Upconversion in Nd(3+)-doped glasses: Microscopic theory and spectroscopic measurements
Upconversion in Nd$^{3+}$-doped glasses: Microscopic theory and spectroscopic measurements

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In this work, we report a systematic investigation of upconversion losses and their effects on fluorescence quantum efficiency and fractional thermal loading in Nd$^{3+}$-doped fluoride glasses. The energy transfer upconversion ($\gamma_{up}$) parameter, which describes upconversion losses, was experimentally determined using different methods: thermal lens (TL) technique and steady state luminescence (SSL) measurements. Additionally, the upconversion parameter was also obtained from energy transfer models and excited state absorption measurements. The results reveal that the microscopic treatment provided by the energy transfer models is similar to the macroscopic ones achieved from the TL and SSL measurements because similar $\gamma_{up}$ parameters were obtained. Besides, the achieved results also point out the migration-assisted energy transfer according to diffusion-limited regime rather than hopping regime as responsible for the upconversion losses in Nd-doped glasses. © 2008 American Institute of Physics. [DOI: 10.1063/1.2826908]

I. INTRODUCTION

Nd$^{3+}$-doped materials have been the most studied laser systems since the first Nd-laser demonstration in 1961. In the last decade, the availability of high power diode lasers enabled a tremendous increase of the output power of compact diode-pumped solid-state lasers (DPSSL). Compared to flash-lamp pumped lasers, these systems operate with localized heat deposition and high inversion densities, bringing more attention to two subjects. First, thermal effects which have limited the power scaling of DPSSL and second, energy transfer among Nd$^{3+}$ ions and other mechanisms that de-populate the excited state. In this sense, several papers have investigated losses in Nd$^{3+}$-doped materials as function of pump intensity in order to elucidate the upconversion mechanisms occurring in laser and amplifiers. Guyot and co-workers obtained the excited state absorption (ESA) spectra of Nd$^{3+}$ in the single crystals Y$_3$Al$_5$O$_{12}$, LiYF$_4$, and LaMgAl$_{11}$O$_{19}$. They observed that the discrepancies between the net gain cross section and the stimulated emission cross section could not be explained only by ESA losses. For a better description of the Nd$^{3+}$ amplifier it was necessary to include the energy transfer upconversion ($^{4}F_{3/2},^{4}F_{3/2} \rightarrow (^{1}I_{1/2},^{2}G_{9/2})$ and $^{4}F_{3/2},^{4}F_{3/2} \rightarrow ^{4}I_{13/2},^{2}G_{7/2}$). A rate equation was solved for the Nd$^{3+}$ $^{4}F_{3/2}$ level in these crystals to describe the transient behavior of the excited level with the upconversion energy transfer term as an adjustable parameter.

Pollnau et al. performed steady state luminescence (SSL) measurements in order to investigate the behavior of $^{4}F_{3/2}$ fluorescence intensity with the pump power for Nd:LiYF$_4$. The $^{4}F_{3/2}$ steady state population was simulated using a set of rate equations taking into account the energy transfer upconversion (ETU) processes. A good agreement was obtained between calculated and experimental curves with the same upconversion parameter previously found in Ref. 5. The same group also studied the effect of upconversion on heat generation and thermal lensing in Nd:yttrium lithium fluoride and Nd:yttrium-aluminum garnet lasers.

In Nd$^{3+}$-doped glasses, ETU parameters were first determined by Payne and co-workers. Although, ETU parameters of glasses are much smaller (~5 times) than in crystals, Descamps et al. observed that in the high pump regime, ETU strongly limits the gain and the energy-storage capability of Nd-doped glasses. Additionally, Doualan et al. calculated the ETU microparameters of Nd$^{3+}$-doped silicate and phosphate glasses from ESA measurements. They predicted that ETU should be the main loss mechanism in regime of high pump fluency, reducing the excited state population to less than half of the values calculated without ETU.

The effect of ETU on excited state population can be monitored by the evolution of gain or fluorescence intensity versus pump power. However, most quantitative upconversion measurements are based on fit of transient luminescence from the $^{4}F_{3/2}$ level, which is proportional to excited state population given by

$$N_e(t) = \frac{N_e(0)\exp(-t/\tau)}{1 + \delta[1 - \exp(-t/\tau)]},$$

where $\delta = N_e(0)\gamma\tau$. Equation (1) is derived assuming an upconversion decay rate given by $\gamma = \gamma N_e$, where $\gamma$ is the upconversion coefficient and $\tau$ is the 1/e decay time of the $^{4}F_{3/2}$ level at low pump regime. However, this method is very imprecise, particularly for small upconversion rate ($\delta < 1$). For instance, to determine the $\gamma$ coefficient in Nd$^{3+}$-doped glasses with approximately 30% uncertainty, most experiments must be conducted close to the damage threshold of the samples. In addition, Zubenko et al. showed that the fluorescence kinetics is too complex to be modeled by rate equations as well as Ostroumov et al. pointed out that Eq. (1) is valid only in some very particular cases when the experimentally determined $N_e(t)$ is close to $N_e(0)$. More precise measurements of ETU parameters and the most appropriate methods are therefore needed.
cases. In spite of the large amount of work on ETU in Nd\textsuperscript{3+}-doped materials, a systematic experimental study with deep analysis of the physical mechanism involved, based on different methodologies and Nd\textsuperscript{3+} concentration, is yet lacking.

