

Tm and Tm–Tb-doped germanate glasses for S-band amplifiers

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Abstract

The mechanism involved in the $\text{Tm}^{3+}({}^3\text{F}_4) \rightarrow \text{Tb}^{3+}({}^7\text{F}_{0,1,2})$ energy transfer as a function of the Tb concentration was investigated in Tm:Tb-doped germanate (GLKZ) glass. The experimental transfer rate was determined from the best fit of the ${}^3\text{F}_4$ luminescence decay due to the Tm \rightarrow Tb energy transfer using the Burshtein model. The result showed that the 1700 nm emission from ${}^3\text{F}_4$ can be completely quenched by 0.8 mol% of Tb^{3+} . As a consequence, the ${}^7\text{F}_3$ state of Tb^{3+} interacts with the ${}^3\text{H}_4$ upper excited state of Tm^{3+} slightly decreasing its population. The effective amplification coefficient $\beta(\text{cm}^{-1})$ that depends on the population density difference $\Delta n = n({}^3\text{H}_4) - n({}^3\text{F}_4)$ involved in the optical transition of Tm^{3+} (S-band) was calculated by solving the rate equations of the system for continuous pumping with laser at 792 nm, using the Runge–Kutta numerical method including terms of fourth order. The population density inversion Δn as a function of Tb^{3+} concentration was calculated by computational simulation for three pumping intensities, 0.2, 2.2 and 4.4 kWcm^{-2} . These calculations were performed using the experimental Tm \rightarrow Tb transfer rates and the optical constants of the Tm (0.1 mol%) system. It was demonstrated that 0.2 mol% of Tb^{3+} propitiates best population density inversion of Tm^{3+} maximizing the amplification coefficient of Tm-doped (0.1 mol%) GLKZ glass when operating as laser intensity amplification at 1.47 μm .

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1. Introduction

Recently Tm-doped tellurite glass has been used for 1.47 μm fiber amplifier [1] based on the ${}^3\text{H}_4 \rightarrow {}^3\text{F}_4$ stimulated transition of Tm^{3+} . However, two intrinsic properties of Tm^{3+} single-doped materials may reduce its capacity of signal light amplification in S band in many oxide glasses where the ${}^3\text{H}_4$ level easily decay to the next lower-level ${}^3\text{H}_5$ via multiphonon relaxation. That is not the case of the germanate (GLKZ) glass used in this work, according to our observation discussed in Section 3.1. Nevertheless, the lifetime of the lower ${}^3\text{F}_4$ level involved in the 1.47 μm emission is considerably longer than that of the upper ${}^3\text{H}_4$ level (~ 6 times is observed in Tm:ZBLAN and Tm:Ge–Ga–As–S–CsBr, and ~ 8.3 times in GLKZ glasses).

To realize population inversion in Tm^{3+} ions, Ho^{3+} or Tb^{3+} ions have been used to codoped the Tm-doped material to depopulate the ${}^3\text{F}_4$ level of Tm^{3+} in fluorindate [2], fluorozirconate (ZBLAN) [3], fluorogermanate [4], tellurite [5] and chalcogenide [6] glasses. Because the energies of ${}^5\text{I}_7$ and ${}^7\text{F}_{0,1,2}$ levels of Ho^{3+} and Tb^{3+} , respectively, coincide with the energy of the ${}^3\text{F}_4$ level, holmium and terbium ions may actuate as deactivator of the ${}^3\text{F}_4$ lowest excited state of Tm^{3+} to improve the population inversion of Tm^{3+} ions in many luminescent solid materials. Besides the ${}^3\text{H}_4$ and ${}^3\text{F}_4$ fluorescence decay effects of Tm^{3+} caused by Tb^{3+} ions have been investigated in fluorindate [2] and more recently in chalcogenide glass containing CsBr [6], a detailed investigation of the mechanisms of ${}^3\text{H}_4$ and ${}^3\text{F}_4$ deactivations are still lacking. Also, a better approach of calculation the population inversion in Tm:Tb and Tm:Ho systems need to be performed based on the numeric solutions of a realistic

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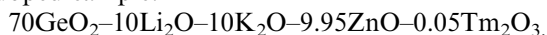
set of rate equations, which can describe the system behavior under continuous pumping of the $^3\text{H}_4$ state. In this work we investigated the time decay of 1470 and 1700 nm emissions of Tm^{3+} in GLKZ glass singly doped with 0.1 mol% of thulium and doubly doped with terbium (0.1, 0.2, 0.4 and 0.8 mol%), due to its favorable optical properties such a wide transmission window (typically 300–5000 nm), high linear (1.65) and nonlinear refractive indices, good corrosion resistance and mechanical stability, and low cut-off phonon energy among oxide materials (800 cm^{-1}). Also this material has high solubility for rare earth doping and low fusion temperature. A depopulation of $^3\text{F}_4$ state of Tm^{3+} by the energy transfer to Tb^{3+} ions is an important phenomena in solids that must be investigated among different host materials to establish a wide comparison of the physical effects in the upper and lower excited states of the $^3\text{H}_4 \rightarrow ^3\text{F}_4$ transition to determine the best deactivator concentration that will improve the population inversion and consequently the gain for light signal amplification at $1.48\ \mu\text{m}$. A deactivation process by means of up-conversion induced by laser pumping at 1064 nm depopulates the $^3\text{F}_4$ in favor of $^3\text{H}_4$ level has been reported in Refs. [7,8]. An internal gain improvement by a factor of 2 has been reported for 795 and 1064 nm dual pump scheme in Tm-doped tellurite fiber operating at $1.48\ \mu\text{m}$ [9]. 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 [10].

In the present work, we have investigated the influence of Tb^{3+} concentration on the luminescence decay of the $^3\text{F}_4$ and $^3\text{H}_4$ excited states of Tm^{3+} in Tm-doped and (Tm:Tb) codoped GLKZ glasses to provide detailed information on the energy transfer mechanisms involved and to determinate the best concentration of Tb^{3+} that maximizes the population inversion based on the numerical solutions obtained using Rung–Kutta method applied to the rate equations system.

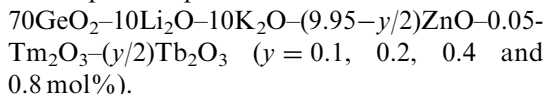
2. Experimental procedure

GLKZ glasses of $\text{GeO}_2\text{--Li}_2\text{O--K}_2\text{O--ZnO}$ (named here as GLKZ) family were prepared as single (Tm) and double-doped (Tm:Tb) for time-resolved luminescence spectroscopy. Two sets of GLKZ glasses were prepared from ultra pure oxide starting materials (P. A. Aldrich) with the following compositions were Tm concentration was kept equal to 0.1 mol%.

(i) Tm-doped sample:



(ii) Tm:Tb codoped samples:



Tm:GLKZ and Tm:Tb:GLKZ glasses were produced by melting the starting materials at $1150\ ^\circ\text{C}$ for 30 min in a

Pt–Au crucible. The liquids were poured into brass molds and annealed at $400\ ^\circ\text{C}$ for 4 h to remove the mechanical stresses. The samples were cut and polished into $15 \times 10 \times 5\ \text{mm}$ pieces.

