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# Excited state dynamics of the $Ho^{3+}$ ions in holmium singly doped and holmium, praseodymium-codoped fluoride glasses

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The deactivation of the two lowest excited states of $Ho^{3+}$ was investigated in $Ho^{3+}$ singly doped and $Ho^{3+}$, $Pr^{3+}$-codoped fluoride (ZBLAN) glasses. We establish that 0.1–0.3 mol % $Pr^{3+}$ can efficiently deactivate the first excited ($^5I_7$) state of $Ho^{3+}$ while causing a small reduction of ~40% of the initial population of the second excited ($^5I_6$) state. The net effect introduced by the $Pr^{3+}$ ion deactivation of the $Ho^{3+}$ ion is the fast recovery of the ground state of $Ho^{3+}$. The Burshstein model parameters relevant to the $Ho^{3+} \rightarrow Pr^{3+}$ energy transfer processes were determined using a least squares fit to the measured luminescence decay. The energy transfer upconversion and cross relaxation parameters for 1948, 1151, and 532 nm excitations of singly $Ho^{3+}$-doped ZBLAN were determined. Using the energy transfer rate parameters we determine from the measured luminescence, a rate equation model for 650 nm excitation of $Ho^{3+}$-doped and $Ho^{3+}$, $Pr^{3+}$-doped ZBLAN glasses was developed. The rate equations were solved numerically and the population inversion between the $^5I_6$ and the $^5I_7$ excited states of $Ho^{3+}$ was calculated to examine the beneficial effects on the gain associated with $Pr^{3+}$ codoping. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2749285]

## I. INTRODUCTION

There has been a significant amount of interest for many decades in the use of sensitizing ions to transfer excitation energy from a pump source to an activator ion. There has been a similar amount of interest in the use of deactivator ions that receive excitation energy from the lower energy level of the luminescent transition of an activator ion; this interest has led to the improvement in several applications particularly in the area of material development for lasers and optical amplifiers. The luminescent $^3F_4$ level of $Tm^{3+}$, for example, can be efficiently depopulated by $Ho^{3+}$ and $Tb^{3+}$ ions in fluorozirconate (ZBLAN), tellurite, Ge–Ga–As–S–CsBr and $GeO_2$–$Li_2O$–$K_2O$–ZnO codoped glasses, making these materials suitable for use as optical amplifiers operating in 1.4–1.5 $\mu$m region of the spectrum.[1–5] For applications requiring laser operation at 2.9 $\mu$m, $Ho^{3+}$-doped $LiYF_4$ (YLF) crystal[6] operating on the $^5I_6 \rightarrow {}^5I_7$ transition has the potential for pulsed laser operation despite the longer ~16 ms lifetime of the lower laser ($^5I_7$) level when compared to the lifetime of the upper laser ($^5I_6$) level which is ~3 ms.[7] Many applications, however, require continuous wave (cw) operation in this spectral range. To achieve this end, a deactivator ion must be introduced in order to quench the excited state population in the $^5I_7$ level. A $^5I_7$ level lifetime reduction to 2.2 ms in the presence of 1.2 mol % $Nd^{3+}$ in codoped YLF crystal[7] has shown some promise, but the population of the upper $^5I_6$ laser level was reduced and the luminescence efficiency of the 2.9 $\mu$m emission decreased by approximately 50%.

Recently,[8] it has been shown that effective deactivation of the $^5I_7$ level of $Ho^{3+}$ using $Pr^{3+}$ ions can lead to cw output from a ZBLAN-based fiber laser. With better choice of both the $Ho^{3+}$ and $Pr^{3+}$ ion concentrations, an unsaturated output power of 2.5 W was obtained from the fiber laser.[9] This recent work extends past investigations[10–12] into the successful use of the $Pr^{3+}$ ion as a deactivator ion for the $^4I_{13/2}$ level of the $^4I_{11/2} \rightarrow {}^4I_{13}$ laser transition of $Er^{3+}$-doped ZBLAN; the current output power of ~9 W from an $Er^{3+}$, $Pr^{3+}$-doped ZBLAN fiber laser demonstrates the power scaling potential of this particular rare-earth ion combination.[13]

In the present study we have carried out a detailed investigation of the luminescence emitted from the excited states of the $Ho^{3+}$ ion in ZBLAN glass and in the presence of $Pr^{3+}$ ions. We have determined the Burshtein model parameters for the luminescent decay and we have calculated the energy transfer rate parameters for the various energy transfer processes present in these glasses. We compare these results with other fluorescent systems involving deactivation and estimate the improvement in the performance of ZBLAN-based lasers operating at 2.9 $\mu$m. In light of potential directly diode pumped $Ho^{3+}$-doped ZBLAN fiber lasers, we numerically solved the rate equations for singly

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$Ho^{3+}$(4 mol %)-doped and $Ho^{3+}$(4 mol %), $Pr^{3+}$(*x* mol %)-codoped ZBLAN glasses under cw pumping at 655 nm to determine the population inversion and its dependence on the $Pr^{3+}$ concentration.

## II. EXPERIMENTAL PROCEDURE

The ZBLAN glasses were prepared as either single ($Ho^{3+}$) or double-doped ($Ho^{3+}$, $Pr^{3+}$) samples for the time-resolved luminescence spectroscopy experiments. The two sets of ZBLAN glasses were prepared from ultrapure fluoride starting materials with the following compositions. (i) $Ho^{3+}$-doped samples: $(100-x)\times[53\ ZrF_4-20\ BaF_2-4\ LaF_3-20\ NaF]-x\ HoF_3$ ($x=2,4,6$ mol %). (ii) $Ho^{3+}$, $Pr^{3+}$-codoped samples which have the $Ho^{3+}$ concentration constant at 4 mol %: $(96-y)\times[53\ ZrF_4-20\ BaF_2-4\ LaF_3-20\ NaF]-4\ HoF_3-y\ PrF_3$ ($y=0.1,0.2,0.3$ mol %).

The $Ho^{3+}$-doped ZBLAN and $Ho^{3+}$, $Pr^{3+}$-codoped ZBLAN glasses were produced by melting the starting materials at 850 °C for 120 min in a Pt–Au crucible. The liquids were poured into brass molds and annealed at 260 °C for 2 h to remove the mechanical stresses. The samples were cut and polished into $15\times10\times5$ $mm^3$ pieces.

The absorption spectra of the glasses were measured using a spectrophotometer (Cary/OLIS 17D) operating in the range of 300–2000 nm. The lifetimes of the $Ho^{3+}$ excited states, i.e., the $^5I_6$ and $^5I_7$ levels, were measured after pulsed laser excitation from a tunable optical parametric oscillator (OPO) that was pumped by the second harmonic of a *Q*-switched Nd:YAG (yttrium aluminum garnet) laser (Brilliant B from Quantel, France). Optical pulse widths of 4 ns at 1151 and 1948 nm were used to directly excite the $^5I_6$ and $^5I_7$ energy levels of $Ho^{3+}$, respectively. Selective optical excitation of the energy levels of $Ho^{3+}$ was carried out in order to isolate the various components to the $Ho^{3+}$ decay. The decay of the luminescence of the energy levels of $Ho^{3+}$ was detected using an InSb infrared detector (Judson model J10D cooled to 77 K) in conjunction with a fast preamplifier (response time of ~0.5 $\mu$s) and analyzed using a digital 200 MHz oscilloscope (Tektronix TDS 410). All the fluorescence decay times were measured at 300 K. To isolate the luminescence signals, bandpass filters with ~80% transmission at 1200 and 2000 nm (each with a half width of 15 nm and an extinction coefficient outside this band of $\sim10^{-5}$) were used.