In this work, we performed a complete investigation of the ETU mechanisms in Nd\textsuperscript{3+}-doped glasses with a concentration from 0.5 to 3 mol% using conventional spectroscopy, Judd–Ofelt calculations, ESA measurements, SSL, and thermal lens (TL) techniques. The TL technique has been successfully used to the determination of thermo-optical parameters and fluorescence quantum efficiencies of solids.\textsuperscript{16–20} The TL signal is proportional to heat released by the sample in the quasicontinuous wave regime and the TL response time is much longer than the fluorescence lifetime. Therefore, the TL experimental data does not rely on any kind of theoretical assumption about the fluorescence kinetics that are usually fitted by Eq. (1). In our investigation, a nonlinear increase of the TL signal with the excitation power was observed, which can be explained by the ETU effect. The upconversion parameters, \( \gamma_{cr} \) were obtained directly from fit of the TL signal with excitation power. Such values are in good agreement with those achieved from SSL measurements. The high sensitivity of the TL method, allowed the detailed study of the power dependence of TL signal, even in the low saturation regime (intensities two orders of magnitude lower than the pump saturation intensity). From the energy transfer microparameters, calculated by means of the energy transfer models and ESA measurements, the ETU mechanism was identified and the upconversion parameters were obtained. The experimental and theoretical approaches indicate the energy transfer assisted by diffusion-limited energy migration as mechanism responsible for the upconversion losses in Nd\textsuperscript{3+}-doped glasses. The influence of the ETU processes on fluorescence quantum efficiency and heat generation as a function of Nd\textsuperscript{3+} concentration and pump power are also discussed.

II. THEORETICAL BACKGROUND

A. Steady state population of the \( ^{4}F_{3/2} \) level

As mentioned earlier, ETU processes are necessary for the description of the nonradiative losses from the \( ^{4}F_{3/2} \) level. ETU involves the interaction of two excited Nd\textsuperscript{3+} ions in the \( ^{4}F_{3/2} \) metastable laser level, such that one ion returns to the \( ^{4}I_{11/2} \) and/or \( ^{4}I_{15/2} \) while the other is promoted to the higher-lying excited following by multiphonon decay (heat generation) to the \( ^{4}F_{3/2} \) level. These processes are represented by the vertical arrows in Fig. 1.

The dynamics of \( ^{4}F_{3/2} \) level considering these mechanisms can be described by

\[
\frac{dN_{e}}{dt} = \sigma I \frac{h\nu_{exc}}{\tau_{0}} - N_{e} \gamma_{cr} N_{g} N_{t} - \gamma_{up} N_{e}^{2},
\]

where \( N_{e}(N_{g}) \) is the population density in the \( ^{4}F_{3/2}(^{4}I_{9/2}) \) level. \( \sigma \) is the absorption cross section for the pump energy \( h\nu_{exc} \). \( I \) is the pump intensity, and \( \tau_{0} \) is the \( ^{4}F_{3/2} \) lifetime, which considers the losses related to the radiative and multiphonon decays. The \( \gamma_{up} N_{e} \) is the upconversion rate and \( \gamma_{up} \) is the ETU parameter. The lifetime concentration dependence is accounted by the decay rate \( \gamma_{up} \), that takes into account nonresonant cross relaxation (CR) mechanisms \( ^{4}F_{3/2},^{4}I_{9/2} \rightarrow ^{4}I_{15/2},^{4}I_{11/2} \) and/or \( ^{4}F_{3/2},^{4}I_{9/2} \rightarrow ^{4}I_{15/2},^{4}I_{13/2} \) enhanced by energy migration (EM) \( ^{4}F_{3/2},^{4}I_{9/2} \rightarrow ^{4}F_{3/2},^{4}I_{9/2} \). Equation (2) has been derived assuming that small density of Nd\textsuperscript{3+} ions is excited to \( ^{4}F_{3/2} \) level by the pump beam. In addition, it is worthwhile to point out that Eq. (2) is similar to that reported in Ref. 2 except for the CR term.

