Time resolved luminescence in (Tm:Ho) doped tellurite glass

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Received 24 February 2004; accepted 17 September 2004
Available online 28 October 2004

Abstract

Thulium (Tm 3+) doped and Holmium (Ho 3+) codoped tellurite glasses with the composition TeO 2–ZnO–Li2O–Bi2O3–CsCl have been investigated in relation to its time decay resolved luminescence, which was used to measure the donor (Tm) and acceptor (Ho) luminescence decays induced by resonant laser excitations. The mechanisms involved in Tm( 3F4) decay and Tm( 3F4)→Ho( 5I7) energy transfer were investigated. The lifetimes of excited Tm( 3H4), Tm(3F4) and Ho( 5I7) were measured by using short pulsed laser excitation at proper wavelength. The behavior from these ions in terms of the luminescence decay was completely different from fluoride and other tellurite glasses found in literature. One explanation about this behavior may be related to the presence of CsCl in the glass matrix that improves, for example, the amplifier performance.

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1. Introduction

TeO 2 based glasses have a wide interest for developing fiber optical amplifier and nonlinear optical devices for telecommunication. Tellurite glass has a wide transmission window (typically 300–5000 nm), high linear and nonlinear refractive indices, good corrosion resistance, high mechanical stability, and low cut-off phonon energy among oxide materials (800 cm−1). This material exhibit also high solubility for rare earth doping and low melting temperature. Because of the favorable structural properties, erbium [1–3] and thulium [4–7] doped fiber amplifiers have proven to be excellent materials for the S-band (1450–1530 nm) optical region. Despite of considerable advance found in the literature on the performance of optical amplifiers based on fluoride glasses, the telecommunication industries have not accepted its use in telecommunication because fluoride fiber fabrication and their splicing with standard silica fiber is difficult. It has been observed in the literature that thulium doped fluoride glass shows an intrinsic problem for optical operation at 1530 nm because the lower (3F4) excited state has a longer lifetime then the upper level (3H4). A deactivation of 3F4 state of Tm3+ is important. A deactivation process by means of up-conversion pumping at 1064 nm that can be used both to excite the 3H4 level and to depopulate the 3F4 level has been reported in the literature [5,6]. In another scheme the thulium doped fiber was codoped with Ho3+ and pumped at 790 nm into the 3H4 level of Tm1+ [4]. Another regime consists of using a cascade process in which the 3F4 is efficiently depopulated by the stimulated emission from 3F4 level at 1860 nm during the optical cycle of laser pumping 790 nm [8].

In view of these difficulties, the aim of this work is the study of Tm and Tm:Ho doped tellurite glasses based

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on the composition TeO$_2$–ZnO–Li$_2$O–Bi$_2$O$_3$–CsCl to characterize the energy transfer process and to discuss some relevant theoretical aspects of the $^3F_4$ deactivation of Tm$^{3+}$ state by Ho$^{3+}$ ions in TZLBC glass.

2. Experimental

Tellurite glasses of TeO$_2$–ZnO–Li$_2$O–Bi$_2$O$_3$–CsCl (TZLBC) family were prepared as single (Tm or Ho) and double doped (Tm:Ho) for time-resolved luminescence spectroscopy. Two sets of TZLBC glasses were prepared from ultra pure oxide starting materials (99.999%) with the following compositions:

(i) $(100 - x)(66\text{TeO}_2 \cdot 15.5\text{ZnO} \cdot 5\text{Li}_2\text{O} \cdot 4\text{Bi}_2\text{O}_3 \cdot 9.5\text{CsCl}) \cdot x\text{TmO}_2$ \quad (x = 0.2, 0.4, 0.8 and 1.5).

(ii) $(99.8 - y)(66\text{TeO}_2 \cdot 15.5\text{ZnO} \cdot 5\text{Li}_2\text{O} \cdot 4\text{Bi}_2\text{O}_3 \cdot 9.5\text{CsCl}) \cdot 0.2\text{TmO}_2 \cdot y\text{HoO}_2$ \quad (y = 0.6, and 1.5).

where $x$ and $y$ are given in mole percent.

