

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

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Abstract

Thulium (Tm^{3+}) doped and Holmium (Ho^{3+}) codoped tellurite glasses with the composition $\text{TeO}_2\text{-ZnO-Li}_2\text{O-Bi}_2\text{O}_3\text{-CsCl}$ 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 $\text{Tm}({}^3\text{F}_4)$ decay and $\text{Tm}({}^3\text{F}_4)\rightarrow\text{Ho}({}^5\text{I}_7)$ energy transfer were investigated. The lifetimes of excited $\text{Tm}({}^3\text{H}_4)$, $\text{Tm}({}^3\text{F}_4)$ and $\text{Ho}({}^5\text{I}_7)$ 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 telecom-

munication 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 (${}^3\text{F}_4$) excited state has a longer lifetime than the upper level (${}^3\text{H}_4$). A deactivation of ${}^3\text{F}_4$ state of Tm^{3+} is important. A deactivation process by means of up-conversion pumping at 1064 nm that can be used both to excite the ${}^3\text{H}_4$ level and to depopulate the ${}^3\text{F}_4$ level has been reported in the literature [5,6]. In another scheme the thulium doped fiber was codoped with Ho^{3+} and pumped at 790 nm into the ${}^3\text{H}_4$ level of Tm^{3+} [4]. Another regime consists of using a cascade process in which the ${}^3\text{F}_4$ is efficiently depopulated by the stimulated emission from ${}^3\text{F}_4$ 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 $\text{TeO}_2\text{-ZnO-Li}_2\text{O-Bi}_2\text{O}_3\text{-CsCl}$ to characterize the energy transfer process and to discuss some relevant theoretical aspects of the ${}^3\text{F}_4$ deactivation of Tm^{3+} state by Ho^{3+} ions in TZLBC glass.

2. Experimental

Tellurite glasses of $\text{TeO}_2\text{-ZnO-Li}_2\text{O-Bi}_2\text{O}_3\text{-CsCl}$ (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) $(100 - x)(66\text{TeO}_2 \cdot 15.5\text{ZnO} \cdot 5\text{Li}_2\text{O} \cdot 4\text{Bi}_2\text{O}_3 \cdot 9.5\text{CsCl}) \cdot x\text{TmO}_2$ ($x = 0.2, 0.4, 0.8$ and 1.5).
- (ii) $(99.8 - y)(66\text{TeO}_2 \cdot 15.5\text{ZnO} \cdot 5\text{Li}_2\text{O} \cdot 4\text{Bi}_2\text{O}_3 \cdot 9.5\text{CsCl}) \cdot 0.2\text{TmO}_2 \cdot y\text{HoO}_2$ ($y = 0.6$, 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 1.5 m/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 $\text{Tm}({}^3\text{F}_4)$ decay and $\text{Tm}({}^3\text{F}_4) \rightarrow \text{Ho}({}^5\text{I}_7)$ energy transfer. The lifetimes of excited $\text{Tm}({}^3\text{H}_4)$, $\text{Tm}({}^3\text{F}_4)$ and $\text{Ho}({}^5\text{I}_7)$ were measured using a pulsed laser excitation (4 ns) 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 776 nm was used to excite the ${}^3\text{H}_4$ Tm state while laser pumping at 1671 nm and 1873 nm were used to excite the ${}^3\text{F}_4$ and ${}^5\text{I}_7$ states of Tm and Ho, respectively. The time-dependent luminescence of the donor (Tm) and the acceptor (Ho) were detected by an InSb (77 K) infrared detector (Judson model J10D) with a fast preamplifier (response time of 0.5 μs) and analyzed using a 200 MHz Tektronix oscilloscope (TDS 410). All the fluorescence decay times were measured at 300 K. Band pass filters (80% transmittance, 10 nm half width and $\sim 10^{-5}$ extinction coefficient) at 1500 nm, 1800 nm and 2000 nm, were used to measure the luminescence of $\text{Tm}({}^3\text{H}_4)$, $\text{Tm}({}^3\text{F}_4)$ and $\text{Ho}({}^5\text{I}_7)$ 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 1470 nm (${}^3\text{H}_4$) and Ho-emission at 2000 nm (${}^5\text{I}_7$), 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 1470 nm emission involves the following Tm-excited level (DD) migration: $\text{Tm}({}^3\text{F}_4, {}^3\text{H}_6) \rightarrow \text{Tm}({}^3\text{H}_6, {}^3\text{F}_4)$. The Tm–Ho energy transfer involves the following excited levels (DA energy transfer): $\text{Tm}({}^3\text{F}_4) \rightarrow \text{Ho}({}^5\text{I}_7)$. This DA energy transfer can be assisted by the Tm–Tm migration according to the notation (or DD migration) $\text{Tm}({}^3\text{H}_4, {}^3\text{H}_6) \rightarrow \text{Tm}({}^3\text{H}_6, {}^3\text{H}_4)$. The Ho–Tm back transfer also occurs according to the following notation (or AD energy transfer) $\text{Ho}({}^5\text{I}_7) \rightarrow \text{Tm}({}^3\text{F}_4)$.