According to Eq. (2), \( 1/e \) decay time at low pump power (negligible upconversion) is given by

\[
\tau^{-1} = \tau_{0}^{-1} + \gamma_{cr} N_{t},
\]

where \( \tau_{0} \) must be compared with the measured decay times of very diluted samples \( (N_{t} \rightarrow 0) \) for which CR and EM are negligible. Equation (2) can be rewritten considering that

\[
\frac{dN_{e}}{dt} = \sigma I \frac{h\nu_{exc}}{\tau_{0}} - N_{e} \gamma_{cr} N_{g} N_{t} - \gamma_{up} N_{e}^{2},
\]
\[ N_i = N_{i0} + N_i \text{, and } n_e = N_e / N_i \text{, where } N_i \text{ is the total Nd}^{3+} \text{ concentration} \]
\[ \frac{dn_e}{dt} = \frac{S}{\tau} - \frac{1}{\tau} n_e - \gamma N_i n_e^2, \]  
where \( \tau \) is given by Eq. (3), \( S/I_0 \) is the pump saturation parameter, \( I_0 = h\nu_{exc}/\sigma \tau \) is the pump saturation intensity, and \( \gamma = \gamma_{p0} - \gamma_{cr} \). Using Eq. (4), for the normalized population density of the metastable level \( \langle 4F_{3/2} \rangle \) in the steady state regime \( (dn_e/dt = 0) \) can be obtained
\[ n_e = \frac{-\left( S + 1 \right) + \sqrt{(S + 1)^2 + 4\beta S}}{2\beta} \]
where \( \beta = \gamma N_i \tau \). Consequently, the quantum efficiency is changed to
\[ \eta_{ETU} = \frac{\tau_{rad}^{-1}}{\tau^{-1} + \gamma n_e N_i} = \frac{\eta}{1 + \beta n_e}, \]
where \( \eta = \tau / \tau_{rad} \) is the quantum efficiency in the absence of ETU mechanisms and \( \tau_{rad} \) is the radiative lifetime. Equation (7) shows that the effect of ETU on \( \eta_{ETU} \) is essentially related to the factor \( \beta n_e \), being negligible when \( \beta n_e \ll 1 \).

### B. Thermal loading

The ETU mechanisms should cause an increase in heat generation as the ions promoted to the higher-lying excited level \( 4I_{13/2} \) and/or \( 4I_{11/2} \) decay via multiphonon relaxation to \( 4F_{3/2} \) metastable level and \( 4I_{9/2} \), respectively. In fluorescent samples, part of the absorbed excitation photon energy \( (h\nu_{exc}) \) is converted into heat and the remaining energy is converted into fluorescence, generating a photon with average energy \( h\nu_{em} \). In this case, the heat efficiency, which is the fraction of absorbed energy converted into heat, is given by \( \varphi = 1 - \eta v_{exc}/\langle \nu_{em} \rangle \). Therefore, considering the reduction of \( \eta \) due to ETU,
\[ \varphi = 1 - \frac{T_{exc}}{1 + \beta n_e} \langle \nu_{em} \rangle. \]

Hence, \( \varphi \) increases as a function of the pump power. It is important to remember that, since ETU populates higher energy levels than metastable level \( 4F_{3/2} \) they may present some upconverted fluorescence. However, these states preferentially decay nonradiatively as their quantum efficiencies are very low (<1%). Therefore, transitions from \( 4F_{3/2} \) level to \( 4I_{9/2}, 4I_{11/2}, \) and \( 4I_{13/2} \) levels are the main fluorescence channels in Nd-doped glasses.

Among the photothermal methodologies that permits to obtain \( \varphi \), the TL technique has proved to be a powerful tool for characterization of rare earth-doped materials. It also provides relevant thermo-optical coefficients such as thermal diffusivity \( (D) \) and temperature coefficient of the optical path length change \( (ds/dT) \). In the TL experiment the samples are exposed to a modulated excitation laser beam with a Gaussian intensity profile. The sample is heated by the fraction of absorbed energy that is converted into heat, generating a radial temperature profile \( \Delta T(r, t) \). As a result of the \( ds/dT \), the sample behaves as a lenslike optical element. The presence of the thermal lens is detected by its effect on the propagation of a probing beam passing through the sample. The temporal evolution of the on-axis probe beam intensity, \( I_{TL}(t) \), is measured in the far field using a pinhole and a photodiode detector. The characteristic time constant of the transient signal is given by \( \tau = w_t^2/4D \), where \( w_t \) is the excitation beam waist. The TL signal is proportional to the phase difference, \( \theta \), of the probe beam at \( r = 0 \) and \( r = 1.4w_t \), induced by the excitation beam. In the transient regime, the parameters \( \theta \) and \( \tau \) can be obtained by fit of experimental data as discussed in Ref. 16. Since \( \theta \) is proportional to absorbed power from the excitation beam, \( P_{abs} \), it is convenient to use the normalized parameter
\[ \Theta = \frac{-\theta}{P_{abs}} = \frac{1}{K\lambda_p} \frac{ds}{dT} \varphi, \]
in which \( \lambda_p \) is the probe beam wavelength, \( K = \rho c D \) is the thermal conductivity, \( \rho \) is the density of the material, \( c \) is the specific heat, and \( D \) is the thermal diffusivity. Substituting Eq. (8) into Eq. (9),
\[ \Theta = C \left[ 1 - \frac{T_{exc}}{1 + \beta n_e} \langle \nu_{em} \rangle \right], \]
where \( C = (K\lambda_p)^{-1}(ds/dT) \). For low doping levels such as the Nd\( ^{3+} \) ZBLAN glasses used in this work, we assumed that both \( C \) and \( v_{exc}/\langle \nu_{em} \rangle \) do not depend on ion concentration. Using \( n_f(S) \) from Eq. (5) into Eq. (10) we obtain a closed expression for \( \Theta(S) \) that is used to fit the experimental data, allowing the determination of \( \beta, \gamma, \) and \( \eta \).