Samples of Tm:TZLBC and Tm:Ho:TZLBC glasses were produced by melting at 800°C for 2h under high purity O$_2$ in a horizontally placed chamber inside of an electrical furnace. The melt was cast into a brass mold, preheated at 280°C, enabling the fabrication of rectangular shaped samples. Annealing at 290°C for 12h was performed after casting. Finally, the samples were face polished to allow the luminescence measurements perpendicularly to the laser excitation. Optical fibers for multimode and monomode operation were produced using the “rod-in-tube” processing method at 480°C with a pulling speed of 1.5m/min.

Selective excitation by tunable OPO laser was used to study the donor (Tm) and acceptor (Ho) luminescence in order to determine the mechanisms involved in Tm($^3F_4$) decay and Tm($^3F_4$)$\rightarrow$Ho($^1I_7$) energy transfer. The lifetimes of excited Tm($^3H_4$), Tm($^3F_4$) and Ho($^1I_7$) were measured using a pulsed laser excitation (4ns) from a tunable optical parametric oscillator (OPO) pumped by the second harmonic of a Q-Switched Quantel Nd:YAG laser Brilliant B. Laser pumping at 776nm was used to excite the $^3H_4$ Tm state while laser pumping at 1671nm and 1873nm were used to excite the $^3F_4$ and $^5I_7$ states of Tm and Ho, respectively. The time-dependent luminescence of the donor (Tm) and the acceptor (Ho) were detected by an InSb (77K) infrared detector (Judson model J10D) with a fast preamplifier (response time of 0.5μs) and analyzed using a 200MHz Tektronix oscilloscope (TDS 410). All the fluorescence decay times were measured at 300K. Band pass filters (80% transmittance, 10nm half width and $\sim 10^{-5}$ extinction coefficient) at 1500nm, 1800nm and 2000nm, were used to measure the luminescence of Tm($^3H_4$), Tm($^3F_4$) and Ho($^1I_7$) excited states, respectively.

3. Results and discussion

3.1. Donor decay and acceptor luminescence transient

Schematic energy level diagrams showing the energy states of Tm$^{3+}$ and Ho$^{3+}$ ions involved in the infrared absorption and emissions with the respective Tm-emission at 1470nm ($^3H_4$) and Ho-emission at 2000nm ($^1I_7$), as well as the possible energy transfers for (Tm:Ho) and (Tm:Tm):TZLBC glasses, are presented in Fig. 1(a) and (b), respectively. The cross-relaxation process that competes with the 1470nm emission involves the following Tm-excited level (DD) migration: Tm($^3F_4$$\rightarrow$Tm($^3H_4$$\rightarrow$Ho($^1I_7$). This DA energy transfer can be assisted by the Tm–Tm migration according to the notation (or DD migration) Tm($^3H_4$,$^3H_6$)$\rightarrow$Tm($^3H_6$,$^3F_4$). The Ho–Tm back transfer also occurs according to the following notation (or AD energy transfer) Ho($^1I_7$)$\rightarrow$Tm($^3F_4$).

One possibility of analyzing the 2000nm luminescence of Ho$^{3+}$ induced by the Tm($^3F_4$)$\rightarrow$Ho($^1I_7$) energy transfer considers that the decay rate of donor (Tm) luminescence is strongly modified by the interaction with all acceptor (Ho) ions included in the excitation volume. In this case, the donor and acceptor time-dependent luminescence is obtained by solving the microscopic rate equation for a typical donor (D$_j$) or

![Fig. 1. A simplified energy level diagram of Tm:Ho:TZLBC glass exhibiting the main energy transfer processes that occur in the Tm→Ho energy transfer are indicated. Fig. 1(a) shows the Tm($^3F_4$,$^3H_4$)$\rightarrow$Tm($^3H_6$,$^3F_4$) migration (process 1), the Tm($^3F_4$)$\rightarrow$Ho($^1I_7$) energy transfer (process 2) and the Ho($^1I_7$)$\rightarrow$Tm($^3F_4$) back transfer (process 3). Fig. 1(b) shows the Tm($^3H_4$,$^3H_6$)$\rightarrow$Tm($^3F_4$,$^3F_4$) cross-relaxation (process 4).](image-url)
acceptor \( (A_k) \) luminescence transients. The microscopic rate equations system is

\[
\frac{d\rho_D}{dt} = -\frac{\rho_D}{\tau_D} - \sum_{i=1}^{N_A} W_{DA}(R_i - R_j)\rho_D,
\]