Absorption spectra were measured using a spectrophotometer Cary/OLIS 17D operating in the range of 300–2000 nm. A selective luminescence excitation by tunable OPO laser was employed to measure the Tm^{3+} luminescence to verify the Tm^{3+} ($^3\text{H}_4$) decay and the Tm^{3+} ($^3\text{F}_4$) \rightarrow Tb^{3+} ($^3\text{F}_{0,1,2}$) energy transfer. The lifetimes of Tm^{3+} excited states, $^3\text{H}_4$ and $^3\text{F}_4$, 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 Nd-YAG laser Brilliant B from Quantel. Laser excitations at 776 and 1671 nm were used to excite the $^3\text{H}_4$ and $^3\text{F}_4$ states of Tm^{3+} , respectively. The time-dependent luminescence of Tm^{3+} was detected by an InSb (refrigerated at 77 K) infrared detector (Judson model J10D) with a fast preamplifier (response time of $0.5\ \mu\text{s}$) and analyzed using a digital 200 MHz oscilloscope from Tektronix (TDS 410). All the fluorescence decay times were measured at 300 K. Band pass filters with 80% of transmittance at 1400 and 1700 nm with a half width of 10 nm and an extinction coefficient of $\sim 10^{-5}$, were used to measure these luminescence signals.

3. Experimental results

3.1. Luminescence effect on the $^3\text{H}_4$ excited state of Tm^{3+}

Fig. 1 shows the absorption spectrum of Tm and Tm:Tb codoped GLKZ glasses measured in the visible and in the infrared range. A clear spectral overlap exists between the ($^3\text{H}_6 \rightarrow ^3\text{F}_4$) absorption of Tm^{3+} centered at 1700 nm with the ($^7\text{F}_6 \rightarrow ^7\text{F}_{0,1,2}$) absorption of Tb^{3+} at 1900 nm, suggests that an efficient energy transfer from $^3\text{F}_4$ (Tm^{3+}) excited state to the $^7\text{F}_{0,1,2}$ (Tb^{3+}) states will happen.

Fig. 2(a) shows the effect on the luminescence decay of the $^3\text{H}_4$ excited state of Tm^{3+} due to the Tm^{3+} ($^3\text{H}_4$) \rightarrow Tb^{3+} ($^7\text{F}_{3,4}$) non-radiative energy transfer in Tm:Tb codoped GLKZ glass. A strong decrease of the 1470 nm luminescence is seen in Fig. 2(a) in Tm:Tb codoped samples. Solid line of Fig. 2(a) represents the best fitting of luminescence signals measured at 1470 nm using the Burshtein model [11]. This model is given by Eq. (1), which includes the donor migration (hopping) in the donor to acceptor energy transfer process for a dipole-dipole interaction as expected for a case when $C_{\text{DD}} \gg C_{\text{DA}}$.

$$I(t) = I_0 \exp\left(\frac{t}{\tau_{\text{D}_i}} - \omega t - \gamma\sqrt{t}\right), \quad (1)$$

where τ_{D_i} is the intrinsic total lifetime of donor and γ is the donor to acceptor energy transfer parameter (direct transfer without migration) and ω is the rate parameter related to the donor to acceptor energy transfer assisted by discrete excitation migration (hopping) among donor ($^3\text{H}_4$) states. The mean lifetime (τ_2) of a non-exponential decay of

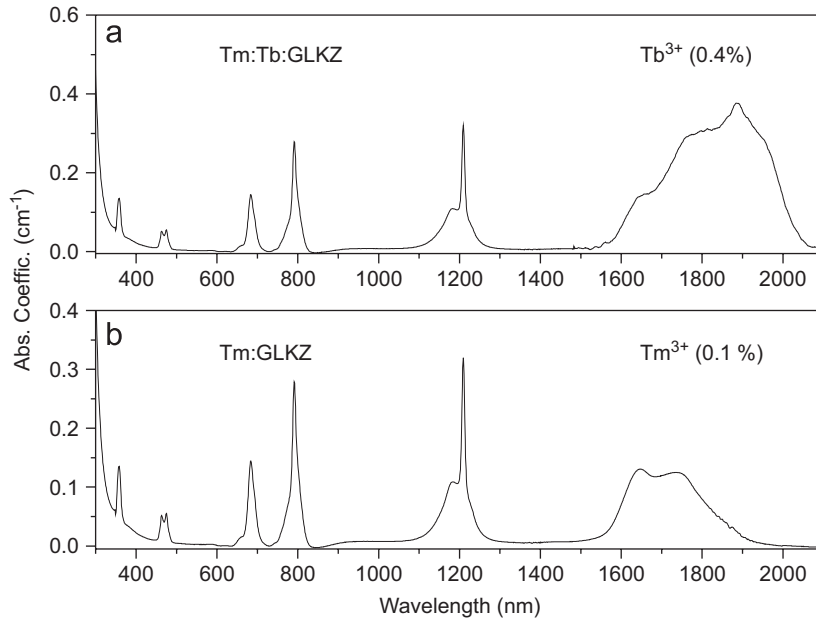


Fig. 1. Absorption spectrum of Tm(0.1) and Tm(0.1):Tb(0.4)-doped GLKZ measured in the visible and in the infrared range, which shows the absorption superposition between the $^3H_6 \rightarrow ^3F_4$ absorption of Tm^{3+} near 1700 nm with the $^7F_6 \rightarrow ^7F_{0,1,2}$ absorption of Tb^{3+} at 1900 nm.

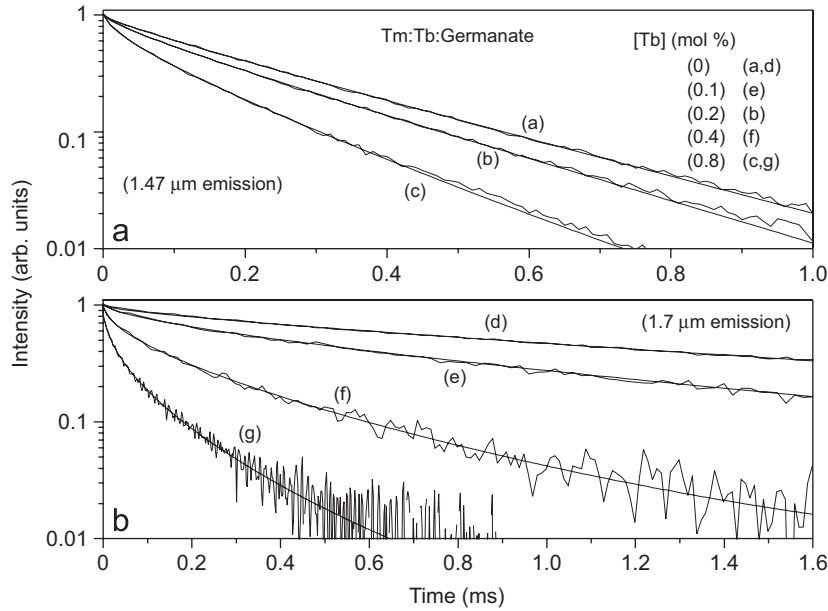


Fig. 2. (a) Tm^{3+} luminescence decay in Tm (0.1) and Tm (0.1):Tb(y):GLKZ using several concentrations of Tb ($y = 0, 0.1, 0.2, 0.4,$ and 0.8 mol%). (a) Shows the 1470 nm luminescence decay of 3H_4 (Tm^{3+}) state using a laser excitation at 776 nm with time duration of 4 ns (10 Hz) and 10 mJ. (b) Shows the 1700 nm luminescence decay of the 3F_4 (Tm^{3+}) state using the laser excitation at 1671 nm of 4 ns (10 Hz) and 10 mJ.