### C. Energy transfer upconversion microparameters

Several theories have been used to describe nonradiative energy transfer mechanisms among impurity ions in host materials. Among them, the Dexter model allows the evaluation of energy transfer rates from the overlap between the pertinent absorption and emission spectra. The Dexter equation for the dipole-dipole energy transfer rate, \( W_{da} \) (s\(^{-1}\)), may be written as
\[ W_{da} = \frac{3C}{8\pi n^2K^2} \int \sigma_{ESA} g_{\lambda} \sigma_{SE}(\lambda) d\lambda, \]
where \( n \) is the refractive index, \( \sigma_{ESA}(\sigma_{SE}) \) is the excited state absorption (stimulated emission) cross section, \( R = \gamma^2/4\pi nN_i \) is the average distance between the two interacting ions, and...
\( N_i \) is the density of ions. The subscript da and superscript up refer to donor-acceptor energy transfer and ETU processes, respectively.

Two energy transfer constants can be defined from Eq. (11) to describe the donor-acceptor interaction
\[
C_{\text{dd}}^\text{up} = W_{\text{dd}}^\text{up} p^\text{dd},
\]
\[
R_{\text{dd}} = (C_{\text{dd}}^\text{up} \tau_0)^{1/6}, \tag{12}
\]
where \( \tau_0 \) is the donor lifetime in the absence of the acceptor ion, as defined in Eq. (2), and \( C_{\text{dd}}^\text{up} \) and \( R_{\text{dd}} \) are the energy transfer microparameter and the critical radius for dipole-dipole nonradiative interaction, respectively. The \( C_{\text{dd}} \) microparameter can also be described by Eq. (11) by using \( \sigma_{\text{GSA}}(\lambda) \) around 870 nm instead of the \( \sigma_{\text{ESA}}(\lambda) \) spectrum. It is important to reinforce that \( C_{\text{dd}}^\text{up} \) and \( C_{\text{dd}} \) stand for dipole-dipole-type energy transfer microparameters associated with the \( 4F_{3/2} \rightarrow 4F_{3/2} \) (\( 4G_{2}^{2+}+2K_{3/2}+4G_{9/2} \)) plus \( 4F_{3/2} \rightarrow 4F_{3/2} \) (\( 4G_{9/2}+2D_{3/2}+4G_{11/2}+2K_{15/2} \)) and \( 4F_{3/2} \rightarrow 4F_{3/2} \) (\( 4F_{3/2} \rightarrow 4F_{3/2} \)) mechanisms, respectively.

The \( C_{\text{dd}}^\text{up} \) and \( C_{\text{dd}} \) microparameters can be used to obtain both total upconversion rate \( (W_{\text{up}}) \) and the \( \gamma_{\text{up}} \) parameter. This calculation might involve static energy transfer described by Förster–Dexter (FD) theory and migration-assisted energy transfers, which can be evaluated by Yokota and Tanimoto (YT) or Burshtein (B) models. In the static transfer model, the first excited Nd ion (donor) can directly transfer energy to an excited acceptor ion (at the \( 4F_{3/2} \) level), which is promoted to a higher-lying excited level. On the other hand, the excitation can migrate over donors before it reaches an acceptor ion at the \( 4F_{3/2} \) level, which is promoted to a higher-lying excited level. The migration mechanism causes an enhancement of the energy transfer to acceptors. The choice between YT or B models depends on the energy migration regime. The YT model is valid for weak donor-donor coupling and strong donor-acceptor coupling. In this case, the excitation energy is not spread in an efficient way through host material so that the energy migration becomes a diffusion-limited process. On the other hand, the B model, also known as hopping regime, assumes that excitation energy jumps among the donors. With that, the excited-state population is redistributed over the donors, until a donor-acceptor interaction or other nonradiative decay occurs, such as energy transfer from rare-earth ion to OH radicals.