(1)

\[
\frac{d\rho_A}{dt} = -\frac{\rho_A}{\tau_A} + \sum_{i=1}^{N_A} W_{DA}(R_i - R_j)\rho_D,
\]

(2)

where \( \rho_A \) and \( \rho_D \) are the respective probability excitation densities of acceptor \( (A_k) \) and donor ions \( (D_j) \). \( \tau_D \) and \( \tau_A \) are the lifetime of isolated donor and acceptor ions measured in a single doped material at low concentration \((\sim 0.2 \text{ mol}%)\). \( N_A \) is the number of acceptor ions in the excitation volume and \( W_{DA}(R_i - R_j) \) is the microscopic energy-transfer rate. The following solutions have been already obtained in Refs. [9,10].

\[
\rho_D(t) = \exp\left(-\frac{t}{\tau_D}\right) \exp\left(-\tau \sum_i W_{DA}(R_i)\right),
\]

(3)

\[
\rho_A(t) = \exp\left(-\frac{t}{\tau_A}\right) - \frac{\sum_i W_{DA}(R_i)}{\sum_i W_{DA}(R_i) + \frac{1}{\tau_D} - \frac{1}{\tau_A}} \times \exp\left(-\frac{t}{\tau_D} - \tau \sum_i W_{DA}(R_i)\right),
\]

(4)

Assuming that ions A and D are randomly distributed in the glass matrix, one finds that the mean probability of donor excitation density at time \( t \) is given by the statistical average of \( \rho_D(t) \) over various possible donor environments. Considering that only a dipole–dipole interaction \((s = 6)\) is important, we have that the microscopic transfer rate is given by \( W_{DA} = (1/\tau_D)(R_{DA}/R_s)^6 \). In this case, the transfer rate \( W_{DA}(R) \) is equal to the intrinsic decay rate \( 1/\tau_D \) of donor state when \( R = R_{DA} \). If the discrete lattice is approximated by a continuum in taking the averages over the interaction volume \( V = (4/3)\pi R^3 \) and making the limit of \( V \rightarrow \infty \), one obtains the Inokuti–Hirayama [9] solution for the donor luminescence decay

\[
\bar{\rho}_D(t) = \exp\left(-\frac{t}{\tau_D}\right) \left(-\frac{c_A}{c_0} \left(\frac{\pi t}{\tau_D}\right)^{1/2}\right),
\]

(5)

where \( c_A \) is the donor concentration and \( c_0 \) is the critical concentration given by \( c_0 = 3/(4\pi R_{DA}^3) \). The transfer parameter is given by \( \gamma = c_A/\sqrt{c_0} \) that is also related to the microscopic transfer constants, \( \gamma(\text{theor}) = 4^{1/2} c_A (C_{DA})^{1/2} \). The following solution has been obtained in Ref. [10] that represents the average luminescence transient of the acceptor derived following the Inokuti–Hirayama approach:

\[
\bar{\rho}_A(t) = C \left[\exp\left(-\frac{t}{\tau_A}\right) - \exp\left(-\gamma\sqrt{t} - \frac{t}{\tau_D}\right)\right],
\]

(6)

where \( \gamma \) is the fitting parameter which is obtained from the best fit of the time-dependent acceptor luminescence.

Eq. (5) is used for the donor luminescence decay and Eq. (6) should be used to describe the acceptor luminescence transient (rise and decay time). Eq. (6) was used to fit the Ho\(^{3+}\) luminescence transient in \((\text{Tm}:\text{Ho})\)-doped tellurite glasses under pulsed laser excitation at 1671 nm (10 mJ, 10 Hz). The decay time of the donor state, \( ^3\text{F}_4(\text{Tm}) \) (or \(^3\text{H}_4(\text{Tm}) \) for \( \text{Tm−Tm} \) cross-relaxation) was calculated using the expression:

\[
\frac{1}{\tau(\text{Tm})} = \frac{1}{\tau(\text{Tm})_{\text{intra}}} + \gamma^2,
\]

(7)

where \( \tau(\text{Tm})_{\text{intra}} \) is the lifetime measured for a single doped \( \text{Tm}(0.2 \text{ mol}%)\)-TZLBC glass.