## III. EXPERIMENTAL RESULTS

### A. Luminescence from the $^5I_7$ excited state of $Ho^{3+}$

The absorption spectrum of $Ho^{3+}$(4 mol %), $Pr^{3+}$(0.3 mol %)-doped ZBLAN glass is shown in Fig. 1. The spectrum was used to calculate the absorption cross section of the $^5I_8\rightarrow{}^5F_5$ absorption transition of $Ho^{3+}$ at 650 nm in ZBLAN glass. The absorption spectrum of the $Ho^{3+}$ and $Pr^{3+}$ ions in ZBLAN codoped glass shows a strong overlap between the $^5I_8\rightarrow{}^5I_7$ absorption transition of $Ho^{3+}$ (centered at 1950 nm) and the $^3H_4\rightarrow{}^3F_2$, $^3H_6$ absorption transition of

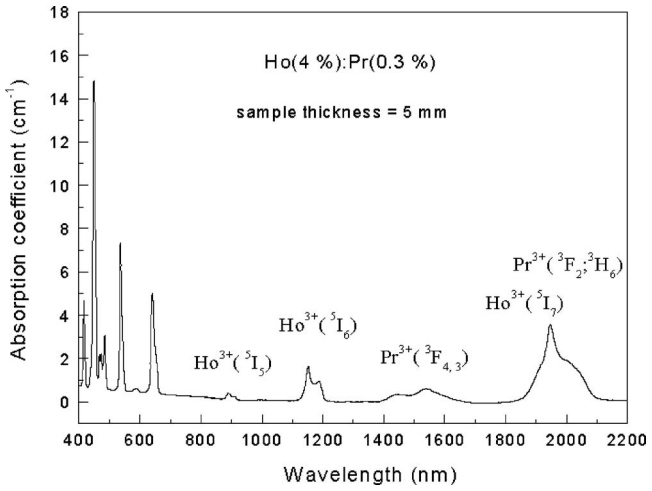


FIG. 1. Absorption spectrum of $Ho^{3+}$(4 mol %), $Pr^{3+}$(0.3 mol %)-doped ZBLAN glass measured at room temperature using the Cary 17D spectrophotometer. The sample thickness was equal to 5 mm. The $Ho^{3+}$ ion concentration of 4 mol % corresponds to $5.5\times10^{20}$ ions $cm^{-3}$.

$Pr^{3+}$ (centered at 2100 nm); it is expected that efficient energy transfer will occur from the $^5I_7$ excited state of $Ho^{3+}$ to the $^3F_2$, $^3H_6$ states of $Pr^{3+}$.

Figure 2 shows the luminescence decay of the $^5I_7$-excited state in $Ho^{3+}$(4 mol %)-doped ZBLAN and $Ho^{3+}$(4 mol %), $Pr^{3+}$(*x* mol %)-codoped ZBLAN glasses. It can be observed that a strong decrease in the $^5I_7$ excited state lifetime takes place for the $Ho^{3+}$(4 mol %), $Pr^{3+}$(0.2 mol %) and $Ho^{3+}$(4 mol %), $Pr^{3+}$(0.3 mol %)-codoped ZBLAN glasses in comparison with the decay of $Ho^{3+}$(4 mol %)-doped ZBLAN glass. The $Ho^{3+}(^5I_7)\rightarrow Pr^{3+}(^3F_2,{}^3H_6)$ nonradiative energy transfer (which we label ET1) is therefore very effective in $Ho^{3+}$, $Pr^{3+}$-codoped ZBLAN glass. The solid lines in Fig. 2 represent the best fit of the $Ho^{3+}(^5I_7)$ state luminescence decay using the Burshtein model,[14] which

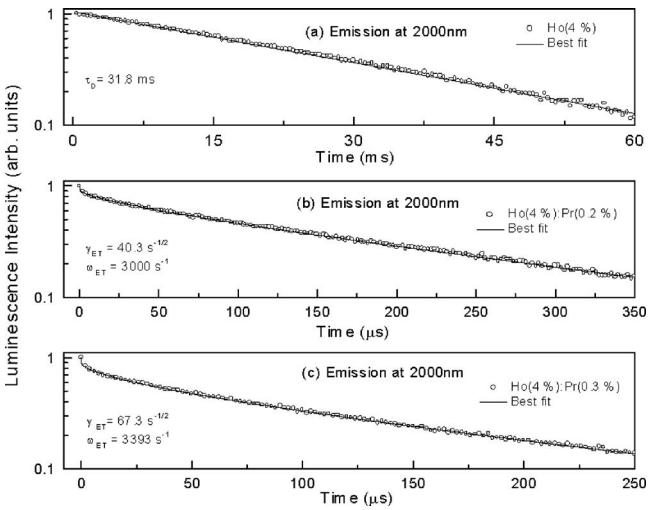


FIG. 2. Luminescence decay of the $^5I_7$ level of $Ho^{3+}$ in (a) singly $Ho^{3+}$(4 mol %)-doped ZBLAN, (b) $Ho^{3+}$(4 mol %), $Pr^{3+}$(0.2 mol %)-co doped ZBLAN, and (c) $Ho^{3+}$(4 mol %), $Pr^{3+}$(0.3 mol %)-co doped ZBLAN induced by laser excitation at 1958 nm with a pulse duration of 4 ns and average energy of 5 mJ (and pulse repletion frequency of 10 Hz). The solid lines represent the best fit using the Burshtein model, and $\omega_{ET}$ and $\gamma_{ET}$ are the derived energy transfer parameters using a least squares fit.

includes donor migration in the energy transfer process. The expression we used to fit the luminescence decay for a dipole-dipole interaction is given by[14]

$$I(t) = I_0 \exp\left(-\frac{t}{\tau_D} - \omega_{ET}t - \gamma_{ET}\sqrt{t}\right), \quad (1)$$

where $\tau_D$ $(=\tau_{D2})$ is equal to 31.8 ms and is the lifetime of $^5I_7$ level measured for $Ho^{3+}$(4 mol %)-doped ZBLAN. Note that this measured lifetime is longer than both the lifetime of the $^5I_7$ state measured in a low concentration system (12 ms for 0.1 mol % $Ho^{3+}$) and the radiative lifetime of 12.6 ms.[15] This longer lifetime relates to the effects from excitation migration of the $^5I_7$ excited states at higher $Ho^{3+}$ concentrations. $\gamma_{ET}$ is the donor to acceptor ($Pr^{3+}$) energy transfer parameter and $\omega_{ET}$ is the transfer parameter which is related to the donor to acceptor energy transfer which is assisted by discrete excitation migration (or hopping) among donor ($^5I_7$) states. The relative luminescence efficiency of the donor state ($^5I_7$) can be calculated by integrating $I(t)$ for the entire decay. Integration of $I(t)$ has been used to calculate the effective lifetime of the $^3H_4(Tm^{3+})$ state due to $Tm^{3+}(^3H_6)$, $Tm^{3+}(^3H_4) \rightarrow Tm^{3+}(^3F_4)$, $Tm^{3+}$ $(^3F_4)$ cross relaxation (CR) among $Tm^{3+}$ ions in $Yb^{3+}$, $Tm^{3+}$-codoped systems.[16] The relative luminescence efficiency ($\eta_\ell$) has been calculated for the nonexponential decay of the donor state using the expression[17]

$$\eta_\ell = \frac{\int_0^\infty I(t)dt}{\int_0^\infty \exp(-t/\tau_D)dt} = \frac{\int_0^\infty I(t)dt}{\tau_D}. \quad (2)$$

In Eq. (2) we have used the normalized luminescence decay $I(t)$ such that $I(0)=I_0=1$, where $I_0$ is the fluorescence intensity at $t=0$ and $I(t\rightarrow\infty)=0$. Using $\eta_\ell = W_D/(W_D+W_{ET})$, where $W_D=\tau_D^{-1}$ is the donor intrinsic decay rate parameter and $W_{ET}$ is the donor to acceptor energy transfer rate parameter, one can obtain

$$W_{ET} = \frac{1}{\tau_D}\left(\frac{1-\eta_\ell}{\eta_\ell}\right). \quad (3)$$

In Eq. (3) $W_{ET}=0$ when $\eta_\ell=1$ and $W_{ET}\rightarrow\infty$ for $\eta_\ell\rightarrow 0$, as expected. The $Ho^{3+}\rightarrow Pr^{3+}$ transfer rate parameter for ET1 (i.e., $W_{ET}=W_{ET1}$) was calculated using Eq. (3) that incorporates the relative luminescence efficiency of the $^5I_7$ $(Ho^{3+})$ state and the intrinsic lifetime of this level $(\tau_D=\tau_{D_2}=31.8$ ms). The values of $W_{ET1}$ are given in Table I.