One possibility of analyzing the 2000 nm luminescence of Ho^{3+} induced by the $\text{Tm}({}^3\text{F}_4) \rightarrow \text{Ho}({}^5\text{I}_7)$ 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

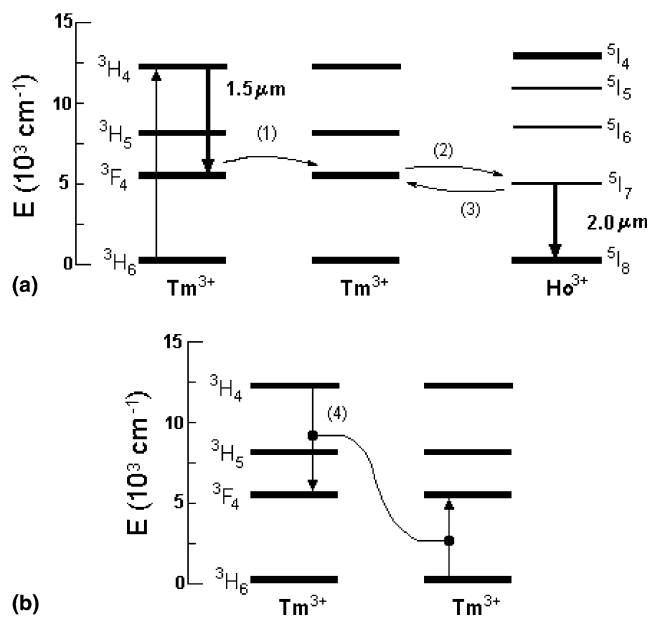


Fig. 1. A simplified energy level diagram of Tm:Ho:TZLBC glass exhibiting the main energy transfer processes that occur in the Tm \rightarrow Ho energy transfer are indicated. Fig. 1(a) shows the $\text{Tm}({}^3\text{F}_4, {}^3\text{H}_6) \rightarrow \text{Tm}({}^3\text{H}_6, {}^3\text{F}_4)$ migration (process 1), the $\text{Tm}({}^3\text{F}_4) \rightarrow \text{Ho}({}^5\text{I}_7)$ energy transfer (process 2) and the $\text{Ho}({}^5\text{I}_7) \rightarrow \text{Tm}({}^3\text{F}_4)$ back transfer (process 3). Fig. 1(b) shows the $\text{Tm}({}^3\text{H}_4, {}^3\text{H}_6) \rightarrow \text{Tm}({}^3\text{F}_4, {}^3\text{F}_4)$ cross-relaxation (process 4).