In view of the earlier considerations, \( W_{\text{up}} \) and \( \gamma_{\text{up}} \) can be calculated on the basis of the microscopic energy transfer parameters by the following equations:
\[
W_{\text{up}} = W_{\text{FD}} + W_{\text{mig}} = (\gamma_{\text{FD}} + \gamma_{\text{mig}}) N_e, \tag{13}
\]
where \( W_{\text{FD}} \) and \( W_{\text{mig}} \) are the upconversion rates related to static energy transfer and migration-assisted energy transfer mechanisms, respectively. The static term is given by
\[
\gamma_{\text{FD}} = 110 C_{\text{dd}}^\text{up} N_e. \tag{14}
\]
The migration-assisted energy transfer term, \( \gamma_{\text{mig}} \), should be calculated according to the YT or B models. When \( C_{\text{dd}} > C_{\text{dd}}^\text{up} \), the B (hopping) model is appropriate.

\[
\gamma_{\text{up}}^R = 40 C_{\text{dd}}^\text{up} N_e, \tag{15}
\]
otherwise, for \( C_{\text{dd}} < C_{\text{dd}}^\text{up} \) according to YT (diffusion-limited) theory
\[
\gamma_{\text{up}}^{\text{YT}} = 42(C_{\text{dd}})^{3/4}(C_{\text{dd}}^\text{up})^{1/4} N_e. \tag{16}
\]
Note that the factor of 2 is already included into Eqs. (14)–(16) to take into account the equivalent nature (indistinguishability) of the Nd\(^{3+} \) excited states.

### III. EXPERIMENTAL

#### A. Samples

The glass samples investigated have the following molar compositions: \((53-\chi)\text{ZrF}_4-29\text{BaF}_2-4.5\text{LaF}_3-3.5\text{AlF}_3-10\text{NaF-}\text{XNdF}_3\), with \( \chi=0.5, 1.0, 2.0, \) and 3.0, henceforth named XNd. The glasses were prepared from the anhydrous fluorides, which were mixed in a platinum crucible and the steps of melting, refining, and casting were carried out in a dry glove box to prevent hydrolysis. Samples were annealed for several hours at a few degrees Celsius below the respective glass transition temperatures. All the prepared samples are crystal free. The refractive index \( n=1.55 \) was measured with an Abbe refractometer. The samples were cut and polished into 1 mm thick slabs.

#### B. Absorption, lifetime, and steady state measurements

Absorption spectra were obtained using a spectrophotometer Perkin-Elmer Lambda-900. The lifetime measurements of the \( 4F_{3/2} \) level were performed using OPO laser tuned around 740 nm (\( 4I_{9/2} \) \( \rightarrow \) \( 4F_{5/2} \) absorption transition). The laser beam diameter on the sample was about 1 cm to assure low pump intensity. The signal was analyzed by a Thermo-Jarrel Ash monochromator and a photomultiplier tube RCA 31034 and recorded by a Tektronix TDS380 oscilloscope. The \( 4F_{3/2} \) luminescence measurements in the steady state regime were performed using a Ti:sapphire laser at 796 nm modulated by a mechanical chopper. The pump beam was focused into the sample with a 10 cm focus length lens and the beam waist was measured with a WM100-Thorlabs beam profiler. The pump power was varied by a Glan–Thompson polarizer in order to maintain the beam waist constant while the excitation power is varied. The emitted light was analyzed using the same apparatus of the lifetime measurements.

#### C. Excited state absorption measurements

Measurements of ESA and stimulated emission (SE) cross-section spectra were carried out using a pump-probe setup. The pump beam was a Ti:sapphire laser operating at 800 nm and the probe beam was a 200-W tungsten halogen lamp. The pump and probe beams were modulated at 14 and 600 Hz, respectively. In general, the recorded signal \( \Delta I/I \), where \( I \) is the transmitted probe intensity and \( \Delta I \) is the variation in the transmitted probe intensity imposed by the pump...
beam, can be related to ground state absorption, stimulated emission and the excited state absorption cross sections by the expression,

\[
\frac{\Delta I}{I} = N_c A L \left[ \sigma_{\text{GSA}} + \sum_i \left( \frac{N_i}{N_c} \right) (\sigma_{\text{SE},i} - \sigma_{\text{ESA},i}) \right],
\]

(17)

where \(N_c\) is the overall excited population, \(A\) is the amplification factor of the lock-in amplifier, \(L\) is the sample thickness, and \(N_i/N_c\) is the ratio between the population of level \(i\) and the total density of excited ions. The fractional population is estimated by the relation between the lifetimes of the excited states. \(\sigma_{\text{GSA}}, \sigma_{\text{SE}},\) and \(\sigma_{\text{ESA}}\) are the ground state, stimulated emission and excited state absorption cross sections, respectively. The collected signal was dispersed by a 0.25-m Thermo Jarrel Ash monochromator and acquired by a Ge detector. The ground state absorption cross-section in a region without stimulated emission and ESA is used to calibrate the spectra and to obtain the product \(N_c A L\). For Nd\(^{3+}\) ions the only metastable level is the \(4F_{3/2}\) level, then \(N_i/N_c = 1\). So, the \((\sigma_{\text{SE}} - \sigma_{\text{ESA}})\) spectrum is achieved by subtracting the ground state absorption cross section from \((\sigma_{\text{GSA}} + \sigma_{\text{SE}} - \sigma_{\text{ESA}})\). A detailed description of the pump-probe setup as well as the calibration procedure can be found in Ref. 28.