3H_4 (or 3F_4) excited state of Tm^{3+} can be calculated by integrating the luminescence decay curve of 3H_4 state in the presence of Tb ions using a normalized luminescence intensity $I(t)$ such as $I(0) = I_0 = 1$ and $I(t \rightarrow \infty) = 0$, according to Eq. (2).

$$\tau_2 = \int_0^\infty I(t) dt \quad (2)$$

The $Tm(^3H_4) \rightarrow Tb(^7F_{3,4})$ energy transfer rate W_2 was calculated from Eq. (3) that uses the mean lifetime τ_2

(obtained from Eq. (2)), the intrinsic lifetime ($\tau_{D_1} = \tau_{D_2}$) of 3H_4 excited level of Tm^{3+} and the Tm–Tm cross-relaxation rate (W_{CR}) of a non-radiative energy transfer between two Tm^{3+} ions, where the excitation of 3H_4 level is transferred to the 3F_4 level in GLKZ glass doped with $[Tm] > 0.01$ mol%.

$$\frac{1}{\tau_2} = \frac{1}{\tau_{D_2}} + W_2 + W_{CR}. \quad (3)$$

The radiative lifetime of 3H_4 excited state of Tm^{3+} in GLKZ was calculated using the Judd–Ofelt theory from

where the Ω_2 , Ω_4 and Ω_6 obtained parameters are 1.14×10^{-19} , 1.17×10^{-19} and $2.0 \times 10^{-20} \text{ cm}^2$, respectively. The calculated value of τ_R was $260 \mu\text{s}$ that is close to the lifetime of $294 \mu\text{s}$ obtained from the best fitting of the non-exponential luminescence decay of the ${}^3\text{H}_4$ state in single Tm-doped GLKZ glass. It means that the ${}^3\text{H}_4$ state is an intrinsically full luminescent state in GLKZ glass and that the non-radiative multiphonon decay channel from this level can be neglected for luminescence measurements made at 300 K. According to this result, we will assume that the intrinsic lifetime of ${}^3\text{H}_4$ state (τ_{D_2}) is equal to $294 \mu\text{s}$. W_{CR} in Eq. (3) is the cross-relaxation rate of an energy transfer process involving two interacting Tm^{3+} ions, which excites two ${}^3\text{F}_4$ states at expenses of the ${}^3\text{H}_4$ and ${}^3\text{H}_6$ states depopulation (*note: this process is named as CR in this work*). This non-radiative interaction is an intrinsic process that infers non-exponential term in the ${}^3\text{H}_4$ luminescence decay of Tm^{3+} in GLKZ doped with low concentration of Tm as 0.1 mol%. Prove of that is given by the observation of a non-vanishing γ value in Tm-doped glass when Tb^{3+} concentration is zero, as shown in Table 1. In fact, the γ parameter includes the intrinsic Tm^{3+} cross relaxation, which makes γ equal to $16.4 \text{ s}^{-1/2}$ when $[\text{Tb}] = 0$. By evaluating the integral of the normalized luminescence decay curve of ${}^3\text{H}_4$ level of Tm^{3+} for the case of $[\text{Tm}] = 0.1$ and $[\text{Tb}] = 0$ (where $\gamma = 16.4 \text{ s}^{-1/2}$) according to Eq. (2), we obtained the integrated decay time τ_2 equal to $236 \mu\text{s}$. By using $\tau_2 = 236 \mu\text{s}$ and $W_2 = 0$ (when $[\text{Tb}] = 0$) in Eq. (3), we obtained the Tm:Tm cross-relaxation rate (or W_{CR}) equal to 836 s^{-1} in Tm-doped GLKZ (0.1 mol%). A Tm–Tm intrinsic cross-relaxation rate of 836 s^{-1} will be considered existing in all the Tm(0.1):Tb(y):GLKZ samples used in this work. The luminescence efficiency of thulium excited states was obtained using $\eta_i = \frac{\tau_i}{\tau_{D_i}}$ where $i = 1$ or

$i = 2$ when referring to the ${}^3\text{F}_4$ and ${}^3\text{H}_4$ excited levels, respectively. Table 1 gives the energy transfer parameters and the total lifetime of ${}^3\text{H}_4$ state (τ_2) and the luminescence efficiency (η_i) due to $\text{Tm}({}^3\text{H}_4) \rightarrow \text{Tb}({}^7\text{F}_{3,4})$ energy transfer. One may obtain the microscopic transfer constant C_{DA} ($\text{cm}^6 \text{ s}^{-1}$) using the following expression that relates this constant with the direct energy transfer parameter γ that has been described by Inokuti–Hirayama model [12] for dipole–dipole interaction according to $C_{DA} = \frac{9\gamma^2}{16\pi^3 c_A^2}$, where c_A is the Tb^{3+} concentration. C_{DA} value of $2 \times 10^{-40} \text{ cm}^6 \text{ s}^{-1}$ was obtained for the $\text{Tm}({}^3\text{H}_4) \rightarrow \text{Tb}({}^7\text{F}_3)$ energy transfer (GLKZ) using the experimental value of $\gamma = (28.7–16.4) = 12.3 \text{ s}^{-1/2}$ from data of Table 1 for $C_A = 0.2 \text{ mol}\%$. The C_{DA} value estimated in GLKZ is four times smaller than the one of $8 \times 10^{-40} \text{ cm}^6 \text{ s}^{-1}$ observed for Tm:Tb Ge–Ga–As–S–CsBr glass [6].

3.2. Luminescence effects on the ${}^3\text{F}_4$ excited state of Tm^{3+}

Fig. 2(b) shows the luminescence decay of the ${}^3\text{F}_4$ excited state of Tm^{3+} observed at 1700 nm due to the $\text{Tm}^{3+}({}^3\text{F}_4) \rightarrow \text{Tb}^{3+}({}^7\text{F}_{0,1,2})$ non-radiative energy transfer in Tm(0.1):Tb(y) codoped GLKZ glass, where $y = 0, 0.1, 0.4$ and $0.8 \text{ mol}\%$. Solid line of Fig. 2(b) represents the best fitting of luminescence decay of donor obtained using Eq. (1), the Burshtein model for a dipole–dipole interaction. It was found that this model gives the best fitting of the non-exponential luminescence decay of the $\text{Tm}^{3+}({}^3\text{F}_4)$ state. Best fitting values of the energy transfer parameters, γ and ω , were given in Table 2. An estimate of the direct energy transfer (*dET or d*) and the migration assisted energy transfer (*mET or m*) contributions were done by integration of normalized Eq. (1) ($t = 0 \rightarrow \infty$). Best fitting