acceptor (A_k) luminescence transients. The microscopic rate equations system is

$$\frac{d\rho_{D_j}}{dt} = -\frac{\rho_{D_j}}{\tau_D} - \sum_{i=1}^{N_A} W_{DA}(\bar{R}_i - \bar{R}_j)\rho_{D_j}, \quad (1)$$

$$\frac{d\rho_{A_k}}{dt} = -\frac{\rho_{A_k}}{\tau_A} + \sum_{i=1}^{N_A} W_{DA}(\bar{R}_i - \bar{R}_j)\rho_{D_j}, \quad (2)$$

where ρ_A and ρ_D are the respective probability excitation densities of acceptor (A_k) and donor ions (D_j). τ_D and τ_A are the lifetime of isolated donor and acceptor ions measured in a single doped material at low concentration (~ 0.2 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].

$$\rho_{D_j}(t) = \exp\left(-\frac{t}{\tau_D}\right) \exp\left(-t \sum_i W_{DA}(R_i)\right), \quad (3)$$

$$\rho_{A_k}(t) = \exp\left(-\frac{t}{\tau_A}\right) - \frac{\sum_i W_{DA}(R_i)}{\sum_i W_{DA}(R_i) + \frac{1}{\tau_D} - \frac{1}{\tau_A}} \times \exp\left(-\frac{t}{\tau_D} - t \sum_i W_{DA}(R_i)\right). \quad (4)$$

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 $\rho_{D_j}(t)$ 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 $W_{DA} = (1/\tau_D)(R_{DA}/R)^6$. 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 $V \rightarrow s\infty$, one obtains the Inokuti–Hirayama [9] solution for the donor luminescence decay

$$\bar{\rho}_D(t) = \exp(-t/\tau_D) \exp\left(-\frac{c_A}{c_0} \left(\frac{\pi t}{\tau_D}\right)^{1/2}\right), \quad (5)$$

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 $\gamma = \frac{c_A}{c_0} \left(\frac{\pi}{\tau_D}\right)^{1/2}$ that is also related to the microscopic transfer constants, $\gamma(\text{theor}) = \frac{4\pi^{3/2}}{3} c_A (C_{DA})^{1/2}$. The following solution has been obtained in Ref. [10] that represents the average luminescence transient of the acceptor derived following the Inokuti–Hirayama approach:

$$\bar{\rho}_A(t) = C \left[\exp\left(-\frac{t}{\tau_A}\right) - \exp\left(-\gamma\sqrt{t} - \frac{t}{\tau_D}\right) \right], \quad (6)$$

where γ 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 $\text{Ho}({}^5\text{I}_7)$ luminescence transient in (Tm: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 Tm–Tm cross-relaxation) was calculated using the expression:

$$\frac{1}{\tau(\text{Tm})} = \frac{1}{\tau(\text{Tm})_{\text{intra}}} + \gamma^2, \quad (7)$$

where $\frac{1}{\tau(\text{Tm})_{\text{intra}}}$ is the lifetime measured for a single doped Tm(0.2 mol%):TZLBC glass.

