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

Carlos Jacinto, Samuel L. Oliveira, Tomaz Catunda
Instituto de Física de São Carlos, Univ. de São Paulo - USP, CEP 13560 - 970, São Carlos - SP, Brazil.
\textit{a)carlosjs@if.sc.usp.br, b)tomaz@if.sc.usp.br}

Acácio A. Andrade
Laboratório de Ciências Físicas, Univ. Estadual do Norte Fluminense, CEP 28015-620, Campos dos Goytacazes-RJ, Brazil.

John D. Myers, Michael J. Myers
Kigre Inc., 100 Marshland Road, Hilton Head Island, SC 29926

Abstract: The thermal lens technique was carried out to experimentally determine the influence of the energy transfer upconversion (ETU) processes on fluorescence quantum efficiency ($\eta$) in Nd$^{3+}$-doped materials. The samples with high Nd$^{3+}$ concentration present a considerable reduction in $\eta$ 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.

©2005 Optical Society of America

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

References and links


(C) 2005 OSA

#6335 - $15.00 US

Received 20 January 2005; revised 4 March 2005; accepted 8 March 2005


1. Introduction

Intense diode pumping of active materials doped with Nd3+ 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 4F3/2 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 4F3/2 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 Nd3+ ions in the 4F3/2 metastable laser level, such that one ion returns to the 4I11/2 and/or 4I13/2 while the other is promoted to the higher-lying excited state (4G7/2, 2K13/2, 4G9/2, 2D3/2, 4G11/2 and 2K15/2). These states decay by fast multiphonon relaxation back to the 4F3/2 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 4F3/2 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 4F3/2 level considering the ETU mechanisms can be described by:

\[
\frac{dN_e}{dt} = \frac{-\sigma I}{h\nu_{ex}} N_e N_g - \frac{N_e}{\tau} - \gamma N_e^2
\]

where \( N_e, N_g, \) and \( N_t = N_e + N_g \) are the excited metastable state (4F3/2), ground state (4I9/2), and total population, respectively. \( \sigma \) is the absorption cross-section at the pump photon energy \( h\nu_{ex}, I \) is the pump intensity, and \( \gamma (\text{cm}^3/\text{s}) \) is the upconversion parameter. In the low pump regime (\( \gamma N_e \ll \tau^{-1} \)) the fluorescence decay is basically exponential with the measured decay rate (\( \tau^{-1} \)) given mainly by the sum of radiative (\( \tau_{rad}^{-1} \)), multiphonon, and cross relaxation
decay rates. The ETU mechanisms cause an additional decay rate $W_{\text{up}} = \gamma N_e$. Since $W_{\text{up}}$ 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 $\eta_0 = \tau_{\text{rad}}/\tau$ (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 $\eta$ is given by [3]:

$$\eta = \frac{\eta_0}{1 + \beta n_e}$$  \hspace{1cm} (2)

where $n_e = N_e/N_t$ is the fraction of ions in the excited state $^4\text{F}_{3/2}$, and $\beta = \gamma N_t$ is a dimensionless parameter related to the strength of ETU processes. It should be noticed that $\tau$ and consequently $\eta_0$ are strongly dependent on $N_t$ due to concentration quenching. In Nd$^{3+}$ doped materials, quenching is related to energy transfers $^4\text{F}_{3/2}, ^4\text{I}_{9/2} \rightarrow ^4\text{I}_{15/2}$, $^4\text{I}_{15/2}$ and $^4\text{F}_{3/2}, ^4\text{I}_{9/2} \rightarrow ^4\text{I}_{9/2}, ^4\text{F}_{3/2}$.[6]

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

$$\phi = 1 - \eta \frac{\langle v_{em} \rangle}{v_{ex}}$$  \hspace{1cm} (3)