Table 1

The energy transfer parameters γ and ω (from best fittings), the total lifetime (τ_2) and luminescence efficiency (η_i) of the ${}^3\text{H}_4$ excited state of Tm^{3+} and the W_2 rate of the $\text{Tm}({}^3\text{H}_4) \rightarrow \text{Tb}({}^7\text{F}_{3,4})$ energy transfer process are given for (Tm:Tb) doped GLKZ glasses

${}^3\text{H}_4(\tau_{D_2} = 294 \mu\text{s})$					
[Tb]	γ ($\text{s}^{-1/2}$) ET (%) ^a	ω (s^{-1}) ET (%) ^b	W_2 (s^{-1})	τ_2 (μs)	η_i
0	16.4	0	0	236	0.80
0.1	26.7 (86)	35 (14)	641	205	0.70
0.2	28.7 (76)	169 (24)	1082	188	0.64
0.4	48.4 (88)	194 (12)	2385	151	0.51
0.8	62.6 (81)	709 (19)	4166	119	0.40

$W_{CR} = 836 \text{ s}^{-1}$ for (${}^3\text{H}_4: {}^3\text{H}_6$) cross-relaxation was obtained by integrating the luminescence decay curve in the case of $[\text{Tb}] = 0$ that exhibits a non-vanishing $\gamma = 16.4 \text{ s}^{-1/2}$.

^aCalculated percentage of direct energy transfer (or direct ET).

^bCalculated percentage of ET assisted by donors migration.

Table 2

The energy transfer parameter γ (from best fitting), the total lifetime (τ_1), luminescence efficiency (η_i) of the ${}^3\text{F}_4$ excited state of Tm^{3+} and W_1 rate of the $\text{Tm}({}^3\text{F}_4) \rightarrow \text{Tb}({}^7\text{F}_{0,1,2})$ energy transfer process are given for (Tm:Tb) codoped GLKZ glasses

${}^3\text{F}_4(\tau_{D_1} = 2.45 \text{ ms})$					
[Tb]	γ ($\text{s}^{-1/2}$) ET (%) ^a	ω (s^{-1}) ET (%) ^b	W_1 (s^{-1})	τ_1 (μs)	η_i
0	10.8	0	0	1570	0.64
0.1	26.9 (82)	87 (18)	620	795	0.32
0.2	52.5 (87)	200 (13)	2156	358	0.15
0.4	71.3 (80)	689 (20)	4265	204	0.08
0.8	157.3 (94)	715 (6)	14288	67	0.03

$W_{\text{other}} = 229 \text{ s}^{-1}$ for the unknown quenching of ${}^3\text{F}_4$ state was obtained by integrating the luminescence decay curve in the case of $[\text{Tb}] = 0$ that exhibits $\gamma = 10.8 \text{ s}^{-1/2}$.

^aCalculated percentage of direct energy transfer (or direct ET).

^bCalculated percentage of ET assisted by donor migration.

value of γ parameter and $\omega = 0$ were used to calculate the mean lifetime of donor state due to dET process. Best fitting value of ω parameter and $\gamma = 0$ were used to calculate the contribution of mET process. The following expressions were used to obtain the direct and migration assisted ET contributions:

$$dET = \left(\frac{1}{\tau_1(d)} - \frac{1}{\tau_{D_1}} \right) \times \frac{1}{(1/\tau_1) - (1/\tau_{D_1})}$$

and

$$mET = \left(\frac{1}{\tau_1(m)} - \frac{1}{\tau_{D_1}} \right) \times \frac{1}{(1/\tau_1) - (1/\tau_{D_1})},$$

where the mean lifetimes $\tau_1(d)$ and $\tau_1(m)$ are due to d and m processes and τ_1 is the total lifetime of donor state. These mean lifetimes were obtained using the following equations:

$$\tau_1(d) = \int_0^\infty \exp\left(-\gamma\sqrt{t} - \frac{t}{\tau_{D_1}}\right) dt,$$

$$\tau_1(m) = \int_0^\infty \exp\left(-\omega t - \frac{t}{\tau_{D_1}}\right) dt$$

and

$$\tau_1 = \int_0^\infty \exp\left(-\gamma\sqrt{t} - \omega t - \frac{t}{\tau_{D_1}}\right) dt,$$

where τ_{D_1} is the intrinsic decay of donor state (3F_4). Experimental results showed that the direct energy transfer 3F_4 (Tm^{3+}) \rightarrow ${}^7F_{0,1,2}$ (Tb^{3+}) has an average contribution of 86% of the total ET1 process. Only 14% of ET1 process is assisted by excitation migration among 3F_4 donor states in the case of Tm(0.1):Tb(y):GLKZ as is seen in Table 2. Similar result was observed for the case of 3H_4 (Tm^{3+}) \rightarrow ${}^7F_{3,4}$ (Tb^{3+}) energy transfer process (ET2), where the direct transfer contribution has an average value of 83% (see Table 1).

A detailed analysis of the 3F_4 (Tm^{3+}) luminescence decay showed that the value of the fitting parameter γ did not vanish when [Tb] concentration is zero in Tm-doped GLKZ glass, but we found $\gamma = 10.8 s^{-1/2}$ as showed in Table 2. This suggests that some unknown impurity contaminant that is present in Tm-doped GLKZ glass can trap and extinguish the migrating excitation of Tm^{3+} (3F_4) state. This mechanism introduces a competitive non-radiative decay of the 3F_4 state with a rate named here as W_{other} . As a result, a luminescence quenching effect is clearly observed by the decrease of the 3F_4 state lifetime from 2.45 ms, expected for isolated Tm^{3+} ions in GLKZ, to 1.57 ms measured in single Tm-doped GLKZ (0.1). W_{other} rate was calculated as

$$W_{other} = \frac{1}{\tau_1} - \frac{1}{\tau_{D_1}} - W_1, \quad (4)$$

where τ_1 is the mean lifetime of 3F_4 state measured in Tm-doped GLKZ and considering $W_1 = 0$ because [Tb] = 0. Using the calculated value of $\tau_1 = 1.57$ ms and $\tau_{D_1} = 2.45$ ms, we obtained $W_{other} = 229 s^{-1}$. This rate

(W_{other}) will be considered existing in all Tm(0.1):Tb(y) codoped GLKZ samples used in this work.