3.2. Analysis of the Tm and Ho luminescence transients

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

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

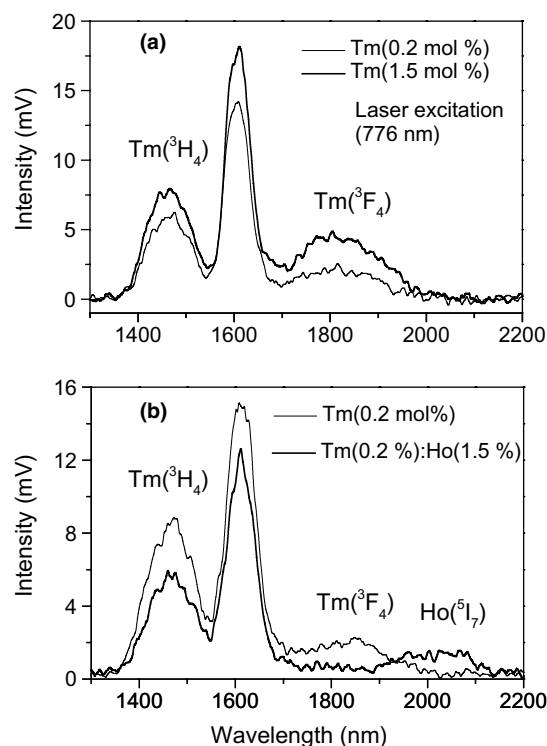


Fig. 2. The infrared luminescence spectra of Tm^{3+} and Ho^{3+} ions in TZLBC glass. Fig. 2(a) shows the spectrum of single doped TZLBC with 0.2 and 1.5 mol% of Tm. Fig. 2(b) shows the spectrum of Tm:Ho:TZLBC after laser excitation at 776 nm with 10 mJ at 300 K. The emission band at 1620 nm is the second 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 ${}^5\text{I}_7 \rightarrow {}^5\text{I}_8$ 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 of $\text{Tm}({}^3\text{H}_4, {}^3\text{H}_6) \rightarrow \text{Tm}({}^3\text{F}_4, {}^3\text{H}_4)$ cross-relaxation process can be seen 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 ${}^3\text{F}_4(\text{Tm})$ 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

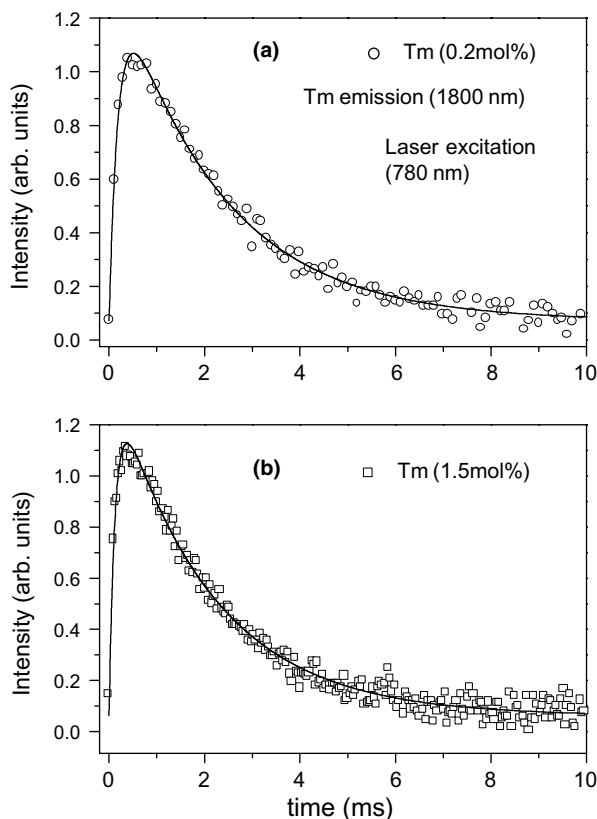


Fig. 3. Fluorescence decay of Tm^{3+} ions after the laser excitation of ${}^3\text{H}_4(\text{Tm})$ at 780 nm with 10 mJ in Tm:Ho:TZLBC glass at 300 K for two Tm concentrations. Circles and squares are the experimental data and solid lines represent the best fitting using two exponentials for rise and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

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

Tm(x):Ho(Y):TZLBC (mol%)	τ (${}^3\text{F}_4$) (exp)	Relative luminescence efficiency
Set (i)		
Tm(0.2):TZLBC	2.28 (ms)	1
Tm(0.4):TZLBC	2.24 (ms)	1
Tm(0.8):TZLBC	2.36 (ms)	1
Tm(1.5):TZLBC	4.02 (ms)	1
Set (ii)		
Tm(0.2):Ho(0.6):TZLBC	260 (μs)	0.044
Tm(0.2):Ho(1.5):TZLBC	67 (μs)	0.012