3.2. Analysis of the Tm and Ho luminescence transients

Two sets of TZLBC glasses were used: (i) \( \text{Tm}(x \text{ mol}%)\)-TZLBC samples with \( x = 0.2, 0.4, 0.8 \) and \( 1.5 \text{ mol}% \), and (ii) \( \text{Tm}(0.2 \text{ mol}%)\):Ho(y)\(\text{TZLBC} \) with \( y = 0.2 \) and \( 1.5 \text{ mol}% \).

Luminescence spectra of Tm and (Tm:Ho) doped samples were measured in the infrared region \((1300–2200 \text{ nm}) \) using the laser excitation at 776 nm and a boxcar technique to discriminate the emission spectrum in

![Fig. 2](image-url) Fig. 2. The infrared luminescence spectra of \( \text{Tm}^{3+} \) and \( \text{Ho}^{3+} \) ions in TZLBC glass. Fig. 2(a) shows the spectrum of single doped TZLBC with 0.2 and 1.5 mol% of Tm. Fig. 2(b) shows the spectrum of Tm:Ho:TZLBC after laser excitation at 776 nm with 10 mJ at 300 K. The emission band at 1620 nm is the second order of \( \text{Tm}(3\text{H}_4) \) emission at 810 nm exhibited for comparison with the 1470 nm emission.
single and codoped telluride glasses. These spectra are shown in Fig. 2(a) and (b). The emissions at 1470 and 1800 nm observed for the single and codoped samples are due to the Tm$^{3+}$ transitions $^3\text{H}_4 \rightarrow ^3\text{F}_4$ and $^3\text{F}_4 \rightarrow ^3\text{H}_6$, respectively. Second order of 810 nm Tm-emission ($^3\text{H}_4 \rightarrow ^3\text{H}_6$) that exhibits a peak in 1620 nm position was included for comparison (see Fig. 2(a) and (b)). Additional emission in the range of 1900–2150 nm was observed in Tm:Ho system due to Tm→Ho energy transfer (see Fig. 2(b)). This luminescence is due to the $^5\text{I}_7 \rightarrow ^5\text{S}_8$ emission of Ho$^{3+}$ ions. It was observed that the Ho-emission at 2000 nm enhances with the increasing of Tm concentration in codoped samples. Evidences the Ho-emission at 2000 nm was observed for the single and codoped samples. Circles and squares are the experimental data plotted in Fig. 2(a) which shows that the Tm fluorescence at 1470 nm decreases with the increasing of Tm concentration in Tm:TZLBC glasses.

The luminescence lifetime of $^3\text{F}_4$(Tm) excited state was measured observing the 1800 nm emission decay induced by 780 nm laser excitation for (i) and (ii) sets. Fig. 3 (a) and (b) show the luminescence decay of single Tm-doped samples and best fittings obtained using two exponentials (rise and decay). The measured luminescence lifetimes of Tm$^{3+}$ are presented in Table 1. All the single doped samples exhibited the luminescence decay with a time constant of 2.2 ms. This result indicates that the concentration effect is not important at least for the maximum Tm-concentration investigated in this work. A weak residual luminescence of Tm$^{3+}$ ions was observed in Tm:Ho system due to Tm→Ho cross-relaxation process.

![Fig. 3. Fluorescence decay of Tm$^{3+}$ ions after the laser excitation of $^3\text{H}_4$(Tm) at 780 nm with 10 mJ in Tm:Ho:TZLBC glass at 300 K for two Tm concentrations. Circles and squares are the experimental data and solid lines represent the best fitting using two exponentials for rise and decay times. Decay time of 2.2 ms was obtained.](image)

### Table 1: Lifetime of $^3\text{F}_4$ excited state of Tm$^{3+}$ measured for two sets of TZLBC glasses: (i) single and (ii) codoped samples

<table>
<thead>
<tr>
<th>Tm(x):Ho(Y):TZLBC (mol%)</th>
<th>$\tau$ ($^3\text{F}_4$) (exp)</th>
<th>Relative luminescence efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set (i)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tm(0.2):TZLBC</td>
<td>2.28 (ms)</td>
<td>1</td>
</tr>
<tr>
<td>Tm(0.4):TZLBC</td>
<td>2.24 (ms)</td>
<td>1</td>
</tr>
<tr>
<td>Tm(0.8):TZLBC</td>
<td>2.36 (ms)</td>
<td>1</td>
</tr>
<tr>
<td>Tm(1.5):TZLBC</td>
<td>4.02 (ms)</td>
<td>1</td>
</tr>
<tr>
<td>Set (ii)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tm(0.2):Ho(0.6):TZLBC</td>
<td>260 (µs)</td>
<td>0.044</td>
</tr>
<tr>
<td>Tm(0.2):Ho(1.5):TZLBC</td>
<td>67 (µs)</td>
<td>0.012</td>
</tr>
</tbody>
</table>

Relative luminescence efficiency from $^3\text{F}_4$(Tm) ions was also included.