D. Thermal lens technique

TL measurements were performed in the dual beam mode-mismatched configuration.\(^{16}\) A He:Ne laser was used as the probe beam and a Ti:saphire the as excitation beam. The Ti:saphire laser was tuned in resonance with the Nd\(^{3+}\)(\(4F_{5/2} + 2H_{9/2}\)) level at 796 nm, which decay nonradiatively, pumping the \(4F_{3/2}\) metastable state. The TL data were recorded in the transient regime and fitted using the standard TL model.\(^{16}\) Accordingly, the parameters \(\theta\) and \(t_s\) (the characteristic TL response time) were determined. The average emission frequency from the \(4F_{3/2}\) level was estimated using the branching ratios \(\beta_i\) by \(\langle \nu_{\text{em}} \rangle = \sum \beta_i \nu_{\text{em},i}\). Therefore, with \(\lambda_{\text{exc}} = 796\) nm, we obtained \(\langle \nu_{\text{em}} \rangle / \nu_{\text{exc}} = 0.77\).

IV. RESULTS

A. Steady state luminescence

SSL measurements from \(4F_{3/2}\) level were performed to study the behavior of the excited state population with excitation power, or \(S\) parameter. Figure 2 shows the results for the samples 0.5Nd (closed circles) and 3Nd (open circles).

The curves indicate that both samples exhibit a nonlinear behavior of \(n_e\) versus \(S\) due to saturation (ground state depletion) and ETU processes. Moreover, a more meaningful nonlinear trend is observed in the 3Nd sample. The \(\beta\) parameters shown in Table I were obtained from fit of the data using Eq. (5).

B. Thermal lens

Figure 3 shows a nonlinear dependence of \(\Theta\) versus \(S\) for Nd\(^{3+}\)-doped ZBLAN glasses, which becomes more evident as the Nd concentration increases. This trend confirms the presence of ETU mechanisms in our glass system, as described by Eq. (10). An increase of \(-10\%\) in the \(\Theta\) values compared to the ones obtained in the low pump power regime was observed in the range of \(S\) values studied. From a qualitative analysis, this behavior is related to the increase of \(\varphi\) with \(S\), which in turn is caused by the efficient ETU processes. In other words, the \(\Theta\) parameter increases as a function of \(S\) due to the factor \(1 + \beta n_e\) in Eq. (10) so that the nonlinear behavior observed is caused by extra deposition of heat owing to the multiphonon decays from higher-lying excited to the \(4F_{3/2}\) level.

From the \(\Theta\) data as a function of \(S\), the \(\beta\) parameters for the Nd samples were achieved using Eq. (10). The solid lines in Fig. 3 show typical fits to the experimental data. The \(\beta\) values are shown in Table I, wherein the subscript TL indicates the results obtained from TL measurements. Besides, the \(\eta\) value for each Nd-doped glass was also obtained from the experimental curves taking into account \(\Theta(S \rightarrow 0)\). Table I exhibits these values and those obtained from the expression \(\eta = 1/\tau_{\text{rad}}\), where \(\tau_{\text{rad}}\) is the radiative lifetime of the \(4F_{3/2}\) level obtained from the Judd–Ofelt theory. The \(\tau_{\text{rad}}\) value in the Nd-ZBLAN glass is 514 \(\mu\)s. The good agreement between the results obtained by these independent measurements indicates the reliability of the measurements performed. As expected, the results indicate that \(\eta\) reduces with Nd concentration due to fluorescence concentration quenching effect associated to the CR energy transfer process enhanced by energy migration mechanism.\(^{30,26}\)

C. Energy transfer upconversion microparameters

Figure 4 shows the excited state absorption \((\sigma_{\text{ESA}})\) and stimulated emission \((\sigma_{\text{SE}})\) cross-section spectra of the Nd\(^{3+}\)-doped ZBLAN glass. Two upconversion channels can be clearly observed and assigned as \(4F_{3/2} \rightarrow (4G_{7/2} + 2K_{13/2} + 4G_{9/2})\) and \(4F_{3/2} \rightarrow (4G_{9/2} + 2D_{3/2} + 4G_{11/2} + 2K_{15/2})\). As mentioned previously, these excited state absorptions from the \(4F_{3/2}\) level are not sufficient to describe the losses from the metastable level so that the \(4F_{3/2} \rightarrow 4I_{13/2}, (4G_{7/2} + 2K_{13/2} + 4G_{9/2})\) and \(4F_{3/2}, 4F_{3/2} \rightarrow 4I_{11/2}, (4G_{9/2} + 2D_{3/2} + 4G_{11/2} + 2K_{15/2})\) ETU mechanisms have been considered. These energy transfer processes are indicated by the vertical arrows in Fig. 1.
The microparameters related to the ETU processes and energy migration can be calculated using Dexter model by means of the overlap between emission spectrum of the donor ion and absorption spectrum of the acceptor ion, as pointed out in Sec. II C. The results obtained are $C_{dd}^{cr} = 19 \times 10^{-40}$ cm$^6$/s and $33 \times 10^{-40}$ cm$^6$/s for $^4F_{3/2} \rightarrow ^4I_{13/2}$, $^2G_{9/2} + ^2D_{3/2} + ^2G_{11/2} + ^2K_{15/2}$ and $^4F_{3/2} \rightarrow ^4I_{13/2}$, $^2G_{7/2} + ^2K_{13/2} + ^2G_{9/2}$ mechanisms, respectively. Accordingly, $C_{dd}^{ap} = 52 \times 10^{-40}$ cm$^6$/s for the summation of the two upconversion mechanisms is obtained. In addition, $C_{dd}^{cr} = 28 \times 10^{-40}$ cm$^6$/s for the energy migration ($^4F_{3/2}, ^4I_{9/2} \rightarrow ^4F_{3/2}, ^4I_{9/2}$) has also been calculated. These values are used for determination of the $\gamma_{ap}$ values of the Nd samples and analysis of the dominant ETU mechanism, as presented in the next section.