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

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 Ho→Tm 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 $C_{\text{AD}}/C_{\text{DA}}$ estimated ratio of 0.034. The microparameters (C_{DD} , C_{DA} and C_{AD}) involved in the energy transfer from the first of $\text{Tm}({}^3\text{F}_4)$ to the $\text{Ho}({}^5\text{I}_7)$ were calculated using:

$$C_{\text{DA}} = \frac{R_{\text{DA}}^6}{\tau_{\text{D}}}, \quad C_{\text{DD}} = \frac{R_{\text{DD}}^6}{\tau_{\text{D}}} \quad \text{and} \quad C_{\text{AD}} = \frac{R_{\text{AD}}^6}{\tau_{\text{A}}},$$

where τ_{D} and τ_{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

$$R_{\text{DD}}^6 = \frac{6c\tau_{\text{D}}}{(2\pi)^4 n^2} \frac{g_{\text{D}}^{\text{low}}}{g_{\text{D}}^{\text{up}}} \int \sigma_{\text{emis}}^{\text{D}}(\lambda) \sigma_{\text{abs}}^{\text{D}}(\lambda) d\lambda, \quad (8)$$

$$R_{\text{DA}}^6 = \frac{6c\tau_{\text{D}}}{(2\pi)^4 n^2} \frac{g_{\text{D}}^{\text{low}}}{g_{\text{D}}^{\text{up}}} \int \sigma_{\text{emis}}^{\text{D}}(\lambda) \sigma_{\text{abs}}^{\text{A}}(\lambda) d\lambda, \quad (9)$$

$$R_{\text{AD}}^6 = \frac{6c\tau_{\text{A}}}{(2\pi)^4 n^2} \frac{g_{\text{A}}^{\text{low}}}{g_{\text{A}}^{\text{up}}} \int \sigma_{\text{emis}}^{\text{A}}(\lambda) \sigma_{\text{abs}}^{\text{D}}(\lambda) d\lambda, \quad (10)$$

where c is the light speed, n is the refractive index of the medium, and $g_{\text{D}}^{\text{low}}$ and g_{D}^{up} are the degeneracy of the respective lower and upper levels of the donor. The emission cross-section of $\text{Tm}({}^3\text{F}_4)$ and $\text{Ho}({}^5\text{I}_7)$ were obtained from the absorption cross-section spectrum using the McCumber relation [11]. The following values of microparameters were obtained for $\text{Tm}({}^3\text{F}_4) \rightarrow \text{Ho}({}^5\text{I}_7)$ nonradiative energy transfer given the following

transfer constants (given in cm^6/s): $C_{\text{DD}} = 1.821 \times 10^{-38}$, $C_{\text{DA}} = 1.872 \times 10^{-40}$ and $C_{\text{AD}} = 6.473 \times 10^{-42}$.

Fig. 4(a)–(c) exhibit the time evolution of $\text{Ho}^{3+}({}^5\text{I}_7)$ 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 $\text{Tm}:\text{Ho}$ codoped samples. Rise-time constant and the experimental transfer rate $\gamma(\text{exp})$ for $\text{Tm}-\text{Ho}$ 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 $\text{Tm}^{3+}({}^3\text{F}_4)$ -emission at 1800 nm was measured after the laser excitation at 1671 nm for