Based on this result, we can establish that the decay of the $^5I_7$ state is practically totally radiative in ZBLAN glass and the nonradiative multiphonon decay rate to the ground state is negligible if these measurements are performed at room temperature. The relative luminescence efficiencies of the two lowest excited states of $Ho^{3+}$ were obtained using the relation $\eta_\ell=\int_0^\infty I_i(t)dt/\tau_{Di}$, where $i=2$ refers to the $^5I_7$ level and $i=3$ to the $^5I_6$ state. Table I gives the energy transfer parameters ($\omega_{ET}$, $\gamma_{ET}$) and the luminescence efficiency ($\eta_\ell$) of $^5I_7$ state, which was diminished by ET1. One may obtain

TABLE I. Energy transfer parameters relating to the $^5I_7$ level The energy transfer parameters were obtained from the best fit to the 2000 nm luminescence of ZBLAN glasses double doped with 4 mol % $Ho^{3+}$ and 0.1, 0.2, or 0.3 mol % $Pr^3$. The energy transfer parameters $\gamma_{ET}$ and $\omega_{ET}$ were obtained using a least squares fit and $\tau_{D2}=31.8$ ms, which was measured independently from a $Ho^{3+}$ (4 mol %)-doped ZBLAN sample. The relative luminescence efficiency $\eta_\ell$ was calculated using the integration of the normalized luminescence decay of $Ho^{3+}$ in $Ho^{3+}$, $Pr^{3+}$-codoped ZBLAN.

| Luminescence from the $^5I_7$ level of $Ho^{3+}$ | | | | |
|---|---|---|---|---|
| $Pr^{3+}$ (mol %) | $C_{DA}$ ($cm^6$ $s^{-1}$) $(10^{-38})$ | $\gamma_{ET}$ ($s^{-1/2}$) | $\omega_{ET}$ ($s^{-1}$) | $\eta_\ell$ |
| 0.1 | 3.1±0.4 | 18.1±0.6 | 1455±3 | $1.428\times10^{-2}$ |
| 0.2 | 3.9±0.7 | 40.3±0.8 | 3000±6 | $5.723\times10^{-3}$ |
| 0.3 | 4.8±0.7 | 67.3±1.1 | 3393±27 | $3.773\times10^{-3}$ |

| Migration assisted $Ho^{3+}(^5I_7)\rightarrow Pr^{3+}$ | | | |
|---|---|---|---|
| $Pr^{3+}$ (mol %) | $W_{ET1}$ ($s^{-1}$) | $\gamma_{ET}^2$ ($s^{-1}$) | $R$ $(=\gamma_{ET}^2/W_{ET1})$ |
| 0.1 | 2171 | 328 | 0.15 |
| 0.2 | 5463 | 1624 | 0.30 |
| 0.3 | 8302 | 4529 | 0.55 |

the microscopic transfer constant $C_{DA}(cm^6\ s^{-1})$ using the following expression that relates this constant with the energy transfer parameter $\gamma_{ET}(s^{-1/2})$,

$$C_{DA} = \frac{9\gamma_{ET}^2}{16\pi^3 c_A^2}, \quad (4)$$

where $c_A$ is the $Pr^{3+}$ concentration. The calculated values of $C_{DA}$ varied from $3.1\times10^{-38}$ to $4.8\times10^{-38}$ $cm^6\ s^{-1}$ as the $Pr^{3+}$ concentration changed from 0.1 to 0.3 mol %, as shown in Table I. The average value of $C_{DA}$ for ET1 obtained in this work was equal to $3.9\times10^{-38}$ $cm^6\ s^{-1}$, which is higher than the microscopic rate constant found in the case of $Ho^{3+}$ $(^5I_7)$ deactivation by $Nd^{3+}$ ions in Ho:Nd:YLF crystal in which case $C_{DA}$ was $8.6\times10^{-41}$ $cm^6\ s^{-1}$.[7]

If one assumes that $\gamma_{ET}{}^2$ relates to direct energy transfer, one can calculate the ratio $R=\gamma_{ET}{}^2/W_{ET}$. which determines the relative contribution of direct energy transfer to the total energy transfer. Table I shows that the contribution of the direct energy transfer to the total energy transfer increases (i.e., $R=0.15\rightarrow0.55$) and the influence of energy migration among donor ions decreases with increasing $Pr^{3+}$ concentration. This situation is expected because with increasing $Pr^{3+}$ concentration each $Ho^{3+}$ excitation finds a $Pr^{3+}$ ion faster, i.e., less energy migration among $Ho^{3+}$ ions is necessary before direct energy transfer to a $Pr^{3+}$ ion takes place.

### B. Luminescence from the $^5I_6$ excited state of $Ho^{3+}$

Figure 3 shows the luminescence decay of the $^5I_6$ excited state of $Ho^{3+}$ observed at 1200 nm due to the $Ho^{3+}(^5I_6)\rightarrow Pr^{3+}(^3F_5, ^3F_4)$, energy transfer process (which we label ET2) in $Ho^{3+}$, $Pr^{3+}$-codoped ZBLAN glass. The solid line in Figs. 3(a) and 3(b) represents the best fit to the luminescence decay using the Burshtein model, i.e., Eq. (1). The energy transfer rate parameter of ET2 with $W_{ET}=W_{ET2}$ was calculated using Eqs. (2) and (3), where $\eta_\ell$ is now the relative luminescence efficiency of the $^5I_6$ excited state and

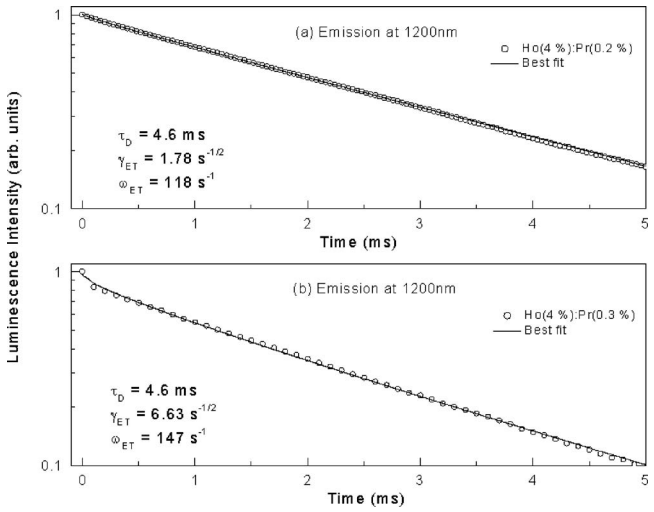


FIG. 3. Luminescence decay of the $^5I_6$ level of (a) $Ho^{3+}$(4 mol %), $Pr^{3+}$(0.2 mol %)-co doped ZBLAN and (b) $Ho^{3+}$(4 mol %), $Pr^{3+}$(0.3 mol %)-co doped ZBLAN. The 1200 nm luminescence was produced by a pulsed laser excitation at 1151 nm with a pulse duration of 4 ns and mean energy of 6 mJ at 10 Hz. The solid lines represent the best fit using the Burshtein model, and $\omega_{ET}$ and $\gamma_{ET}$ are the derived energy transfer parameters using a least squares fit.

$\tau_D = \tau_{D3} = 4.6$ ms. The values of $W_{ET2}$ and $\gamma_{ET}^2$ are given in Table II. The values of $R$ shown in Table II show that in a similar manner to ET1 the influence of direct energy transfer increases (i.e., $R = 0.009 \rightarrow 0.15$) and the influence of energy migration among donor ions decreases with increasing $Pr^{3+}$ concentration. The ratio of direct energy transfer to the total energy transfer is smaller for ET2 compared to ET1, which suggests that more energy migration is required for ET2 compared to ET1.

Table II gives the energy transfer parameters ($\omega_{ET}$, $\gamma_{ET}$) and the relative luminescence efficiency ($\eta_\ell$) of the $^5I_6$ state due to ET2. The microscopic transfer constant $C_{DA}$ varies from $0.18 \times 10^{-41}$ to $3.51 \times 10^{-41}$ $cm^6\ s^{-1}$ in the case of the $Ho^{3+}$ ($^5I_6$) deactivation by the $Pr^{3+}$ ($^3F_4, ^3F_3$) states, when the $Pr^{3+}$ concentration changes from 0.1 to 0.3 mol %. The average value of $C_{DA}$ for ET2 is $2.05 \times 10^{-41}$ $cm^6\ s^{-1}$ is three order of magnitude smaller than the $C_{DA}$ value for ET1 and is approximately 36 times bigger than the corresponding parameter determined for the case of $Ho^{3+}$ ($^5I_6$) deactivation by $Nd^{3+}$ in Ho:Nd:YLF crystal ($C_{DA} = 5.6 \times 10^{-42}$ $cm^6\ s^{-1}$).[7] This indicates that the deactivation of the $Ho^{3+}$ ($^5I_6$) state by energy transfer to $Pr^{3+}$ ions will potentially have a larger impact on the population inversion of the 2.9 $\mu$m laser transition compared to deactivation of the $Ho^{3+}$($^6I_6$) state that would be introduced by $Nd^{3+}$ ions.