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

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, $\theta$, of the probe beam between the beam center $r = 0$ and $r = \sqrt{2} w_c$, induced by the TL [16]. Here, $r$ is the radial distance from the beam center in the sample. Since $\theta$ is proportional to the absorbed power of the excitation beam, $P_{\text{abs}}$, it is convenient to use the normalized parameter:

$$\Theta = -\frac{\theta}{P_{\text{abs}}} = \frac{\phi}{K \lambda_p} \frac{ds}{dT}$$  \hspace{1cm} (4)

in which $\lambda_p$ is the probe beam wavelength, $K = \rho c D$ is the thermal conductivity, $\rho$ 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 $\eta$, the expression for $\Theta$ becomes (see Eqs. 2-4):

$$\Theta = C \left[ 1 - \left( \frac{\eta_0}{1 + \beta n_e} \frac{\langle v_{em} \rangle}{v_{ex}} \right) \right]$$  \hspace{1cm} (5)

where $C = (K \lambda_p)^2 ds/dT$. 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.
our experiments, regime, ETU causes a nonlinear increase of the TL signal (Θ) as observed in many experiments, including Nd3+ doped glasses [14]. In the high power 2.0x10²⁰ ions/cm³ of Nd3+, Guyot et al. [7] have achieved attributed to the increase of τβ parameter.

The Ti:sapphire laser was tuned in resonance with the Nd³⁺ (4F⁵/2 + 2H⁹/2) level (~800nm), which decay nonradiatively, pumping the 2F⁵/2 metastable state. The TL measurements were performed in the transient regime, where the parameters θ and tᵢ = wᵣ/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 Nd³⁺ 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 ⁴G⁷/₂, ⁴K₁₃/₂, ⁴G₉/₂, ⁴D₂/₂, ⁴G₁₁/₂, and ⁴F₃/₂ for ⁴F₃/₂. 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) nₑ = S(1 − βS) and η = ηᵣ[1 − βS + (βS)²]. Consequently, Θ depends on three parameters: C, β, and ηᵣ<νₑ>/. The factor <νₑ>/νₑ 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 <νₑ>/νₑ do not depend on ion concentration as previously verified [12,15]. The parameters β(Nt) and C were determined by fitting the data in Fig. 1(b) using ηᵣ(Nt) and <νₑ> 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 β(Nt) and π(Nt). 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 Nᵣ = 2.5x10²⁰ cm⁻³, Payne et al. [1] obtained γ = (4.6 ± 1.4)x10¹⁷cm³/s. For this same concentration, we estimate γ = (6.0 ± 0.5)x10¹⁷cm³/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 (βS = 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 2.0x10²⁰ ions/cm³ of Nd³⁺, Guyot et al. [7] have achieved γ = (1.7 ± 1.0) x10¹⁶ cm³/s. We achieved γ = (1.9 ± 0.2)x10¹⁶ cm³/s for an YLF crystal with 1.7x10²⁰ ions/cm³.
Fig. 1. (a) TL amplitude, θ; (b) θ normalized by the absorbed power, Θ; and (c) η normalized by η_0, 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_0 values were gathered from refs. [12,13,15].

<table>
<thead>
<tr>
<th>Sample</th>
<th>N_t (10^{20} \text{ cm}^{-3})</th>
<th>τ (µs)</th>
<th>η_0^{TL}</th>
<th>η_0^{JO}</th>
<th>β</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q-98 (Kigre)</td>
<td>1.1</td>
<td>346</td>
<td>0.90</td>
<td>0.88</td>
<td>1.54</td>
</tr>
<tr>
<td></td>
<td>3.3</td>
<td>300</td>
<td>0.78</td>
<td>0.77</td>
<td>11.10</td>
</tr>
<tr>
<td></td>
<td>6.7</td>
<td>202</td>
<td>0.53</td>
<td>0.52</td>
<td>31.00</td>
</tr>
<tr>
<td></td>
<td>10.3</td>
<td>186</td>
<td>0.48</td>
<td>0.47</td>
<td>69.00</td>
</tr>
<tr>
<td>PGIZCa</td>
<td>1.2</td>
<td>421</td>
<td>0.89</td>
<td>0.94</td>
<td>2.34</td>
</tr>
<tr>
<td></td>
<td>2.3</td>
<td>367</td>
<td>0.78</td>
<td>0.82</td>
<td>5.40</td>
</tr>
<tr>
<td></td>
<td>4.2</td>
<td>248</td>
<td>0.52</td>
<td>0.55</td>
<td>13.10</td>
</tr>
<tr>
<td></td>
<td>6.5</td>
<td>164</td>
<td>0.48</td>
<td>0.37</td>
<td>20.70</td>
</tr>
<tr>
<td>ZBLAN</td>
<td>0.9</td>
<td>515</td>
<td>0.99</td>
<td>1.03</td>
<td>1.42</td>
</tr>
<tr>
<td></td>
<td>1.9</td>
<td>460</td>
<td>0.88</td>
<td>0.92</td>
<td>3.66</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>380</td>
<td>0.73</td>
<td>0.76</td>
<td>10.18</td>
</tr>
<tr>
<td></td>
<td>5.2</td>
<td>260</td>
<td>0.50</td>
<td>0.52</td>
<td>15.93</td>
</tr>
<tr>
<td>YLF</td>
<td>1.7</td>
<td>520</td>
<td>0.90</td>
<td>0.94</td>
<td>16.80</td>
</tr>
</tbody>
</table>