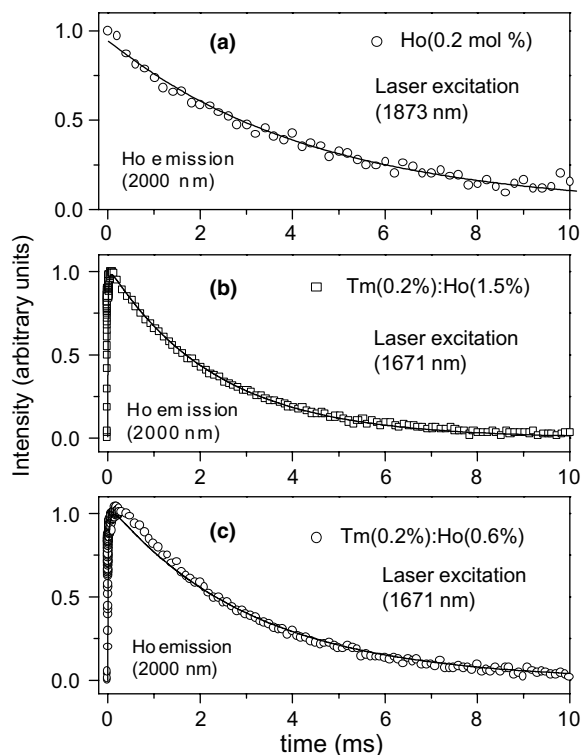


Fig. 4. Fluorescence decay of $\text{Ho}^{3+}({}^5\text{I}_7)$ at 2000 nm excited with laser excitation at 1873 nm for Ho-single doped sample (a) and with 1671 nm (10 mJ) for $\text{Tm}:\text{Ho}$ codoped samples (see (b) and (c)). Solid line of (a) was obtained from best fitting using an exponential decay time and the solid lines of (b) and (c) were obtained from the best fitting using the Inokuti–Hirayama solution for the acceptor luminescence transient (Ho^{3+}) ion.

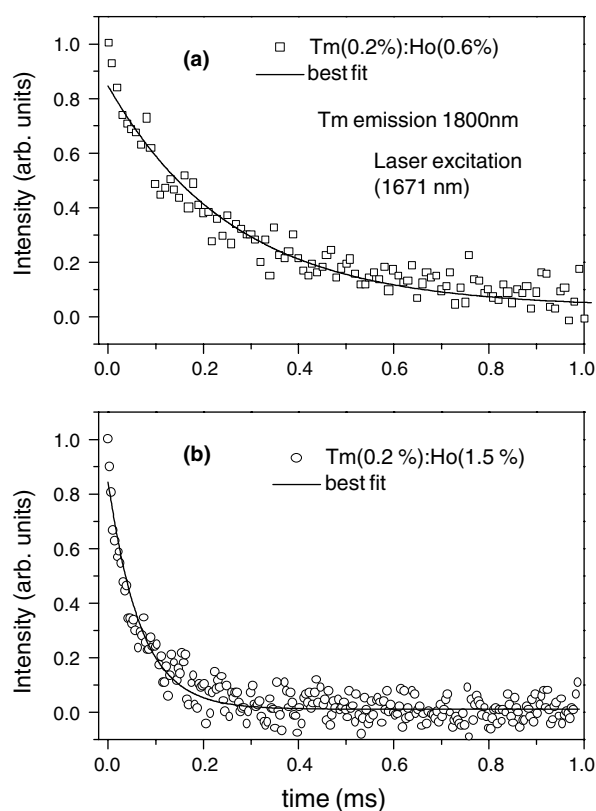


Fig. 5. Fluorescence decay of $\text{Tm}^{3+}({}^3\text{F}_4)$ at 1800 nm excited with laser excitation 1671 nm (10 mJ) measured for $\text{Tm}(0.2\text{mol}\%):\text{Ho}(\gamma):\text{TZLBC}$ where $\gamma = 0.6\text{mol}\%$ (a), and $\gamma = 1.5\text{mol}\%$ (b). Solid lines were obtained from the best fitting using the Inokuti–Hirayama solution for the donor (Tm^{3+}) luminescence decay.

Table 2

The experimental values of energy transfer parameter ($\gamma(\text{exp})$) obtained for the best fitting of 2000 nm luminescence of $\text{Ho}^{3+}({}^5\text{I}_7)$ using the Inokuti–Hirayama solution for the acceptor luminescence transient for $\text{Tm}(x):\text{Ho}(y):\text{TZLBC}$

Tm(x):Ho(y):TZLBC (mol%)		Transfer and time constants				
(x)	(y)	Ho(${}^5\text{I}_7$)				Tm(${}^3\text{F}_4$)
		γ ($\text{s}^{-1/2}$) (theor) ^a	γ ($\text{s}^{-1/2}$) (exp) ^b	τ (rise) (μs) ^c	K_d (s^{-1}) ^d	τ (decay) (μs) (exp) ^e
0.2	0.6	13.3	382.2	9.3	495	260
0.2	1.5	32.7	416.9	5.8	1216	67

Theoretic values of γ 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 donors states (diffusion model) were included for comparison. The measured decay time of remaining Tm^{3+} excited ions from ${}^3\text{F}_4$ 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 $\gamma(\text{exp})$.