TABLE II. Energy transfer parameters relating to the $^5I_6$ level. The energy transfer parameters were obtained from the best fit to the 1200 nm luminescence of ZBLAN glasses double doped with 4 mol % $Ho^{3+}$ and 0.1, 0.2, or 0.3 mol % $Pr^3$. The energy transfer parameters $\gamma_{ET}$ and $\omega_{ET}$ were obtained using a least squares fit and $\tau_{D2} = 4.6$ ms, which was measured independently from a $Ho^{3+}$(4 mol %)-doped ZBLAN sample. The relative luminescence efficiency $\eta_\ell$ was calculated using the integration of the normalized luminescence decay of $Ho^{3+}$ in $Ho^{3+}$, $Pr^{3+}$-doped ZBLAN.

| Luminescence from the $^5I_6$ level of $Ho^{3+}$ | | | | |
|---|---|---|---|---|
| $Pr^{3+}$ (mol %) | $C_{DA}$ ($cm^6\ s^{-1}$) ($10^{-40}$) | $\gamma_{ET}$ ($s^{-1/2}$) | $\omega_{ET}$ ($s^{-1}$) | $\eta_\ell$ |
| 0.1 | 0.69±0.08 | 0.85±0.05 | 67.0±0.1 | 0.7285 |
| 0.2 | 0.76±0.06 | 1.78±0.06 | 118.0±0.3 | 0.5949 |
| 0.3 | 4.69±0.29 | 6.63±0.21 | 147.0±1.2 | 0.4433 |
| Migration assisted $Ho^{3+}(^5I_6) \rightarrow Pr^{3+}$ energy transfer | | | | |
| $Pr^{3+}$ (mol %) | $W_{ET2}$ ($s^{-1}$) | $\gamma_{ET}^2$ ($s^{-1}$) | $R$ ($=\gamma_{ET}^2/W_{ET2}$) | |
| 0.1 | 81 | 0.73 | 0.009 | |
| 0.2 | 148 | 3.2 | 0.021 | |
| 0.3 | 273 | 44 | 0.161 | |

### C. Energy transfer upconversion (ETU) from the lowest excited states of $Ho^{3+}$

Two emission bands centered at 1200 and 655 nm were observed in $Ho^{3+}$ (4 mol %) -doped ZBLAN produced by pulsed laser excitations at 1958 and 1151 nm, respectively. The temporal characteristics of both upconversion emissions were observed to be dependent on the excitation energy density up to the limit of ~0.2 $J/cm^3$. For larger energy densities we observed a constant upconversion transient response. (The excitation energy densities were determined for constant energies of 3.1 mJ at 1958 nm and 8 and 12 mJ at 1151 nm. Four focus positions provided excitation volumes of $3.9 \times 10^{-3}$, $7.6 \times 10^{-3}$, $15.7 \times 10^{-3}$, and $35.3 \times 10^{-3}$ $cm^3$.) This observation cannot be applied to the luminescence decay of the lower excited (or donor) level involved in the upconversion process because one finds that the initial part of the decay curve of the donor level changes its slope as the pulse energy is varied. When we measured the intrinsic $^5I_7$ and $^5I_6$ fluorescence decays, we used a 6 mJ pulse energy (i.e., 1.9 mJ absorbed) to minimize the effects from ETU. This is demonstrated by the fact that the best fit of the $^5I_7$ (and $^5I_6$) luminescence decay curve is purely exponential, as seen in Fig. 2(a). The upconversion luminescence at 1200 nm was produced by a phonon-assisted ETU process, which we label ETU1 that can be represented by $Ho^{3+}(^5I_7, ^5I_7) \rightarrow Ho^{3+}(^5I_6, ^5I_8)$. Figure. 4 displays the 1200 nm luminescence decay of $^5I_6$ level when directly excited at 1151 nm [Fig. 4(a)] and when indirectly excited at 1958 nm by the ETU1 process [Fig. 4(b)].

A second upconversion luminescence at 655 nm was produced after two interacting $^5I_6$ states promote excitation to the $^5F_5$ level by way of a similar ETU process, labeled here as ETU2 and which can be represented by $Ho^{3+}(^5I_6, ^5I_6) \rightarrow Ho^{3+}(^5F_5, ^5I_8)$. Figures 5(a) and 5(b) show the luminescence transient measured at 655 nm from the $Ho^{3+}$ ($^5F_5$) excited state of $Ho^{3+}$ (4 mol %)-doped ZBLAN. This 655 nm luminescence was produced by two distinct ways using (i) excitation at 532 nm to produce the $^5I_8 \rightarrow {}^5S_2$ absorption transition which was followed by fast (~20 $\mu$s) decay to $^5F_5$ state, see Fig. 5(a); (ii) indirect excitation at 1151 nm to produce the $^5I_8 \rightarrow {}^5I_6$ absorption transition which was followed by ETU2, see Fig. 5(b). Despite the fact that 655 nm upconversion luminescence has also been observed in $Ho^{3+}$, $Pr^{3+}$-codoped ZBLAN, we measured the ETU2 rate parameter using singly $Ho^{3+}$-doped ZBLAN in

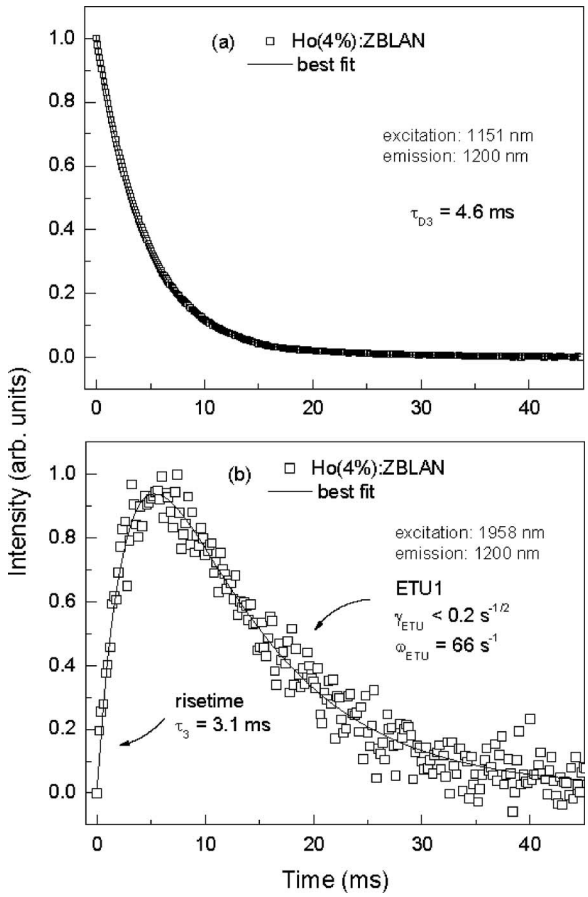


FIG. 4. (a) Luminescence decay of the $^5I_6$ excited state at 1200 nm measured after pulsed laser excitation at 1151 nm in singly $Ho^{3+}$(4 mol %)-doped ZBLAN (density of excited $^5I_7$ states of $\sim 5 \times 10^{17}$ $cm^{-3}$) and (b) the upconversion luminescence at 1200 nm induced by pulsed laser excitation at a wavelength of 1958 nm (pulse energy=3.1 mJ in 4 ns) having a density of excited ($^5I_7$) states of $1.56 \times 10^{18}$ $cm^{-3}$. The solid line represents the best fit using the Burshtein model, and $\omega_{ETU}$ and $\gamma_{ETU}$ are the ETU1 parameters using a least squares fit.