Table 2 exhibits the mean lifetime values (τ_1) of the 3F_4 (Tm^{3+}) state measured for Tm and Tm:Tb codoped GLKZ glasses. Using these mean lifetimes in Eq. (4) we obtained the $Tm^{3+}({}^3F_4) \rightarrow Tb^{3+}({}^7F_{0,1,2})$ energy transfer rate (W_1) for Tm:Tb systems (see data of Table 2). According to the results of this section, we have seen that W_1 rate has a power dependence on Tb^{3+} concentration in Tm(0.1):Tb(y) GLKZ according to the expression $W_1 = c [Tb]^{1.68}$, where $c = 25.7 \times 10^3 s^{-1}$ and Tb^{3+} concentration given in mol%. W_1 did not exhibit saturation effect with the Tb^{3+} concentration up to 0.8 mol%. Neither a residual 1700 nm luminescence from the 3F_4 state due to some isolated Tm^{3+} ions with intrinsic lifetime of 1.57 ms has been seen. This result is in agreement to what has been reported about the luminescence effects on the 3F_4 state decay of Tm^{3+} in (Tm:Ho) tellurite [5] and (Tm:Tb) chalcogenide [6] glasses, respectively. On the other hand, a residual luminescence from 3F_4 excited state, corresponding to 25% of the Tm^{3+} excited ions, remaining with the intrinsic lifetime of ~ 8.9 ms in Tm(0.5 mol%):Ho(0.5 or 1 mol%):ZBLAN glass, has been observed [3]. C_{DA} constant equal to $2.1 \times 10^{-39} cm^6 s^{-1}$ was obtained for the $Tm^{3+}({}^3F_4) \rightarrow Tb^{3+}({}^7F_{0,1,2})$ energy transfer using the experimental value of $\gamma = (52.5-10.8) = 41.7 s^{-1/2}$ shown in Table 2 considering $C_A = 0.2$ mol%. The C_{DA} value obtained for GLKZ is bigger than the value ($C_{DA} = 1 \times 10^{-39} cm^6 s^{-1}$) verified in Ge-Ga-As-S-CsBr glass [6]. It means that the 3F_4 state deactivation caused by direct energy transfer to Tb^{3+} ions in GLKZ is about two times stronger than the one observed in Ge-Ga-As-S-CsBr glass, which favors the required population inversion between the 3H_4 and 3F_4 states in GLKZ system for 1450 nm light signal amplification.

4. Discussion

4.1. Rate equations for the Tm and Tm:Tb codoped GLKZ glasses

Fig. 3 shows the schematic energy levels diagram used for the Tm:Tb system considered for continuous laser pumping at 792 nm. Based on the mechanisms showed in Fig. 3 we derived three rate equations for the system. n_0 , n_1 and n_2 are the 3H_6 , 3F_4 and 3H_4 normalized populations (given in mol fraction), respectively, exhibited in the diagram scheme of Fig. 3, n_3 , n_4 are the ground (7F_6) and the excited state (${}^7F_{0,1,2}$) population of Tb^{3+} . Obviously, n_4 population of Tb^{3+} was considered negligible ($n_4 = 0$) in the rate equations because the ${}^7F_{0,1,2}$ excited state should strongly be depopulated by fast multiphonon decays to the lowest 7F_3 and 7F_4 levels that are close to the 7F_6 ground state by $\sim 500 cm^{-1}$. A very fast ground state population recovering of few nanoseconds is expected to happen in the Tb^{3+} excited ion that validates our consideration that n_4 is negligible and n_3 is equal to

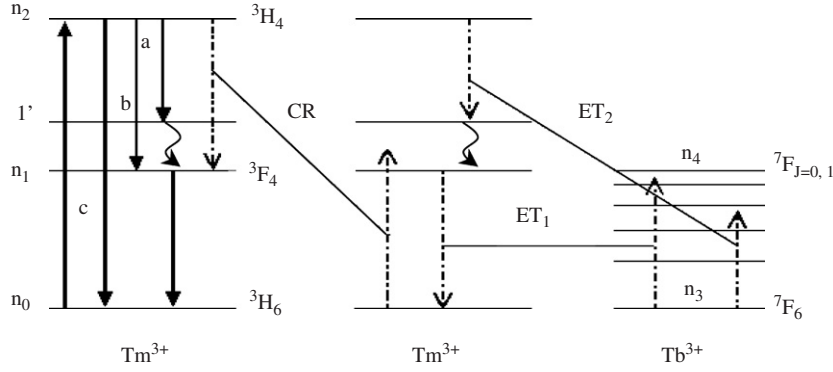


Fig. 3. A schematic energy levels diagram used for the (Tm:Tb) system considered for continuous laser pumping at 792 nm (solid up-arrow). n_0, n_1, n_2 are the populations of the Tm^{3+} and the n_3 and n_4 are the populations of Tb^{3+} ions (n_i are given in mol fraction). Tm–Tm cross-relaxation process is represented by CR that has a transfer rate W_{CR} . Tm–Tb energy transfer processes are represented by ET_1 and ET_2 that have transfer rates W_1 and W_2 , respectively. Radiative transitions are: $a = 2300$ nm ($\beta_{21'} = 0.02$); $b = 1470$ nm ($\beta_{21} = 0.08$); $c = 800$ nm ($\beta_{20} = 0.90$).

Tb^{3+} concentration (or y).

$$\frac{dn_0}{dt} = -\sigma_{02} \frac{I_P}{h\nu} n_0 + \frac{n_1}{\tau_{D_1}} + \frac{B_{20}}{\tau_{D_2}} n_2 - W_{\text{CR}} n_0 n_2 + W_1 n_1 y + W_{\text{other}} n_1, \quad (5)$$

$$\frac{dn_1}{dt} = 2W_{\text{CR}} n_0 n_2 + \frac{(B_{21} + B_{21'})}{\tau_{D_2}} n_2 - \frac{n_1}{\tau_{D_1}} - W_1 n_1 y + W_2 n_2 y - W_{\text{other}} n_1, \quad (6)$$

$$\frac{dn_2}{dt} = \sigma_{02} \frac{I_P}{h\nu} n_0 - \frac{n_2}{\tau_{D_2}} - W_{\text{CR}} n_0 n_2 - W_2 n_2 y, \quad (7)$$

where σ_{02} is the absorption cross section at 792 nm. I_P used in Eqs. (5) and (7) is the pumping intensity (W cm^{-2}) and $h\nu$ is the photon energy of pumping at 792 nm τ_{D_1} and τ_{D_2} are the intrinsic total lifetime of ${}^3\text{H}_4$ and ${}^3\text{F}_4$ levels of Tm^{3+} . W_{CR} is the Tm–Tm cross-relaxation rate equals to 836 s^{-1} , W_1 and W_2 are the rates of the Tm–Tb energy transfer processes represented by ET_1 and ET_2 in Fig. 3. Luminescence branching ratio of ${}^3\text{H}_4$ level (Tm^{3+}) used are $\beta_{21'} = 0.02$, $\beta_{21} = 0.08$ and $\beta_{20} = 0.90$ for the emissions with peaks at 2300, 1470 and 800 nm, respectively.