Additional emission in the range of 1900–2150 nm was included for comparison (see Fig. 2(a) and (b)). The emissions at 1470 and 2000 nm were due to the Tm$^{3+}$ transitions $^3\text{H}_6$ and $^3\text{H}_4$, respectively. Second order of 810 nm Tm-emission ($^3\text{H}_4 \rightarrow ^3\text{H}_6$) that exhibits a peak in 1620 nm position was included for comparison (see Fig. 2(a) and (b)). Additional emission in the range of 1900–2150 nm was observed in Tm:Ho system due to Tm→Ho energy transfer (see Fig. 2(b)). This luminescence is due to the $^5\text{I}_7 \rightarrow ^5\text{S}_8$ emission of Ho$^{3+}$ ions. It was observed that the Ho-emission at 2000 nm enhances with the increasing of Tm concentration in codoped samples. Evidences the Ho-emission at 2000 nm was observed for the single and codoped samples. Circles and squares are the experimental data plotted in Fig. 2(a) which shows that the Tm fluorescence at 1470 nm decreases with the increasing of Tm concentration in Tm:TZLBC glasses.

The luminescence lifetime of $^3\text{F}_4$(Tm) excited state was measured observing the 1800 nm emission decay induced by 780 nm laser excitation for (i) and (ii) sets. Fig. 3 (a) and (b) show the luminescence decay of single Tm-doped samples and best fittings obtained using two exponentials (rise and decay). The measured luminescence lifetimes of Tm$^{3+}$ are presented in Table 1. All the single doped samples exhibited the luminescence decay with a time constant of 2.2 ms. This result indicates that the concentration effect is not important at least for the maximum Tm-concentration investigated in this work. A weak residual luminescence of Tm$^{3+}$ ions was observed in double-doped samples. This residual luminescence was produced by a small fraction of (1.2–4.4%) of remaining Tm ions in the $^3\text{F}_4$ state due to the Tm→Ho back transfer. This back transfer process represents 3.3% of the direct Tm→Ho energy transfer in double-doped samples, which is justified by the observed $C_{AD}/C_{DA}$ estimated ratio of 0.034. The microparameters ($C_{DD}$, $C_{DA}$) and $C_{AD}$ involved in the energy transfer from the first of Tm($^3\text{F}_4$) to the Ho($^5\text{I}_7$) were calculated using:

$$C_{DA} = \frac{R_{DA}^6}{\tau_D}, \quad C_{DD} = \frac{R_{DD}^6}{\tau_D} \quad \text{and} \quad C_{AD} = \frac{R_{AD}^6}{\tau_A},$$

where $\tau_D$ and $\tau_A$ are the total lifetime of the donor and the acceptor state, respectively, both measured in single doped samples. The critical radii $R_{DD}$, $R_{DA}$ and $R_{AD}$ were calculated using the overlap integral method based on the calculation of the emission (donor) and the absorption (acceptor) cross-section superposition. The following expressions were used

$$R_{DD}^6 = \frac{6c\tau_D}{(2\pi)^3n^2} \int \sigma_{\text{emis}}(\lambda)\sigma_{\text{abs}}^D(\lambda) d\lambda,$$

$$R_{DA}^6 = \frac{6c\tau_D}{(2\pi)^3n^2} \int \sigma_{\text{emis}}(\lambda)\sigma_{\text{abs}}^A(\lambda) d\lambda,$$

$$R_{AD}^6 = \frac{6c\tau_A}{(2\pi)^3n^2} \int \sigma_{\text{emis}}^D(\lambda)\sigma_{\text{abs}}^A(\lambda) d\lambda,$$