^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 $\text{Tm}(^3\text{F}_4)$ in the presence of Ho (0.6 and 1.5 mol%) are presented in Table 2. The decay-time constant of $\text{Tm}(^3\text{F}_4)$ is 67 μs for $\text{Tm}(0.2\text{ mol}\%):\text{Ho}(1.5\text{ mol}\%)$, which is still little longer than the measured rise-time constant of $\text{Ho}(^5\text{I}_7)$ acceptor state. This residual thulium emission with this peculiar lifetime (67 μs) represents only 1.4% of the total Tm luminescence of $^3\text{F}_4$ excited state and maybe due to a small class of Tm^{3+} modified neighborhoods in TZLBC glass containing 9.5 mol% of CsCl.

Fig. 5(a) and (b) exhibit the luminescence decay curves of $\text{Tm}(^3\text{F}_4)$ at 1800 nm for single (Tm) and co-doped (Tm:Ho) TZLBC samples after the laser excitation of Tm^{3+} at 1671 nm. The decay-time constant of $^3\text{F}_4(\text{Tm})$ for codoped samples were obtained from the best fitting of 1800 nm 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 $\text{Tm}(^3\text{H}_4)$ at 1470 nm for Tm doped TZLBC samples after the laser excitation at 776 nm. The value of Tm–Tm cross-relaxation energy transfer parameter, $\gamma(\text{exp})$, was obtained

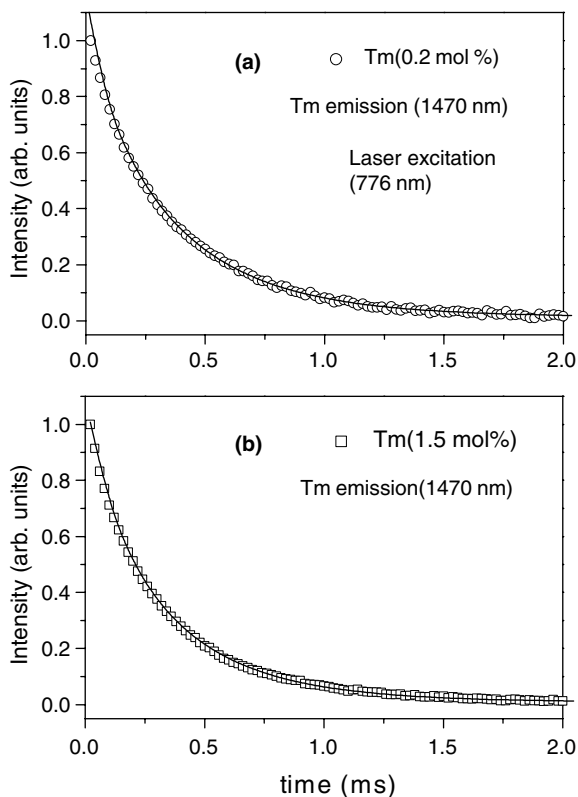


Fig. 6. Fluorescence decay of $\text{Tm}^{3+}(^3\text{H}_4)$ at 1470 nm emission measured in $\text{Tm}(x):\text{TZLBC}$ with $x = 0.2\text{ mol}\%$ (a), and $x = 1.5\text{ mol}\%$ (b), after laser excitation at 776 nm (10 mJ). Solid lines were obtained from the best fitting using the Inokuti–Hirayama solution for the donor (Tm^{3+}) decay (Eq. (5)).