The absorption cross section σ_{02} was calculated using the absorption spectrum of Tm(0.1):GLKZ (Fig. 1), the thulium density ($2.53 \times 10^{19} \text{ cm}^{-3}$) and the sample thickness (0.25 cm), which resulted $\sigma_{\text{abs}} = 1.10 \times 10^{-20} \text{ cm}^2$ at 792 nm. The emission cross sections for the ${}^3\text{H}_4 \rightarrow {}^3\text{H}_6$ and ${}^3\text{H}_4 \rightarrow {}^3\text{F}_4$ transitions of Tm^{3+} , respectively, centered at 800 and 1470 nm, were calculated using the integration relation [13] given by

$$\sigma_{\text{emis}}(\bar{\lambda}) = \frac{\bar{\lambda}^4 \beta_{ij}}{8\pi n^2 \tau_{R_i} c} \frac{I(\lambda)}{\int I(\lambda) d\lambda}, \quad (8)$$

where $I(\lambda)$ is the measured luminescence intensity, c is the speed of light and $n = 1.65$. One may use that $(I(\lambda)/\int I(\lambda) d\lambda) = (1/\Delta\lambda)$ where $\Delta\lambda$ is the emission bandwidth at half height and $\bar{\lambda}$ is the mean value of the emission

wavelength. The following experimental parameters were used in this calculation: (i) for ${}^3\text{H}_4 \rightarrow {}^3\text{H}_6$ emission: $\bar{\lambda} = 800$ nm, $\tau_{R_2} = 294 \text{ } \mu\text{s}$, $\beta_{20} = 0.90$ and $\Delta\lambda = 55$ nm; (ii) for ${}^3\text{H}_4 \rightarrow {}^3\text{F}_4$ emission: $\bar{\lambda} = 1470$ nm, $\tau_{R_2} = 294 \text{ } \mu\text{s}$, $\beta_{20} = 0.08$ and $\Delta\lambda = 190$ nm. Calculated values of the emission cross sections are $1.13 \times 10^{-20} \text{ cm}^2$ for 800 nm and $3.5 \times 10^{-21} \text{ cm}^2$ for 1470 nm.

Numerical calculations of the rate equations system were performed for Tm-doped and Tm:Tb codoped GLKZ taking the Tm concentration equal to 0.1 mol% and [Tb] equal to $y = 0, 0.1, 0.2, 0.4$ and 0.8 mol%, using a home made program based on Scilab language.

Fig. 4 shows the time evolution of $n_1(t)$ and $n_2(t)$ populations after switching the CW laser (792 nm) laser ON at $t = 0$, and the time past to drive them to equilibrium for Tm(0.1), Tm(0.1):Tb(0.2) and Tm(0.1):Tb(0.4):GLKZ glasses for an pumping intensity equal to 0.9 kW cm^{-2} . Population difference Δn (in mol fraction) was taken at the longest time after the population densities getting the equilibrium. Fig. 5 shows the population density difference ΔN (ions cm^{-3}) $= (n_2 - n_1) N_0$ obtained from rate equations as a function of Tb concentration for several pumping rates $R_p = 10, 100$ and 200 s^{-1} . These pumping rates are consistent with the pumping intensities I_P used, 0.2, 2.2 and 4.4 kW cm^{-2} , respectively, considering that the absorption cross section of Tm^{3+} at 792 nm is equal to $\sigma_{02} = 1.10 \times 10^{-20} \text{ cm}^2$. As a result of this calculation, Fig. 5 shows ΔN positive for Tm:Tb codoped GLKZ, which exhibits a maximum for 0.2% of Tb^{3+} , according to our computational simulation. A population density inversion has been reported in Ref. [6] for the (Tm:Tb) codoped Ge–Ga–As–S–CsBr glass for the ${}^3\text{H}_4 \rightarrow {}^3\text{F}_4$ transition of Tm^{3+} by solving a set of rate equations of the system, without considering the crossing product between Tm^{3+} populations (${}^3\text{H}_4, {}^3\text{F}_4$) and Tb^{3+} ground state population (${}^7\text{F}_0$). As a consequence of this, best Tb^{3+} concentration that exhibits the maximum ΔN in the curve of ΔN versus Tb^{3+} concentration was not clearly obtained in Ref. [6]. However, a maximum ΔN of

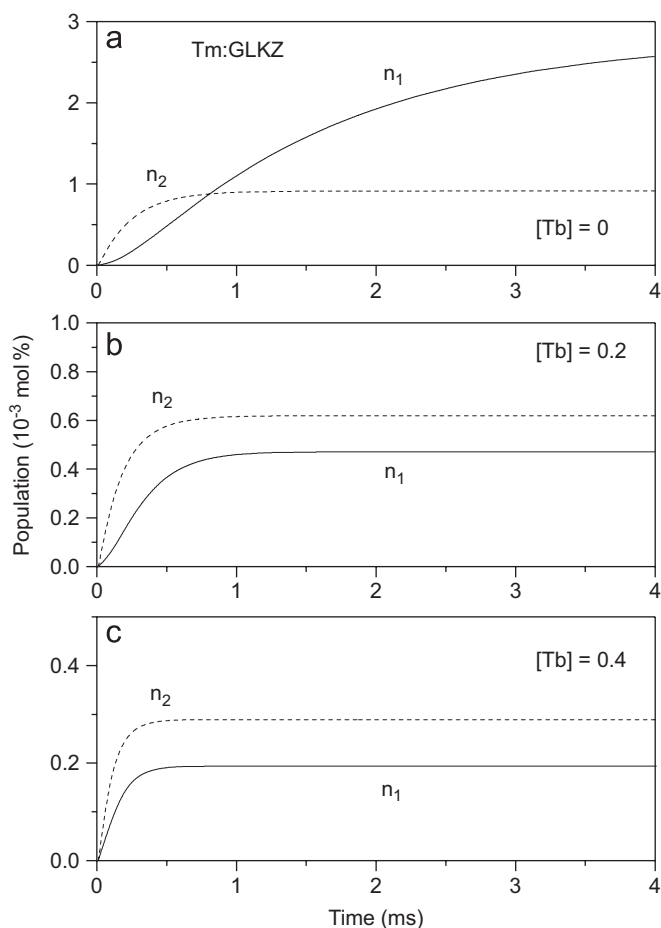


Fig. 4. This figure shows the time evolution of $n_1(t)$ and $n_2(t)$ populations after the CW laser pumping at 792 nm application at $t = 0$, and the time past to drive them to equilibrium. Tm(0.1) and Tm(0.1):Tb(y):GLKZ were considered where $y = 0.2$ and 0.4 mol%. The pumping intensity used was 0.89 kW cm^{-2} .

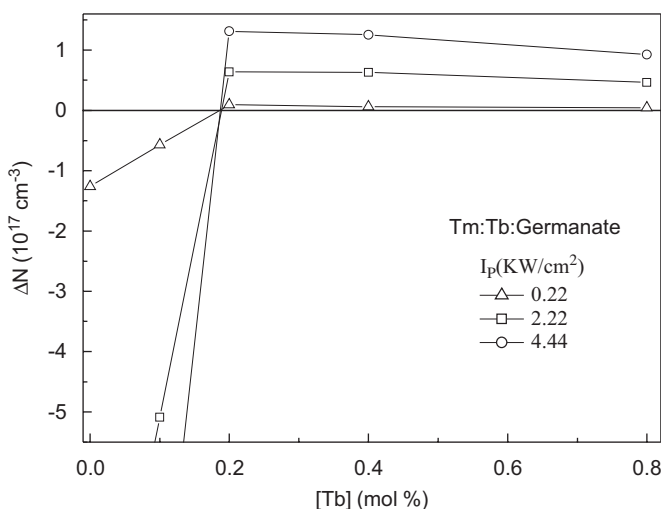


Fig. 5. This figure shows the population density difference $\Delta N = (n_2 - n_1)N_0$ obtained from rate equations as a function of Tb^{3+} concentration for the pumping rates $R_p = 10, 100$ and 200 s^{-1} that are consistent with the pumping intensities $I_p = 0.22, 2.22$ and 4.44 kW cm^{-2} , respectively, considering the absorption cross section $\sigma_{02} = 1.10 \times 10^{-20} \text{ cm}^2$ at 792 nm.