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:

\[ W_{up} = W_{FD} + W_B = (\gamma_{FD} + \gamma_B)n_e N_t \]  

(6)

where \( \gamma_{FD} = 2(4/3)^2 \pi^3 (R_{up}^{FD})^6 N_e / \tau_{rad} \) and \( \gamma_B = 2 \pi (2\pi/3)^{5/2} (R_B^{mig})^3 (R_{up}^{mig})^5 N_e / \tau_{rad} \). \( R_{up}^{mig} \) is called the critical radius for Auger upconversion and \( R_{mig} \) is the critical radius for the energy
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 (\( \gamma_B \)) should give the main contribution to ETU. This hypothesis is corroborated by the linear behavior of \( \gamma \) 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**: \( \gamma = (-0.2 \pm 0.3) \times 10^{-17} + (3.49 \pm 0.05) N_t \times 10^{-37} \) cm\(^3\)/s
- **PGIZCa**: \( \gamma = (0.8 \pm 0.5) \times 10^{-17} + (2.8 \pm 0.1) N_t \times 10^{-37} \) cm\(^3\)/s
- **ZBLAN**: \( \gamma = (0.8 \pm 0.5) \times 10^{-17} + (2.1 \pm 0.2) N_t \times 10^{-37} \) cm\(^3\)/s

These \( \gamma \) values can also be calculated from the excited-state absorption spectra. Using the data from Doualan et al. [2] for phosphate glass LHG-8, \( \gamma = 3.2 N_t \times 10^{-37} \) cm\(^3\)/s was evaluated for low excitation regime \( (n_e << 1) \). Note that ref. [2] presents a general theoretical expression for \( \gamma \), i.e., for low and high excitation densities. This \( \gamma \) value of the LHG-8 glass is very similar to our experimental result for Q-98, \( (3.49 \pm 0.05) N_t \times 10^{-37} \) cm\(^3\)/s.

For the modeling of Nd:glass lasers it is interesting to define a critical inversion density \( N_{ec} = (\chi \tau)^{-1} \), i.e., the \( N_t \) value where \( W_{W} = \tau \tau = W_t/2 \). Fig. 2(b) shows that \( (\chi \tau)^{-1} \) 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 \( \tau \) decreases by \( -2 \), indicating that \( (\chi \tau)^{-1} \) is proportional to \( (N_t \tau)^{-1} \) (B model) and it should really diminish. However, for high intensity this behavior could be different, since \( \gamma \) will be proportional to \( N_e \) and \( N_t \).

It is very important to note that due to high sensitivity of the TL technique, the power levels used for \( \gamma \) 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 \( \eta \) with the increasing excitation power due to the efficient ETU processes. Migration-assisted energy transfer (Burstein) is the main
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 \(\gamma\) 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.

Acknowledgments
We are thankful to CNPq and FAPESP for the financial support of this work. The authors thank to A. S. S. de Camargo, M. J. V. Bell, and D. N. Messias for careful reading of the manuscript.