Table 3

Intrinsic lifetime constant (intra center lifetime) of $^3\text{H}_4$ excited state of Tm^{3+} ions measured for $\text{Tm}(x\text{ mol}\%):\text{TZLBC}$ samples and the energy transfer parameter (cross-relaxation), $\gamma(\text{exp})$, obtained from best fitting of 1470 nm luminescence decay using the Inokuti–Hirayama solution for donor decay

$\text{Tm}(x):\text{TZLBC}$ (mol%)	τ_{intra} (μs) (exp)	γ ($\text{s}^{-1/2}$) (exp)	η ($^3\text{H}_4$)
0.2	490	24.9	0.76
0.4	509	26.9	0.74
0.8	507	28.2	0.72
1.5	486	33.4	0.64

The calculated luminescence efficiency from $^3\text{H}_4(\text{Tm})$ ions was also included.

from the best fitting of $^3\text{H}_4(\text{Tm})$ luminescence decay using Eq. (5). The results are shown in Table 3. The luminescence efficiency of 1470 nm luminescence of $^3\text{H}_4(\text{Tm})$ state was calculated using the expression

$$\eta = \frac{\tau_{\text{intra}}^{-1}}{\tau_{\text{intra}}^{-1} + \gamma^2}, \quad (11)$$

where γ is the transfer parameter involved in the $\text{Tm} \rightarrow \text{Tm}$ cross-relaxation mechanism. It was observed that Ho^{3+} ions do not introduce an effective deactivation process of the $^3\text{H}_4(\text{Tm})$ excited level since none significant lifetime decreasing was observed in Tm:Ho codoped systems compared to the Tm-single doped one.

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

$$K_d = 21c_{\text{Tm}}c_{\text{Ho}}(C_{\text{DD}}^3 C_{\text{DA}})^{\frac{1}{4}}$$

(see data of Table 2 for comparison).

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 $\text{Ho}(^5\text{I}_7)$ 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, $\gamma(\text{exp})$, is larger than the theoretical value, $\gamma(\text{theor})$. 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 ($\gamma^2(\text{exp})$) 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 occur-

rence among Tm^{3+} (donors) ions, before starting the direct $\text{Tm} \rightarrow \text{Ho}$ 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 $^3\text{F}_4$ 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, $C_{\text{AD}}/C_{\text{DA}} = 0.033$, estimated for this system. This indicates that $\sim 97\%$ of initially excited Tm ions in the $^3\text{F}_4$ state can transfer its excitation to $^5\text{I}_7$ state of Holmium with a short time constant (9.8–5.8 μs). These physical properties of Tm:Ho luminescence indicate that Ho^{3+} ion is an important deactivator of the first excited state ($^3\text{F}_4$) 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).

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References

- [1] A. Mori, Y. Ohishi, S. Sudo, *Electron. Lett.* 33 (1997) 863.
- [2] M. Yamada, A. Mori, H. Ono, K. Kobayashi, T. Kanamori, Y. Ohishi, *Electron. Lett.* 34 (1998) 370.
- [3] A. Mori, K. Kobayashi, M. Yamada, T. Kanamori, K. Oikawa, Y. Nishida, Y. Ohishi, *Electron. Lett.* 34 (1998) 887.
- [4] E.R. Taylor, Li NaNg, N.P. Sessions, H. Buerger, *J. Appl. Phys.* 92 (2002) 112.
- [5] B. Bourliaguet, E. Emond, A-C. Jacob-Poulin, P.Y. Cortes, L. Lauzon, *Electron. Lett.* 38 (2002) 447.
- [6] R.M. Percival, J.R. Williams, *Electron. Lett.* 30 (1994) 1684.
- [7] S. Shen, A. Jha, E. Zhang, S.J. Wilson, *Comp. Rend. Chim.* 5 (2002) 921.
- [8] R. Allen, L. Esterowitz, I. Aggarwal, *IEEE J. Quant. Electron.* 29 (1993) 303.
- [9] M. Inokuti, F. Hirayama, *J. Chem. Phys.* 43 (1965) 1978.
- [10] L.D. da Vila, L. Gomes, L.V.G. Tarelho, S.J.L. Ribeiro, Y. Messaddeq, *J. Appl. Phys.* 93 (2003) 3873.
- [11] D.E. McCumber, *Phys. Rev.* 136 (1964) A954.
- [12] R.C. Powell, in: R.C. Powell (Ed.), *Physics of Solid-State Laser Materials*, Springer, New York, 1998, Chapter 5.