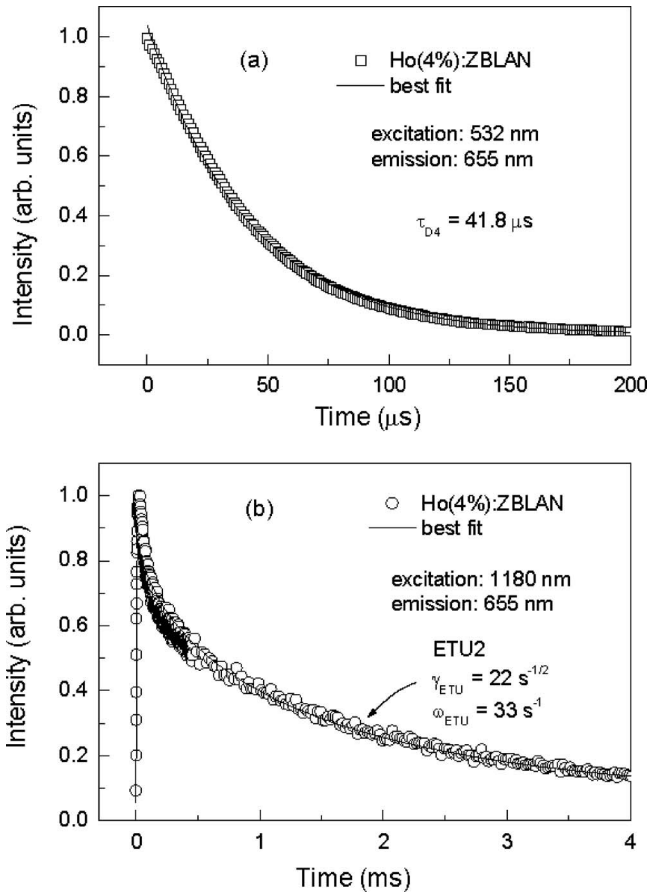


FIG. 5. The $^5F_5$ excited state luminescence of $Ho^{3+}$ observed at 655 nm in singly $Ho^{3+}$(4 mol %)-doped ZBLAN glass after (a) direct excitation at 532 nm and (b) exciting the $^5I_6$ state at a wavelength of 1151 nm (pulse energy=8 mJ in 4 ns) having a density of excited ($^5I_6$) states of $1.17 \times 10^{18}$ $cm^{-3}$. The solid line represents the best fit using the Burshtein model, and $\omega_{ETU}$ and $\gamma_{ETU}$ are the ETU2 parameters using a least squares fit.

order to eliminate the influence of ET2. The solid lines in Figs. 4(b) and 5(b) represent the best fit to the 1200 and 655 nm emissions using Eq. (5) that has been derived for the acceptor luminescence transient where the energy transfer involves the Burshtein (or Inokuti-Hirayama) model for a dipole-dipole energy transfer.[18] The relation is given by

$$I = I_0\left[\exp\left(-\frac{t}{\tau_D} - \omega_{\mathrm{ETU}}t - \gamma_{\mathrm{ETU}}\sqrt{t}\right) - \exp\left(-\frac{t}{\tau_A}\right)\right], \quad (5)$$

where $\tau_A$ is the total lifetime of the acceptor excited state and $\tau_D$ is the intrinsic lifetime of the donor excited ($Ho^{3+}$) ion. The first term in Eq. (5) gives the nonexponential decay of the donor excited state directly involved in the ETU process. The second term is the acceptor excited state decay. The adjustable transfer parameters $(\omega_{\mathrm{ETU1}}, \gamma_{\mathrm{ETU1}})$ and $(\omega_{\mathrm{ETU2}}, \gamma_{\mathrm{ETU2}})$ in Eq. (5) relate to ETU1 and ETU2 processes, respectively. The best fit to the upconversion luminescence gave (a) $\omega_{\mathrm{ETU1}}=66$ $s^{-1}$ and $\gamma_{\mathrm{ETU1}}<0.2$ $s^{-1/2}$ for 1200 nm emission; (b) $\omega_{\mathrm{ETU2}}=33$ $s^{-1}$ and $\gamma_{\mathrm{ETU2}}=22$ $s^{-1/2}$ for 655 nm emission, measured for $Ho^{3+}$(4 mol %)-doped ZBLAN. The luminescence efficiency of the donors in the lower state that are involved in the ETU process was obtained using the following expression:

$$\eta_\ell = \frac{1}{\tau_D}\int_0^\infty \exp\left(-\frac{t}{\tau_D} - \omega_{\mathrm{ETU}}t - \gamma_{\mathrm{ETU}}\sqrt{t}\right)dt, \quad (6)$$

in which $I_0=1$ for $t=0$, according to Eq. (2). The ETU rate parameter ($W_{\mathrm{ETU}}$) was obtained using an expression similar to Eq. (3). The relative luminescence efficiencies ($\eta_\ell$) due to ETU1 and ETU2 were obtained using $\tau_D(^5I_7)=31.8$ ms and $\tau_D(^5I_6)=4.6$ ms in Eq. (6). The ETU rate parameters $W_{\mathrm{ETU1}}$ and $W_{\mathrm{ETU2}}$ were obtained for the $Ho^{3+}$-doped ZBLAN system, using an equation similar to Eq. (3). By observing the 655 nm luminescence transient shown in Fig. 5(b), one observes that the fluorescence decay is consistent with the measured mean decay time ($\tau$) of the donor ($^5I_6$) state involved in the ETU2 process ($\tau=1.33$ ms). On the other hand, the 655 nm luminescence has a short decay time of $\sim 41.8$ $\mu$s when this level is directly excited at 532 nm by the short laser pulse of 4 ns duration and a pulse energy of 5 mJ, as shown in Fig. 5(a) for the $Ho^{3+}$(4 mol %)-doped ZBLAN glass. The 655 nm emission exhibits the shortened decay time of 42 $\mu$s compared to the intrinsic 290 $\mu$s due to the phonon-assisted CR interaction $Ho^{3+}$ $(^5F_5, ^5I_6) \rightarrow Ho^{3+}(^5I_8, ^5I_7)$ that depopulates this state in a highly con-

TABLE III. Parameters used in the rate equation modeling.

| Luminescence branching ratio and radiative lifetimes of $Ho^{3+}$[a] | | | | |
|---|---|---|---|---|
| Transition | $\beta$ | $\tau_R$ | $\tau$ (expt) | $W_{nr}$ ($s^{-1}$) |
| $^5F_5\rightarrow$ | | 500 $\mu$s | 290 $\mu$s | 1448 |
| $^5I_6$ | 0.05 | | | |
| $^5I_7$ | 0.18 | | | |
| $^5I_8$ | 0.77 | | | |
| $^5I_6\rightarrow$ | | 5.9 ms | 3.5 ms | 116.2 |
| $^5I_7$ | 0.09 | | | |
| $^5I_8$ | 0.91 | | | |
| $^5I_7\rightarrow{}^5I_8$ | 1 | 12.6 ms | 12 ms | |

| $Ho^{3+}\rightarrow Ho^{3+}$ energy transfer rate parameters (expt)[b] | | |
|---|---|---|
| $Ho^{3+}$ (mol %) | $W_{CR}$ ($s^{-1}$) | $\eta_\ell(^5F_5)$ |
| 2 | 107 76 | 0.2424 |
| 4 | 194 87 | 0.1503 |
| 6 | 251 23 | 0.1207 |

| $Ho^{3+}\rightarrow Pr^{3+}$ energy transfer rate parameters (expt)[b] | | | | |
|---|---|---|---|---|
| $Pr^{3+}$ (mol %) | $W_{ET1}$ ($s^{-1}$) | $W_{ET2}$ ($s^{-1}$) | $\eta_\ell(^5I_7)$ | $\eta_\ell(^5I_6)$ |
| 0.1 | 2171 | 81 | $1.427\times10^{-2}$ | 0.7285 |
| 0.2 | 5463 | 148 | $5.723\times10^{-3}$ | 0.5949 |
| 0.3 | 8302 | 273 | $3.773\times10^{-3}$ | 0.4433 |

[a]Values obtained from the literature (Ref. 15).
[b]Experimental relative luminescence efficiencies and calculated rate values (this work).

centrated system, i.e., for $[Ho^{3+}]>0.5$ mol %. The luminescence decay of the $^5F_5$-excited state was measured for three $Ho^{3+}$-doped ZBLAN samples (2, 4, and 6 mol %) by direct excitation at 532 nm. The relative luminescence efficiency of the $^5F_5$ state was obtained for the three $Ho^{3+}$-doped ZBLAN samples using the integration of the luminescence decay curve previously described by Eq. (2). The values obtained are given in Table III as well the corresponding CR rate parameter $W_{CR}$ that was calculated using a similar equation to Eq. (3) with $\tau_D=\tau_{D4}=290$ $\mu$s. The calculated values are given in Table III.