$\sim 2.4 \times 10^{17} \text{ Tm}^{3+} \text{ cm}^{-3}$ was obtained for a simulated pumping intensity of 1.6 kW cm^{-2} at 792 nm [6] that is consistent with the population inversion exhibited in Fig. 5.

Fig. 6 shows the population density difference ΔN (ions/ cm^3) obtained from the numerical solutions for the steady state regime as a function of the (CW) laser pumping intensity at 792 nm for Tm(0.1) and Tm(0.1):Tb(0.2) codoped GLKZ glasses. Open squares of Fig. 6(a) exhibit the hypothetical population density difference ΔN gotten if the presence of Tb (0.2%) would not deactivate the 3H_4 excitation what is equivalent to make W_2 equal to zero in the rate equations. This consideration gives an insight of how a perfect deactivator would work. One may compare the hypothetical system (open squares in Fig. 6(a)) with the real system (solid

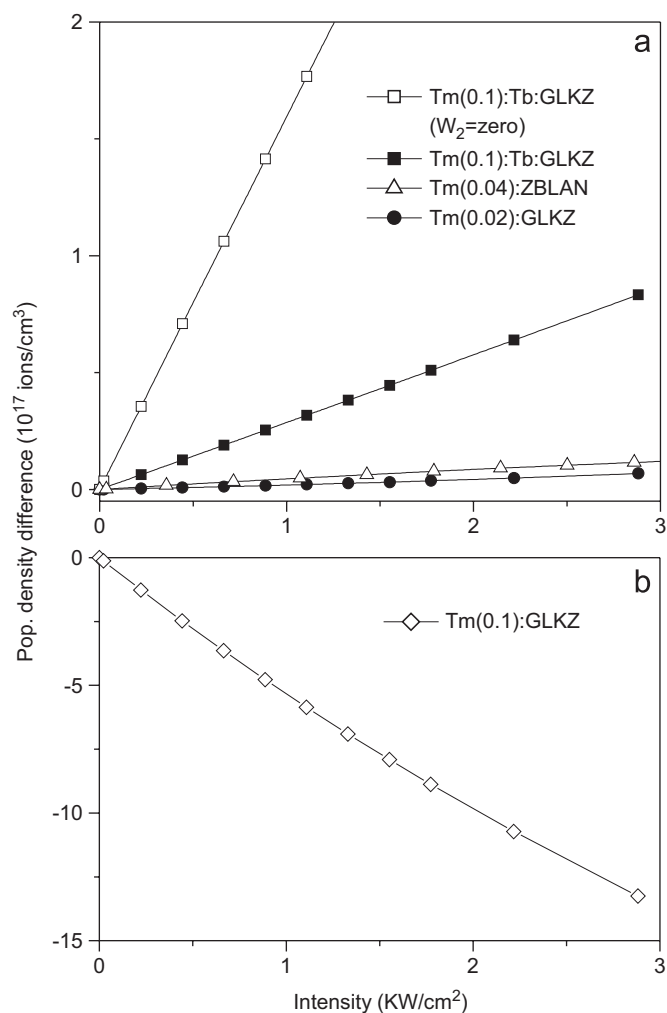


Fig. 6. This figure shows the population density difference ΔN obtained for the steady state regime as a function of the laser pumping intensity at 792 nm. Tm(0.02), Tm(0.1) and Tm(0.1):Tb(0.2) codoped GLKZ and Tm(0.04):ZBLAN glasses were used. The curve with open squares in (a) exhibits ΔN gotten for a hypothetical system constituted by Tm(0.1):Tb(0.2):GLKZ where it has W_2 transfer rate negligible for comparison with the real case (solid squares in (a) and (b) shows that ΔN is negative in Tm(0.1):GLKZ due to W_{CR} value that is 836 s^{-1} . In opposite, Tm(0.02):GLKZ system has a positive Δn because W_{CR} value has decreased to 134 s^{-1} .

squares in Fig. 6(a)). The results exhibited in Fig. 6(b) also show that the population density difference is negative for Tm(0.1):GLKZ because the Tm:Tm cross-relaxation rate ($W_{CR} = 836 \text{ s}^{-1}$) transfers excitation from $^3\text{H}_4$ to $^3\text{F}_4$ excited state so decreasing the population inversion. On the other hand, if we consider the GLKZ glass doping with $x \text{ mol}\%$ of thulium, the expected Tm:Tm cross-relaxation rate will decrease according to

$$W_{CR}(x) = \left(\frac{1}{\tau_2(x)} - \frac{1}{\tau_{D_2}} \right) \times \frac{1}{(1/\tau_2) - (1/\tau_{D_2})} \times W_{CR}.$$

By using $\tau_{D_2} = 296 \mu\text{s}$, $\tau_2 = 236 \mu\text{s}$, $W_{CR} = 836 \text{ s}^{-1}$ and $\tau_2(x = 0.02) = 284 \mu\text{s}$, which were obtained by means of integration (Eq. (2)), and $\gamma(x = 0.02) = 3.2 \text{ s}^{-1/2}$ that was obtained from $\gamma(x) = (x/0.1)\gamma$ (considering that $\gamma = 16.4 \text{ s}^{-1/2}$).

By solving the rate equations system for Tm(0.02):GLKZ system that has $W_{CR}(x = 0.02) = 134 \text{ s}^{-1}$, a positive population density difference was found as exhibited by the curve of solid circles in Fig. 6(a). Similar magnitude of population inversion (ΔN) and linear dependence of ΔN as a function of the pumping intensity (given in kW cm^{-2}) verified for the Tm(0.02):GLKZ (solid circles in Fig. 6(a)) is also observed in Tm(0.04):ZBLAN (open triangles in Fig. 6(a)) glass, besides the differences of the optical constants of both systems. The Tm:Tm cross-relaxation is negligible in Tm(0.04):ZBLAN ($W_{CR} \sim 5 \text{ s}^{-1}$) while it is not negligible in Tm(0.02):GLKZ ($W_{CR} = 134 \text{ s}^{-1}$). The lifetime of $^3\text{H}_4$ and $^3\text{F}_4$ states of Tm^{3+} in Tm(0.04):ZBLAN, 1.5 and 8.9 ms, respectively, are longer than the corresponding lifetimes observed in Tm(0.02):GLKZ glass, which are 283 μs and 1.57 ms, respectively. The absorption cross section measured at 792 nm for Tm:ZBLAN that values $2.7 \times 10^{-21} \text{ cm}^2$, is smaller than the one measured for Tm:GLKZ glass ($1.10 \times 10^{-20} \text{ cm}^2$).