where $c$ is the light speed, $n$ is the refractive index of the medium, $\sigma_{\text{emis}}^D$ and $\sigma_{\text{abs}}^A$ are the degeneracy of the respective lower and upper levels of the donor. The emission cross-section of Tm($^3\text{F}_4$) and Ho($^5\text{I}_7$) were obtained from the absorption cross-section spectrum using the McCumber relation [11]. The following values of microparameters were obtained for Tm($^3\text{F}_4$)→Ho($^5\text{I}_7$) nonradiative energy transfer given the following
transfer constants (given in cm$^6$/s): $C_{DD} = 1.821 \times 10^{-38}$, $C_{DA} = 1.872 \times 10^{-40}$ and $C_{AD} = 6.473 \times 10^{-42}$.

Fig. 4(a)–(c) exhibit the time evolution of Ho$^{5I7}$ luminescence at 2000 nm for the single (set i) and codoped samples (set ii) after laser excitation (Tm$^{3+}$). Laser excitation at 1873 nm was used for single Ho-doped TZLBC(0.6 mol%) and laser excitation at 1671 nm was used to excite Tm$^{3+}$ ions in Tm:Ho co-doped samples. Rise-time constant and the experimental transfer rate $\gamma$(exp) for Tm–Ho were obtained from the best fit of Ho-emission (2000 nm) using Eq. (6) (see solid lines in Fig. 4(b) and (c)). The results are shown in Table 2. The lifetime of the Tm($^3F_4$)-emission at 1800 nm was measured after the laser excitation at 1671 nm for

Table 2

<table>
<thead>
<tr>
<th>Tm(x):Ho(y):TZLBC (mol%)</th>
<th>Transfer and time constants</th>
<th>Ho($^5I7$)</th>
<th>Tm($^3F_4$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(x) (y)</td>
<td>$\gamma$ ($s^{-1/2}$) (theor)$^a$</td>
<td>$\gamma$ ($s^{-1/2}$) (exp)$^b$</td>
<td>$\tau$ (rise) ($\mu$s)$^b$</td>
</tr>
<tr>
<td>0.2 (0.6)</td>
<td>13.3</td>
<td>382.2</td>
<td>9.3</td>
</tr>
<tr>
<td>0.2 (1.5)</td>
<td>32.7</td>
<td>416.9</td>
<td>5.8</td>
</tr>
</tbody>
</table>

Theoritic values of $\gamma$ parameters and $K_d$ were obtained from the microscopic theory of energy transfer based on the random walk problem involving excitation migration by diffusion through the donors states (diffusion model) were included for comparison. The measured decay time of remaining Tm$^{3+}$ excited ions from $^3F_4$ state was also included for comparison.

$^a$ Calculated values using the Inokuti–Hirayama theory (Ref. [9]).
$^b$ Experimental data obtained from best fit of the acceptor luminescence transient obtained using the Inokuti–Hirayama approach, Eq. (6).
$^c$ Calculated values using $\gamma$(exp).
$^d$ Calculated values using the diffusion model (Ref. [12]).
$^e$ Experimental data obtained from best fit of the donor luminescence decay using an exponential decay.
Tm:Ho doped samples (see Fig. 5(a) and (b)). Best fittings were obtained using two exponentials, i.e. one for rising and another for the decay time (solid lines of Fig. 5(a) and (b)). The rise- and decay-time constants for Tm($^3F_4$) in the presence of Ho (0.6 and 1.5mol%) are presented in Table 2. The decay-time constant of Tm($^3F_4$) is 67 μs for Tm(0.2mol%):Ho(1.5mol%), which is still little longer than the measured rise-time constant of Ho($^4I_1$) acceptor state. This residual thulium emission with this peculiar lifetime (67 μs) represents only 1.4% of the total Tm luminescence of $^3F_4$ excited state and maybe due to a small class of Tm$^{3+}$ modified neighborhoods in TZLBC glass containing 9.5mol% of CsCl.