### D. Model for ETU in $Ho^{3+}$-doped ZBLAN

A detailed investigation of the time dependence of the ETU luminescence transient was carried out by monitoring the upconverted luminescence at 1200 and 655 nm as a function of the absorbed excitation energy density and hence the density of excited $Ho^{3+}$ ions. We made a fit to the luminescence transient using the Burshtein model given by Eq. (5) for a dipole-dipole interaction. The rate parameters for ETU were obtained using the integration method given by Eq. (6) and a similar equation to Eq. (3). The results are presented in Table IV. Figures 6(a) and 6(b) display the ETU rate parameters for ETU2 and ETU1 as a function of the density of excited $Ho^{3+}$ ions. It can be observed that the rate parameter of both ETU processes reaches a constant rate when the excited $Ho^{3+}$ ion density reaches a value of $2\times10^{18}$ $cm^{-3}$; this behavior suggests that there exists a critical distance $R_C$ between excited $Ho^{3+}$ ions for both ETU processes. Based on a statistically random separation between the excited $Ho^{3+}$ ions in the glass lattice, we can say that the fraction of excited

TABLE IV. Parameters relating to the proposed model for the ETU processes observed in $Ho^{3+}$(4 mol %)-doped ZBLAN.

| $Ho^{3+}\rightarrow Ho^{3+}$ ETU rate parameters (expt) | | |
|---|---|---|
| | ETU1 | ETU2 |
| $K_0$ ($s^{-1}$) | 72 | 650 |
| $N_C$ ($cm^{-3}$) | $3.6\times10^{17}$ | $2.94\times10^{17}$ |
| $R_C$ (Å) | 87 | 70 |

$Ho^{3+}$ ions $fdR$, which have another excited $Ho^{3+}$ ion as the closest neighbor between distance $R$ and $R+dR$, is given by,[19]

$$fdR = 4\pi R^2 N_{Ho}\frac{N^*}{N_{Ho}}\left(1-\frac{N^*}{N_{Ho}}\right)^{[\pi/3R^3N_{Ho}-2]}dR, \tag{7}$$

where $N^*$ is the concentration of $Ho^{3+}$ excited ions ($cm^{-3}$) and $N_C$ is the critical concentration of excited $Ho^{3+}$ ions which is related to $R_C$. Integrating Eq. (7) between $R_m$ (the minimum distance between $Ho^{3+}$ ions) and $R=\infty$ yields the ETU efficiency as a function of $N^*$ according to

$$\eta_{ETU} = \int_{R_m}^{R_C} fdR\times 1 + \int_{R_c}^{\infty} fdR\times 0 = 1-\exp(-N_C/N^*), \tag{8}$$

where we use $\int_{R_C}^{\infty} fdR=\exp(-N_C/N^*)$, which has been determined previously.[19] The observation that the ETU rate pa-

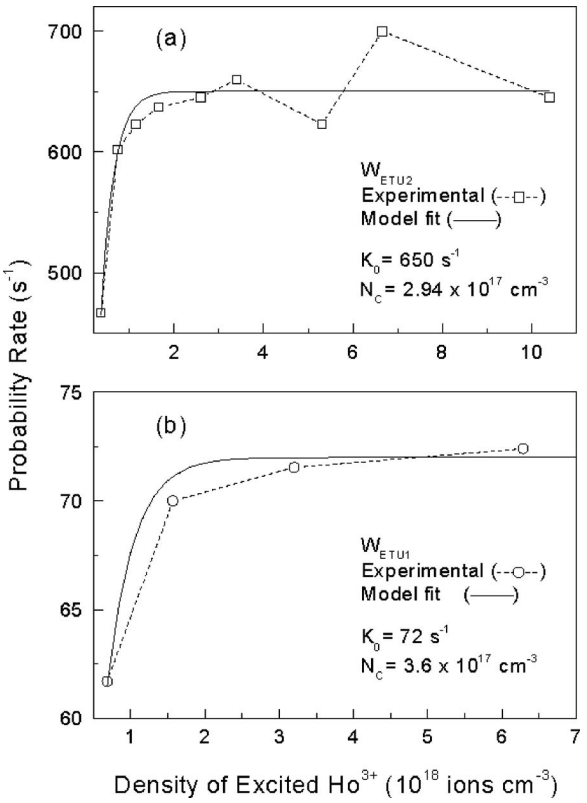


FIG. 6. ETU rate parameter as a function of the experimental excited $Ho^{3+}$ ion density ($N^*$) obtained by measuring the luminescence transient of (a) the $^5F_5$ level after excitation at 1151 nm and (b) the $^5I_6$ level after excitation at 1958 nm. The solid lines represent the best fit using the proposed model for ETU.

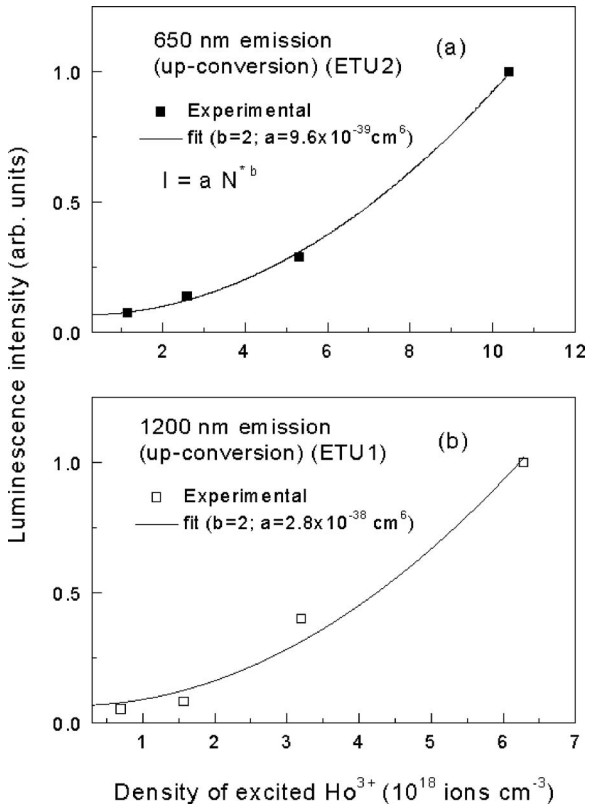


FIG. 7. Measured dependence of (a) 650 nm and (b) 1200 nm emission as a function of the excited $Ho^{3+}$ ion density. The solid line represents $I=aN^{*b}$, where $b=2$ for both ETU processes.

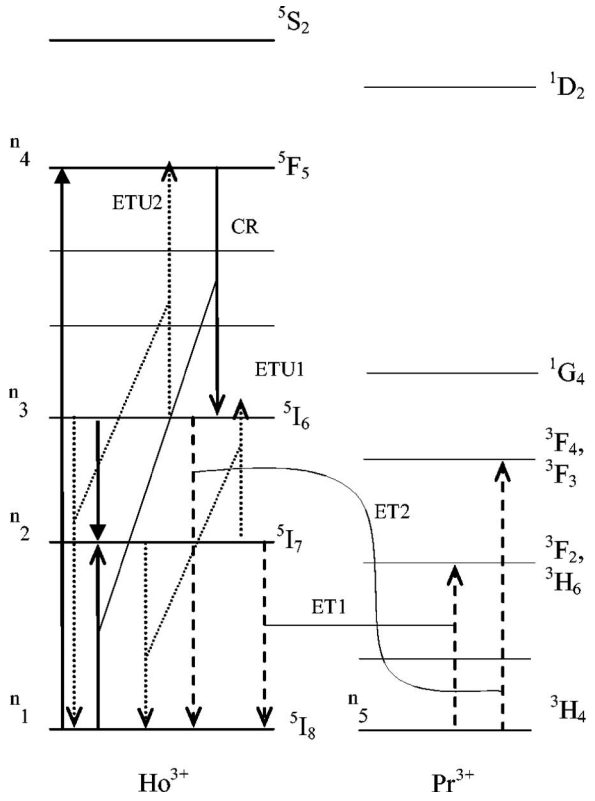


FIG. 8. Simplified energy level diagram for the $Ho^{3+}$, $Pr^{3+}$ system used for the rate equations modeling. The diagram shows the optical pumping at 650 nm, the 2900 nm laser emission from the $^5I_6$ excited state of $Ho^{3+}$, and the $Ho^{3+} \rightarrow Pr^{3+}$ energy transfer processes.