V. DISCUSSIONS

From the $\beta$ values obtained from TL or SSL measurements, $\gamma = \gamma_{ap} - \gamma_{cr}$ can be directly calculated using Eq. (6). Therefore, $\gamma_{cr}$ has to be previously determined in order to be used in the $\gamma_{ap}$ calculation. The CR processes ($^4F_{3/2}, ^4I_{9/2} \rightarrow ^4I_{15/2}, ^4I_{13/2}$ and/or $^4F_{3/2}, ^4I_{9/2} \rightarrow ^4I_{13/2}, ^4I_{13/2}$) are nonresonant, since the overlap integral between emission (donor) and absorption (acceptor) spectra [Eq. (11)] is approximately zero. Consequently, the $\gamma_{cr}$ parameter cannot be obtained from Dexter model described in Sec. II C, as these CR energy transfer mechanisms must be phonon assisted.

An alternative procedure to estimate $\gamma_{cr}$ is based on concentration dependence of $1/e$ $^4F_{3/2}$ lifetime in the low pump regime. In Nd-doped fluoride and phosphate glasses, the CR mechanism is enhanced by energy migration according to the hopping model since $C_{dd}^{cr} \gg C_{dd}^{ap}$, where $C_{dd}^{cr}$ is the microparameter related to the CR process, as depicted in Fig. 1. Hence, the fluorescence concentration quenching can be described by Eq. (3) with $\gamma_{ap}^{cr} = 40 \sqrt{C_{dd}^{cr} C_{dd}^{ap}} N_t$. Note that this expression is equivalent to Eq. (15) for ETU process. In the low excitation regime, $N_t \gg N_s$, so substituting $\gamma_{ap}^{cr}$ in Eq. (3) results in:

$$\tau^{-1} = \tau_0^{-1} + 40 C_{dd}^{cr} N_t^2.$$  (18)

with $p = 2$ and $Q^2 = N_t / \tau_0 \gamma_{cr}$. The Eq. (18) is usually adopted to fit the concentration dependence of experimental lifetime data. Note that $Q$ is equivalent to the concentration needed to reduce the lifetime to $\tau_0 / 2$ (one-half of its zero concentration value). Figure 5 shows the lifetime concentration quenching for the ZBLAN glasses. The curve is well fitted by Eq. (18) with $p = 2$, resulting in $Q = 5.5 \times 10^{20}$ (cm$^3$) and consequently $\gamma_{cr} = 6.4 \times 10^{39}$ N$^{-1}_t$ (cm$^3$/s). Table I exhibits the $\gamma_{ap}$ parameter for Nd$^{3+}$-doped ZBLAN glasses achieved using $\beta$ and $\gamma_{cr}$ values. It can be seen a good agreement among the $\gamma_{ap}$ values obtained from different methodologies. The results also reveal that $\gamma_{ap}$ is greater than $\gamma_{cr}$ parameter, at least two orders of magnitude, so that $\beta = (\gamma_{ap} - \gamma_{cr}) N_t \tau = \gamma_{ap} N_t \tau$.

Figure 6 depicts the normalized excited state population $S = I/I_0$ for the 0.5Nd and 2Nd samples as a function of $S$. These curves were obtained using the Eqs. (5) and (6) considering the $\gamma_{ap}$ values achieved by means of the TL technique. In the low pump intensity regime used in the TL measurements, $S$