Fig. 5(a) and (b) exhibit the luminescence decay curves of Tm($^3F_4$) at 1800nm for single (Tm) and co-doped (Tm:Ho) TZLBC samples after the laser excitation of Tm$^{3+}$ at 1671nm. The decay-time constant of $^3F_4$(Tm) for codoped samples were obtained from the best fitting of 1800nm Tm-luminescence using the Inokuti–Hirayama solution obtained for the donor (Tm) luminescence decay (Eq. (5)). Fig. 6(a) and (b) exhibit the luminescence decay curves of Tm($^3H_4$) at 1470nm for Tm doped TZLBC samples after the laser excitation at 776nm. The value of Tm–Tm cross-relaxation energy transfer parameter, $\gamma$(exp), was obtained from the best fitting of $^3H_4$(Tm) luminescence decay using Eq. (5). The results are shown in Table 3. The luminescence efficiency of 1470nm luminescence of $^3H_4$(Tm) state was calculated using the expression

$$\eta = \frac{\tau_{\text{intra}}^{-1}}{\tau_{\text{intra}} + \gamma^2}$$

where $\gamma$ is the transfer parameter involved in the Tm–Tm cross-relaxation mechanism. It was observed that Ho$^{3+}$ ions do not introduce an effective deactivation process of the $^3H_4$(Tm) excited level since none significant lifetime decreasing was observed in Tm:Ho co-doped systems compared to the Tm-single doped one.

It was observed that the experimental value of $\gamma$(exp) obtained for the Tm:Ho energy transfer is always larger than the predicted value of $\gamma$ by the Inokuti–Hirayama model (see data of $\gamma$(theor) in Table 2 for comparison). Also, the experimental transfer rate, $\gamma^2$(exp), was observed to be higher than the transfer rate predicted by the migration model ($K_d$) that can be calculated using the expression [12]:

$$K_d = 21c_{\text{Tm}}c_{\text{Ho}}(C_{\text{DD}}^3C_{\text{DA}})^{\frac{1}{3}}$$

(see data of Table 2 for comparison).

### Table 3

<table>
<thead>
<tr>
<th>Tm(x):TZLBC (mol%)</th>
<th>$\tau_{\text{intra}}$ (μs) (exp)</th>
<th>$\gamma$ (s$^{-1/2}$) (exp)</th>
<th>$\eta$ ($^3H_4$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>467</td>
<td>0.76</td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>504</td>
<td>0.76</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>507</td>
<td>0.72</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>486</td>
<td>0.64</td>
<td></td>
</tr>
</tbody>
</table>

The calculated luminescence efficiency from $^3H_4$(Tm) ions was also included.

4. Conclusions

Our main conclusion is that the fast excitation diffusion occurs in a very short time changing the initial excitation distribution among Tm$^{3+}$ ions strongly affecting the mechanism of Tm–Ho energy transfer. The measured time dependence of Ho($^4I_1$-) luminescence is compatible with an energy transfer mechanism given in the Inokuti–Hirayama approach not involving excitation migration. However, the experimental values of the transfer parameter, $\gamma$(exp), is larger than the theoretical value, $\gamma$(theor). The observation that Ho-luminescence transient follows the acceptor solution of Inokuti–Hirayama model in addition to the fact that it happens with a transfer rate ($\gamma^2$(exp)) bigger than the diffusion model predicted rate ($K_d$), in which the energy transfer process is assisted by excitation migration among donors state, reinforces the fast exciton diffusion occurr-
rence among Tm$^{3+}$ (donors) ions, before starting the direct Tm—Ho transfer that was recently reported in the Yb:Er:ZBLAN glass [10].

Another relevant physical aspect of Tm:Ho:TZLBC glass is the observation of a very small Tm-luminescence from $^3F_4$ state in the presence of 0.6–1.5 mol% of Ho ions (1.2–4.4%). This small residual Tm-luminescence is consistent with the back transfer ratio, $C_{AD}/C_{DA} = 0.033$, estimated for this system. This indicates that $\sim 97\%$ of initially excited Tm ions in the $^3F_4$ state can transfer its excitation to $^5I_7$ state of Holmium with a short time constant (9.8–5.8 $\mu$s). These physical properties of Tm:Ho luminescence indicate that Ho$^{3+}$ ion is an important deactivator of the first excited state ($^3F_4$) of Thulium in TZLBC glass, which makes this material a strong candidate for optical fiber producing and amplifier performance testing when operating in the infrared range (1450–1530 nm).

Acknowledgments

The authors thank the financial support from CE-POF, FAPESP (Grants No. 1995/4166-0 and No. 2000/10986-0) and CNPq. One of the authors L.D. da Vila thanks FAPESP for the fellowship No. 2000/06798-4.

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