rameter dependence on $N^*$ in Figs. 6(a) and 6(b) displays a constant probability rate for higher excitation densities indicates that the ETU relative efficiency for large values of $N^*$ should be given by $\eta_{ETU}(N^*)=W_{ETU}/K_0$, where $K_0$ is the rate parameter constant. The solid lines in Figs. 6(a) and 6(b) represent the best fit using the model, which gave $N_C=2.94\times10^{17}$ cm$^{-3}$ and $K_0=650$ s$^{-1}$ for ETU2 and $N_C=3.6\times10^{17}$ cm$^{-3}$ and $K_0=72$ s$^{-1}$ for ETU1. These values for $K_0$ should be used in a rate equation system simulating the operation of a laser because under these circumstances, higher excited $Ho^{3+}$ ion densities ($N^*\sim10^{19}$ cm$^{-3}$) are usually present.

The luminescence intensities at 1200 and 655 nm produced by the ETU1 and ETU2 processes, respectively as a function of the excited $Ho^{3+}$ density are presented in Figs. 7(a) and 7(b). It can be observed that the emissions are dependent on the square of $N^*$, as represented by the solid and open squares in Figs. 7(a) and 7(b). The proposed model for ETU predicts an ETU rate linearly dependent on the $N^*$ for $N^* \ll N_C$, i.e., $W_{ETU} \alpha N^*$, as has been previously reported for ETU process between two $Nd^{3+}$ ions in the $^4F_{3/2}$ state.[20]

## IV. DISCUSSION

The rate parameters for ETU1 correspond to 11% of the rate parameters for ETU2, consequently ETU does not favor a population inversion between the $^5I_6$ and $^5I_7$ energy levels in singly $Ho^{3+}$-doped ZBLAN glass. The opposite situation has been observed in the case of $Er^{3+}$-doped ZBLAN glass, where the corresponding rate parameter values for ETU1 are three times larger than the corresponding rate parameter values for ETU2 and ETU contributes positively to a population inversion.[21] (The ETU processes in $Er^{3+}$ involve similarly positioned energy levels as in $Ho^{3+}$.) The ET1 energy transfer process has a larger rate parameter than the ETU2 process in $Ho^{3+}$ (4 mol %), $Pr^{3+}$ (0.3 mol %)-doped ZBLAN, which will minimize the negative effect of ETU on the laser gain. ET1 effectively quenches the $^5I_7$ intrinsic lifetime of 31.8 ms to such an extent that the mean decay time is only 120 $\mu$s for $Ho^{3+}$ (4 mol %), $Pr^{3+}$ (0.3 mol %)-codoped ZBLAN glass. Similar effects have been observed on the lower laser level of $Er^{3+}$ (8.75 mol %), $Pr^{3+}$ (1.55 mol %)-codoped ZBLAN glass, where the $Er^{3+}$ ($^4I_{13/2}$) intrinsic lifetime of 9 ms is reduced to 20 $\mu$s due an efficient $Er^{3+}(^4I_{13/2}) \rightarrow Pr^{3+}(^3F_3, ^3F_4)$ energy transfer process.[21]

### A. Rate equations for the $Ho^{3+}$, $Pr^{3+}$-codoped ZBLAN system

Figure 8 shows a simplified energy level scheme of the $Ho^{3+}$, $Pr^{3+}$ system considered for cw diode laser pumping at 650 nm. $n_1$, $n_2$, $n_3$, and $n_4$ are the $^5I_8$, $^5I_7$, $^5I_6$, and $^5F_5$ populations of $Ho^{3+}$, respectively. For the $Pr^{3+}$ ion, only the ground state $^3H_4$ ($n_5$) population was considered because the $^3F_4$, $^3F_3$, $^3F_2$, $^3H_6$, and $^3H_5$ excited state populations of $Pr^{3+}$ are strongly depopulated by fast multiphonon decay to the ground state and consequently they were neglected in the

model. The rate equations comprising the model using the fact that $n_1+n_2+n_3+n_4=0.04$ for a $Ho^{3+}$ concentration of 4 mol % are

$$\frac{dn_1}{dt} = -\sigma_{14}n_1\frac{I_P}{h\nu} + \frac{n_2}{\tau_2} + \frac{B_{31}}{\tau_{R_3}}n_3 - W_{CR}n_1n_4 + W_{ET1}n_2n_5 + W_{ET2}n_3n_5 + W_{ETU1}n_2^2 + W_{ETU2}n_3^2 + \frac{\beta_{41}}{\tau_{R_4}}n_4, \quad (9)$$

$$\frac{dn_2}{dt} = W_{CR}n_1n_4 + \left(\frac{B_{32}}{\tau_{R_3}} + W_{nR}(32)\right)n_3 - \frac{n_2}{\tau_2} - W_{ET1}n_2n_5 + \frac{\beta_{42}}{\tau_{R_4}}n_4 - 2W_{ETU1}n_2^2, \quad (10)$$

$$\frac{dn_3}{dt} = W_{CR}n_1n_4 - \frac{n_3}{\tau_3} - W_{ET2}n_3n_5 - 2W_{ETU2}n_3^2 + \left(\frac{\beta_{43}}{\tau_{R_4}} + W_{nR}(43)\right)n_4 + W_{ETU1}n_2^2, \quad (11)$$

$$\frac{dn_4}{dt} = \sigma_{14}n_1\frac{I_P}{h\nu} + W_{ETU2}n_3^2 - W_{CR}n_1n_4 - \frac{n_4}{\tau_4}, \quad (12)$$

where $I_P$ is the pump intensity given in W $cm^{-2}$ and $h\nu$ is the photon energy at 650 nm. $\beta_{ij}$ represents the luminescence branching ratio and $\tau_{R_i}$ is the radiative lifetime of $^5F_5$, $^5I_6$ and $^5I_7$ excited states of $Ho^{3+}$ labeled as $i=4$, 3, and 2, respectively.

### B. Numerical simulation of the rate equation system

Calculations were performed for the singly $Ho^{3+}$- and the $Ho^{3+}$, $Pr^{3+}$-codoped ZBLAN glasses containing 4 mol % $Ho^{3+}$ and 0.1, 0.2, and 0.3 mol % $Pr^{3+}$ using a computer program incorporating the Runge-Kutta numerical method. Figure 9 shows the time evolutions of $n_2(t)$, $n_3(t)$, and $\Delta n(t)=n_3(t)-n_2(t)$, the population inversion of $Ho^{3+}$ after switching the pump laser on at $t=0$ (using a pump rate of 80 $s^{-1}$ at 650 nm). Equilibrium in the populations was obtained after 10 ms in the $Ho^{3+}$ (4 mol %), $Pr^{3+}$ (0.3 mol %)-doped ZBLAN system, see Fig. 9(b). At that stage, the value for $\Delta n$ was obtained. On the other hand, equilibrium in the value for $\Delta n$ in the singly $Ho^{3+}$-doped ZBLAN system is established at a comparatively longer time, see Fig. 9(a). In addition, $n_3<n_2$ and $\Delta n<0$ for most of the calculation for the singly $Ho^{3+}$-doped ZBLAN system.

Figure 10 shows $\Delta n$ obtained for 2.92 $\mu$m laser emission from $Ho^{3+}$ in both singly $Ho^{3+}$-doped and $Ho^{3+}$, $Pr^{3+}$-codoped ZBLAN systems as a function of the pump rate ($R_P$) for the three $Pr^{3+}$ concentrations used in this work. The pump rates can be converted to pump intensities $I_P$ (W/$cm^2$) using $I_P=(h\nu R_P)/\sigma_{abs}$, where $\sigma_{abs}(^5I_8\rightarrow{}^5F_5)=8.56\times10^{-20}$ $cm^2$ at 650 nm. The results presented in Fig. 10 show that 0.3 mol % $Pr^{3+}$, which produces a strong quenching of the $^5I_7$ level decay time, leads to $\Delta n>0$. The similar $Ho^{3+}$ (3 mol %), $Pr^{3+}$ (0.3 mol %)-codoped ZBLAN glass has been shown experimentally to provide efficient 2.92 $\mu$m laser emission.[9] Thus we have shown both experimentally and theoretically that the $Pr^{3+}$ ion is a very effective deactivator for the 2.92 $\mu$m $^5I_6\rightarrow{}^5I_7$ laser transition of $Ho^{3+}$.