<table>
<thead>
<tr>
<th>Sample</th>
<th>$N_t$ (10$^{20}$ cm$^{-3}$)</th>
<th>$\tau$ (μs)</th>
<th>$\eta_{TL}$</th>
<th>$\eta_{SS}$</th>
<th>$\beta_{SSL}$</th>
<th>$\gamma_{ap}^{SSL}$ (10$^{-17}$ cm$^3$ s$^{-1}$)</th>
<th>$\beta_{TL}$</th>
<th>$\gamma_{ap}^{TL}$ (10$^{-17}$ cm$^3$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5Nd</td>
<td>0.9</td>
<td>514</td>
<td>0.99</td>
<td>1.03</td>
<td>0.61</td>
<td>1.3</td>
<td>1.4</td>
<td>3.0</td>
</tr>
<tr>
<td>1Nd</td>
<td>1.9</td>
<td>460</td>
<td>0.88</td>
<td>0.92</td>
<td>4.2</td>
<td>4.8</td>
<td>3.7</td>
<td>4.2</td>
</tr>
<tr>
<td>2Nd</td>
<td>3.5</td>
<td>380</td>
<td>0.73</td>
<td>0.76</td>
<td>10.5</td>
<td>7.9</td>
<td>10.2</td>
<td>7.7</td>
</tr>
<tr>
<td>3Nd</td>
<td>5.2</td>
<td>260</td>
<td>0.50</td>
<td>0.52</td>
<td>21.6</td>
<td>16.0</td>
<td>16.0</td>
<td>12.0</td>
</tr>
</tbody>
</table>

**FIG. 3.** $\Theta$ values vs excitation parameter for Nd$^{3+}$-doped ZBLAN glasses. The solid line represents fit to the experimental data using Eq. (10).

**FIG. 4.** Excited state absorption cross-section ($\sigma_{ESA}$, solid line) and stimulated emission cross-section ($\sigma_{SE}$, dashed line) spectra of the Nd$^{3+}$-doped ZBLAN glass.
<0.04, the normalized excited state populations were smaller than 0.03 ($N_e < 0.03N_t$). As a result, although the $\gamma_{up}$ values determined by the TL technique are similar to the ones obtained from transient measurements reported in Ref. 13, the TL method is approximately 20 times more sensitive than that reported by Payne et al.13 because in their measurements the normalized excited state population was around 0.63.

To estimate the value of $\gamma_{up}$ as a function of Nd$^{3+}$ concentration and identify the dominant ETU mechanism from microscopic treatment, we used the energy transfer microparameters previously determined. As the relation $C_{dd} < C_{dp}^{up}$ is reached, it is expected that the ETU mechanisms in Nd$^{3+}$-doped ZBLAN glasses occur in a diffusion limited regime instead of hopping regime (Burshtein model), which have been considered in previous studies of ETU in Nd-doped silicate, fluoride, and phosphate glasses,7,13,20 even when the condition $C_{dd} < C_{dp}^{up}$ is clearly satisfied.7

In this microscopic picture, the $\gamma_{up}$ parameter can be calculated as $\gamma_{up}^{FD} + \gamma_{up}^{YT} = (5.7n_e + 1.4n_g)10^{-37}N_p$, where the first and second terms on the right side are related to static transfer and migration-assisted energy transfer according to diffusion-limited regime, respectively. From this equation and Eqs. (5) and (6), the normalized excited state populations as a function of $S$ for the 0.5Nd and 2Nd samples were obtained, Fig. 6. The data demonstrate that the microscopic treatment provided by the energy transfer models is corroborated by the results achieved from the TL and SSL measurements. Therefore, any one of these methodologies can be used to evaluate ETU losses in Nd-doped materials. The results also reveal that in the low pump regime ($N_e < 0.1N_t$) the ETU losses should be mainly attributed to migration-assisted energy transfer (diffusion-limited regime) instead of the static transfer mechanism because the ratio between YT and FD contributions is higher than 2.2.

Figure 7 shows the effect of upconversion losses on fluorescence quantum efficiency ($\eta_{ETU}$) and fractional thermal loading ($\varphi$) versus $S$ parameter. These data were obtained from the $\beta$ and $n_e$ values achieved in the thermal lens measurements. It can be observed a reduction of $\eta_{ETU}$, and increase of $\varphi$ values up to 10% for the range $S$ values. Therefore, the strong effect of the pump power due to the ETU processes on both parameters cannot be neglected in highly doped samples and high pump power regime. It is interesting to point out that when ETU is negligible ($\beta n_e \rightarrow 0, S \rightarrow 0$), $\varphi$ increases with Nd$^{3+}$ concentration due to fluorescence concentration quenching effect.30,26

VI. CONCLUSIONS

In conclusion, we have performed an investigation of the effect of the upconversion energy transfer mechanisms on $\eta_{ETU}$ and $\varphi$ values as a function of pump power in a set of Nd$^{3+}$-doped fluoride glasses by means of the thermal lens and luminescence techniques and energy transfer models. The good agreement between experimental and theoretical approaches indicate the migration-assisted energy transfer
according to diffusion-limited regime rather than hopping regime as responsible by the upconversion losses in Nd-doped fluoride glasses.

The samples with high dopant concentration present a considerable reduction in the quantum efficiency as well as an increase in the thermal loading as a function of $S$ due to the efficient ETU processes. The results also show that, while the $\gamma_{SP}$ absolute values can be determined from several techniques, the thermal lens technique is confirmed as a good option because it matches more sensitivity and simple experimental apparatus.

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