomes more evident as shown in Fig. 1(c). The theoretical fit of Fig. 1(b) was obtained by Eq. (5) using $n_e(S)$ achieved from Eq. (1). It should be noticed that Θ depends on three parameters: C, β, and $\eta_o<\nu_{em}>/\nu_{ex}$. The factor $<\nu_{em}>/\nu_{ex}$ can be obtained from luminescence data and the parameter C is related only to the physical properties of the host material. For the doping levels used in this work, C and $<\nu_{em}>/\nu_{ex}$ do not depend on ion concentration as previously verified [12,15]. The parameters $\beta(N_t)$ and C were determined by fitting the data in Fig. 1(b) using $\eta_o(N_t)$ and $<\nu_{em}>$ values from previous TL measurements [12,13,15]. The results for β are shown in Table I. The C values achieved are in agreement with those obtained previously [12,13,15]. This corroborates our assumption that C is concentration independent.

Figure 2(a) depicts the concentration dependence of γ values, calculated from $\beta(N_t)$ and $\tau(N_t)$. It is interesting to compare the γ values determined by TL technique and those obtained from transient emission measurements reported elsewhere**.** For instance, for a ZBLAN sample with $N_t = 2.5\text{x}10^{20}$ cm^{-3}, Payne et al. [1] obtained $\gamma = (4.6 \pm 1.4)\text{x}10^{-17}cm^3/s$. For this same concentration, we estimate $\gamma = (6.0 \pm 0.5)\text{x}10^{-17}cm^3/s$ from our data. It is worth noting that, in order to obtain reasonable accuracy (error ~30%), the measurements of Ref. [1] were performed at high excitation levels ($\beta S \approx 0.63$), near the damage threshold of the samples. In our experiments, γ was determined with higher accuracy (error ~10%) with much lower excitation levels, corresponding to the βS in the range of 0.015-0.06. For YLF doped with $2.0\text{x}10^{20}$ ions/cm^3 of Nd^{3+}, Guyot et al. [7] have achieved $\gamma = (1.7 \pm 1.0)\text{ x}10^{-16}$ cm^3/s. We achieved $\gamma = (1.9 \pm 0.2)\text{x}10^{-16}$ cm^3/s for an YLF crystal with $1.7\text{x}10^{20}$ ions/cm^3.

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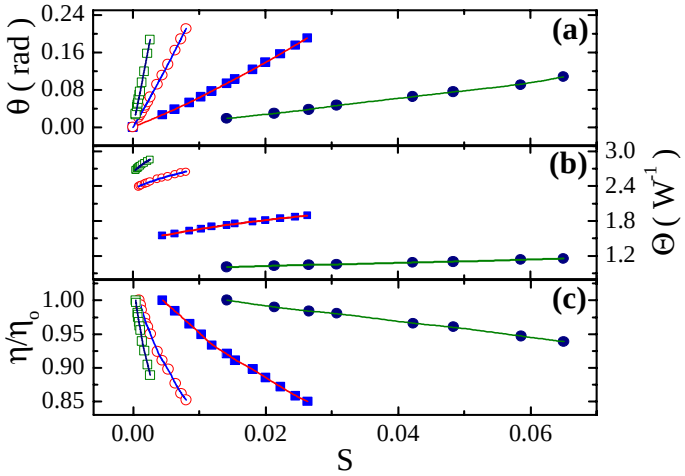

Fig. 1. (a) TL amplitude, θ, (b) θ normalized by the absorbed power, Θ, and (c) η normalized by η_o, versus excitation parameter $S=I/I_s$ at λ_{ex} = 801.6 nm for phosphate Q-98 glasses doped with 1.1 (closed circles), 3.3 (closed squares), 6.7 (open circles), and 10.3 (open squares) x10^{20} ions/cm^3 of Nd^{3+}. The lines in (b) represent the theoretical fit of experimental data.

Table 1. β parameter for Phosphate (Q-98), Fluoroindate (PGIZCa), and Fluorozirconate (ZBLAN) glasses and Nd:YLF crystal. The τ and η_o values were gathered from refs. [12,13,15].

Sample	**N_t (10^{20} cm^{-3})**	**τ (μs)**	**η_o^{TL}**	**η_o^{JO}**	**β**
Q-98 (Kigre)	1.1	346	0.90	0.88	1.54
	3.3	300	0.78	0.77	11.10
	6.7	202	0.53	0.52	31.00
	10.3	186	0.48	0.47	69.00
PGIZCa	1.2	421	0.89	0.94	2.34
	2.3	367	0.78	0.82	5.40
	4.2	248	0.52	0.55	13.10
	6.5	164	0.48	0.37	20.70
ZBLAN	0.9	515	0.99	1.03	1.42
	1.9	460	0.88	0.92	3.66
	3.5	380	0.73	0.76	10.18
	5.2	260	0.50	0.52	15.93
YLF	1.7	520	0.90	0.94	16.80

We will now analyze the physical mechanisms involved in ETU. The upconversion processes involve static transfer (Förster-Dexter - "FD" model) and migration-assisted energy transfer (Burstein - "B" model) [1,2]. In the FD theory the initially excited Nd ions remain fixed in space, in other words, the donor excitation is transferred to an acceptor directly. In the B model, the excitation migrates over donors before it reaches an acceptor, from where energy can be transferred to acceptors in the most efficient way, so the migration mechanism causes an enhancement of the energy transfer to acceptors. The total upconversion rate is given by:

$$W_{up} = W_{FD} + W_B = (\gamma_{FD} + \gamma_B) n_e N_t \tag{6}$$

where $\gamma_{FD} = 2(4/3)^2 \pi^3 \left(R_{up}^{FD}\right)^6 N_e / \tau_{rad}$ and $\gamma_B = 2\pi(2\pi/3)^{5/2} \left(R_{up}^{B}\right)^3 \left(R_{mig}\right)^3 N_g / \tau_{rad}$. R_{up} is called the critical radius for Auger upconversion and R_{mig} is the critical radius for the energy