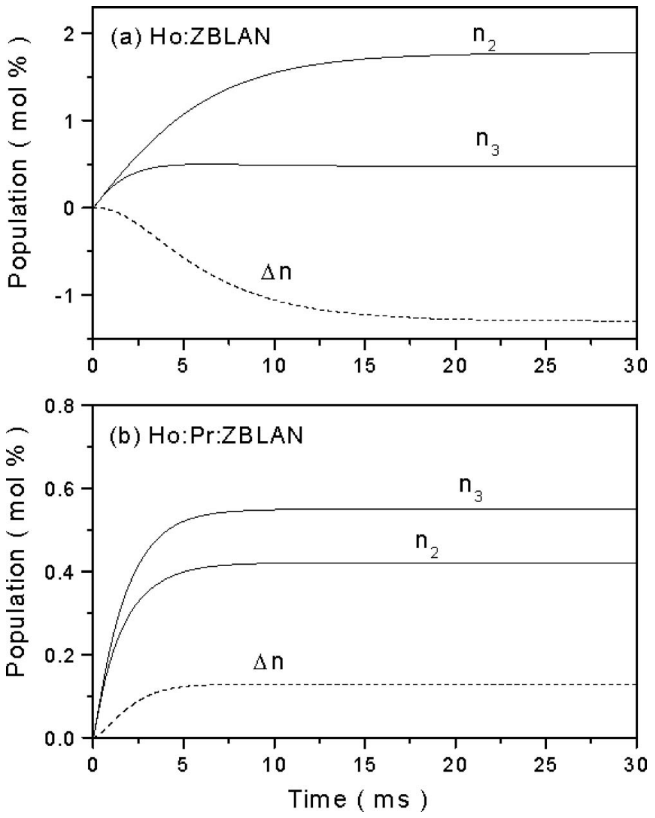


FIG. 9. Calculated evolution of the excited state populations (in mol %) of $Ho^{3+}$ obtained by numerical simulation of the rate equations for (a) $Ho^{3+}$(4 mol %)-doped ZBLAN and (b) $Ho^{3+}$(4 mol %), $Pr^{3+}$(0.3 mol %)-codoped ZBLAN. The simulations were obtained under a continuous pump rate of 80 $s^{-1}$ at 650 nm.

It is important to clarify that we have dealt with the total population inversion between the $^5I_6$ and $^5I_7$ multiplet levels without considering Stark splitting. We can, however, sketch out how the $^5I_7$ multiplet splitting will affect the calculated population inversion. The $^5I_7$ multiplet has three main sublevels localized at 4835, 5049, and 5243 $cm^{-1}$ (Ref. 15) having Boltzmann occupation factors $f_i$ equal to 0.676, 0.234, and 0.090, respectively. For the purposes of calculating the population inversion, the $^5I_6$ multiplet is located at 8544 $cm^{-1}$ with $f=1$. Three main emission lines are observed at 2.8 $\mu$m (1), 2.94 $\mu$m (2), and 3.11 $\mu$m (3). The population inversion for each $^5I_6\rightarrow{}^5I_7(i)$ transition will be given by $\Delta n_i=n_3-n_2f_i=n_2[(n_3/n_2)-f_i]$. In the case of $Ho^{3+}$ (4 mol %)-doped ZBLAN, we have seen that $n_3/n_2\ll f_3=0.09$, so $\Delta n_i<0$ for all the emission lines involved in the $^5I_6\rightarrow{}^5I_7$ transition. A positive but smaller population inversion can be obtained for the 2.94 and 3.11 $\mu$m emission lines in $Ho^{3+}$ (4 mol %), $Pr^{3+}$ (0.2 mol %)-codoped ZBLAN compared to $Ho^{3+}$ (4 mol %), $Pr^{3+}$ (0.3 mol %)-codoped ZBLAN.

## V. CONCLUSIONS

We have investigated in detail the deactivation of the $^5I_7$ excited state level of $Ho^{3+}$ in the presence of $Pr^{3+}$ ions in ZBLAN glasses. Two energy transfer upconversion pro-

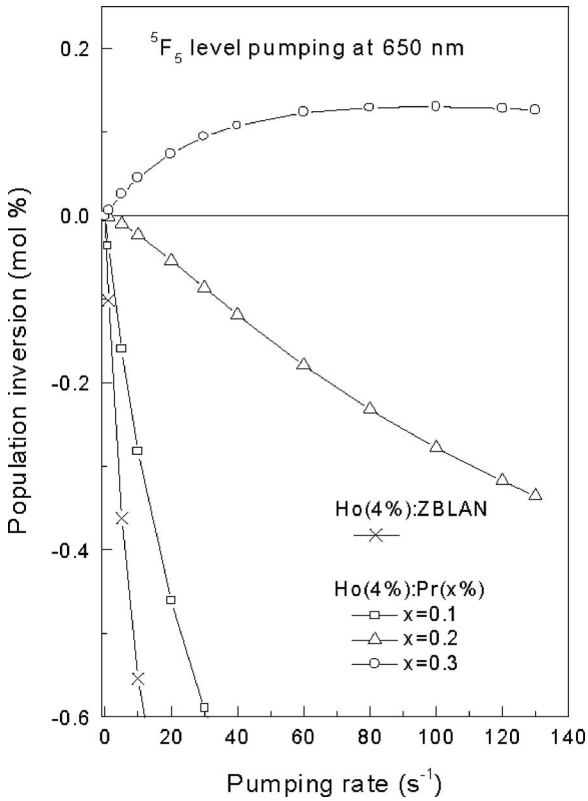


FIG. 10. Calculated population inversion (in mol %) for the laser emission at 2.9 $\mu$m obtained for a simulation with continuous laser pumping at 650 nm for (a) $Ho^{3+}$(4 mol %)-doped ZBLAN and (b) $Ho^{3+}$(4 mol %), $Pr^{3+}$($x$ mol %)-codoped ZBLAN glasses, where $x$=0.1, 0.2, and 0.3 mol %. Note that the $Ho^{3+}$ ion concentration of 1 mol % corresponds to $1.375 \times 10^{20}$ ions $cm^{-3}$.

cesses ETU1 and ETU2 which lead to the excitation of the $^5I_6$ and $^5F_5$ states were shown to occur in singly $Ho^{3+}$-doped ZBLAN glass. The rate parameters for these ETU processes were determined and it was established that the rate parameters for ETU2 were higher than those for ETU1. The rate parameter of the CR process involving the excited $^5F_5$ level and the $^5I_8$ ground state of $Ho^{3+}$ was determined from a best fit to the 655 nm luminescence. With all the relevant energy transfer rate parameters available, we numerically solved the rate equations for the ZBLAN system under cw laser pumping at 650 nm. The results established that the $Ho^{3+}$ (4 mol %)-doped ZBLAN glass that was codoped with 0.3 mol % $Pr^{3+}$ showed considerable improvement in the value of $\Delta n$ as compared to the corresponding singly $Ho^{3+}$-doped ZBLAN glass because of strong depopulation of the $^5I_7$ level of $Ho^{3+}$ by ET1. As a consequence, the doubly doped glass exhibited a maximum population inversion equal to ~3.3% of total $Ho^{3+}$ population for a cw pump rate of 80 $s^{-1}$. These facts indicate that $Ho^{3+}$, $Pr^{3+}$-codoped ZBLAN glass is a promising candidate for high power laser operation at 2.9 $\mu$m using diode laser pumping at 650 nm. The effect of $^5I_7$ deactivation by $Pr^{3+}$ ions on the population inversion of the $^5I_6 \rightarrow {}^5I_7$ transition in $Ho^{3+}$, $Pr^{3+}$-codoped ZBLAN glass is comparable to the gain improvement reported for $Er^{3+}$, $Pr^{3+}$-codoped ZBLAN glass.

## ACKNOWLEDGMENTS

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