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migration mechanism [1]. Note that a factor of two has been added to both equations to account for the indistinguishability of Nd excited states. Our measurements were performed at low excitation such that $n_e < 0.04$, so $N_e << N_g \approx N_t$. Therefore, in this regime, migration (γ_B) should give the main contribution to ETU. This hypothesis is corroborated by the linear behavior of γ versus N_t observed for all studied glasses, shown in Fig. 2(a). From linear adjustments of data in Fig. 2(a), the following information were obtained:

- **Q-98:** $\gamma = [(-0.2 \pm 0.3)x10^{-17} + (3.49 \pm 0.05).N_t x10^{-37}]$ cm^3/s
- **PGIZCa:** $\gamma = [(0.8 \pm 0.5)x10^{-17} + (2.8 \pm 0.1).N_t x10^{-37}]$ cm^3/s
- **ZBLAN:** $\gamma = [(0.8 \pm 0.5)\ x10^{-17} + (2.1 \pm 0.2).N_t x10^{-37}]$ cm^3/s

These γ values can also be calculated from the excited-state absorption spectra. Using the data from Doualan et. al. [2] for phosphate glass LHG-8, $\gamma = 3.2N_t x10^{-37}$ cm^3/s was evaluated for low excitation regime ($n_e << 1$). Note that ref. [2] presents a general theoretical expression for γ, i.e., for low and high excitation densities. This γ value of the LHG-8 glass is very similar to our experimental result for Q-98, $(3.49 \pm 0.05).N_t x10^{-37}$ cm^3/s.

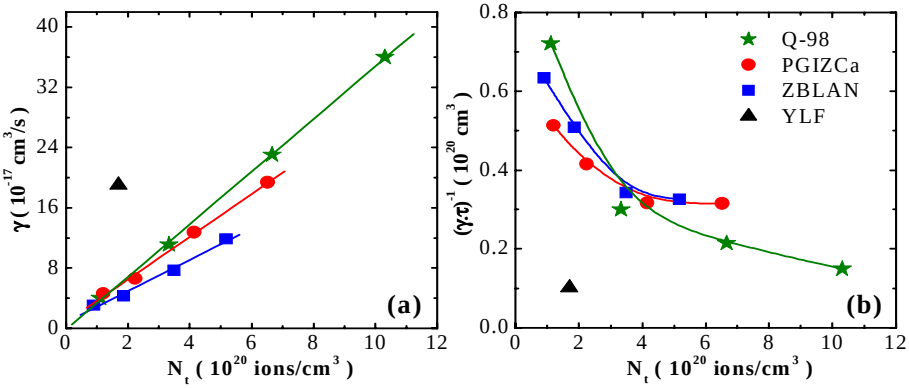

Fig. 2. (a) Upconversion parameter (γ) and (b) inversion density $(\gamma\tau)^{-1}$ for Phosphate (Q-98), Fluoroindate (PGIZCa), and Fluorozirconate (ZBLAN) glasses as a function of the Nd^{3+} concentration (N_t). The values for only one concentration are showed for YLF. The lines in (a) are linear fitting, and in (b) are only guides for eyes.

For the modeling of Nd:glass lasers it is interesting to define a critical inversion density $N_{ec} = (\gamma\tau)^{-1}$, i.e., the N_e value where $W_{up} = \tau^{-1} = W_t/2$. Fig. 2(b) shows that $(\gamma\tau)^{-1}$ is not concentration independent as previously suggested for high power regime [1], but it decreases with N_t for all studied glasses. It should be noticed that for Fig. 2(b) data N_t increases by a factor 6 – 10 whereas τ decreases by ~2, indicating that $(\gamma\tau)^{-1}$ is proportional to $(N_t\tau)^{-1}$ (B model) and it should really diminish. However, for high intensity this behavior could be different, since γ will be proportional to N_g and N_e.

It is very important to note that due to high sensitivity of the TL technique, the power levels used for γ determination are very low, corresponding to low inversion regime, $n_e < 0.1$. It should also be noticed that in this regime static (FD) processes are negligible while in the high excitation regime both FD and B mechanisms are relevant.

4. Conclusions

In summary, we have demonstrated that the nonlinear dependence of the TL signal with excitation power can be used to study the energy-transfer upconversion in Nd-doped materials. As a photothermal technique, this method does not require any knowledge on fluorescence kinetics, which is usually a complex phenomenon. The samples with high Nd^{3+} concentration present a considerable reduction in η with the increasing excitation power due to the efficient ETU processes. Migration-assisted energy transfer (Burstein) is the main

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mechanism responsible for the upconversion losses in our measurements. Besides, it was verified that the critical inversion density $(\gamma.\tau)^{-1}$ decreases with increasing Nd content. The approach based on TL technique appears as a good alternative for γ determination because of the high sensitivity of the method. Consequently, the measurements can be performed in a pump power regime that avoids damages in the investigated materials. Another advantage is the use of a cw pump source instead of a pulsed one. This reduces uncertainties in the pump intensity (related to beam power and waist) increasing the experiment accuracy.

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