4.2. The amplification coefficient $\beta(\text{cm}^{-1})$

If a small volume of (Tm:Tb) codoped GLKZ glass is considered be uniformly excited by a diode laser through a small length depth z with an intensity I_P (W cm^{-2}) at 792 nm, it might be able to accumulate amplification potential for 1470 nm laser radiation resonant with the $^3\text{H}_4 \rightarrow ^3\text{F}_4$ transition (Tm^{3+}) for Tm and (Tm:Tb) codoped systems. When the probe laser beam (1470 nm) of intensity I_0 (W cm^{-2}) passes through the excited cylinder volume in the z direction, it will be amplified or absorbed depending on Δn value is positive or negative according to

$$I = I_0 \exp(-\sigma_{\text{abs}} n_1 N_0 z) \exp(\sigma_{\text{emis}} n_2 N_0 z) = I_0 \exp(\sigma_{\text{emis}} \Delta N z), \quad (9)$$

considering that $\sigma_{\text{abs}}(1470 \text{ nm}) \sim \sigma_{\text{emis}}(1470 \text{ nm}) = 3.5 \times 10^{-21} \text{ cm}^2$, ΔN the population density difference ($\text{Tm}^{3+} \text{ cm}^{-3}$) and z the gain length (cm) and N_0 the number of $\text{Tm}^{3+} \text{ cm}^{-3}$ in the Tm(0.1):GLKZ. The use of $\sigma_{\text{abs}}(1470 \text{ nm}) \sim \sigma_{\text{emis}}(1470 \text{ nm})$ in Eq. (9) justifies considering that the $^3\text{F}_4 \rightarrow ^3\text{H}_4$ absorption band of Tm^{3+} in GLKZ

is unknown and cannot be measured by standard absorption technique, once this transition involves an excited state absorption that strongly overlaps the correspondent emission spectrum. Using the composition formula of Tm(0.1):GLKZ glass and its density of 3.95 g cm^{-3} , we could estimate $N_0 = 2.53 \times 10^{19} \text{ Tm}^{3+} \text{ cm}^{-3}$. By inspecting Eq. (9) one concludes that the probe laser beam will be absorbed or amplified if ΔN would be negative or positive, respectively. ΔN positive means that the $^3\text{H}_4$ excited state population exceeds the $^3\text{F}_4$ state population when the system gets a steady state regime. The medium gain, $g(\text{cm}^{-1})$, was calculated taking the difference between the stimulation coefficient $\beta(\text{cm}^{-1})$ and the absorption coefficient $\alpha(\text{cm}^{-1})$ according to

$$g = \beta - \alpha = \sigma_{\text{emis}} N_2 - \sigma_{\text{abs}} N_1 \text{ (or } \approx \sigma_{\text{emis}} \Delta N). \quad (10)$$

Fig. 7(a) shows the amplification coefficient $\beta(\text{cm}^{-1})$ as a function of the pumping intensity I_P for the Tm(0.1):Tb(0.2):GLKZ. On the other hand, Fig. 7(b)

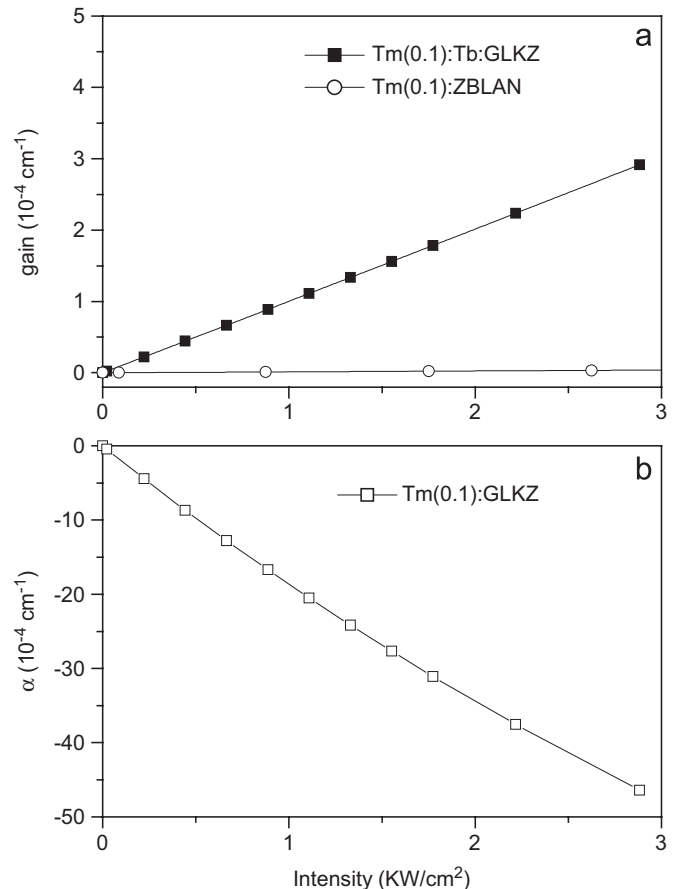


Fig. 7. Gain (g) or attenuation (α) coefficients were calculated for a signal probe laser of 1470 nm passing through the glass material for many laser pumping intensities at 792 nm (CW regime) for Tm(0.1) and Tm(0.1):Tb(0.2):GLKZ, and for Tm(0.1):ZBLAN glasses for comparison. It was used $N(\text{Tm}) = 2.53 \times 10^{19} \text{ ions cm}^{-3}$ and $N(\text{Tm}) = 1.76 \times 10^{19} \text{ ions cm}^{-3}$, respectively, for GLKZ and ZBLAN doped with 0.1 mol% of Tm. $\sigma_{\text{emis}} = 3.5 \times 10^{-21} \text{ cm}^2$ and $\sigma_{\text{emis}} = 2.8 \times 10^{-22} \text{ cm}^2$ were used for GLKZ and ZBLAN glasses, respectively, for the 1470 nm emission of Tm^{3+} to calculate the gain coefficient.

shows that absorption of the 1470 nm laser probe will happen instead of amplification in the case of Tm (0.1)-doped GLKZ. In contrast, the numerical calculation applied to the Tm(0.1)-doped ZBLAN glass exhibits small laser probe amplification at 1470 nm.

5. Conclusions

In this work, we investigated the amplification properties of the GLKZ glass operating for 1470 nm wavelength. Despite the lower absorption coefficient produced by the low Tm concentration used (0.1 mol%) to minimize the (Tm:Tm) cross-relaxation effect on $^3\text{H}_4$ luminescent level, the Tb^{3+} codoped system showed capability for laser radiation amplification tuned in the S-band of telecommunication because $\beta > \alpha$. Best Tb^{3+} concentration was found to be in the order of 0.2 mol%. It was shown that Tm(0.1):Tb(0.2):GLKZ has β amplification coefficient about 14 times higher than one estimate for Tm(0.1):ZBLAN glass for a typical intensity of 0.93 kW cm^{-2} . It was verified that the Tm(0.1):GLKZ will exhibit intensity attenuation of a laser probe at 1470 nm, because $\beta < \alpha$ due to the cross-relaxation rate (836 s^{-1}) involving the $^3\text{H}_4$ upper state. However, Tm(0.02%):GLKZ glass shows positive gain because the cross-relaxation rate decreased to 134 s^{-1} . The main conclusion is that the Tm(0.1%):GLKZ glass codoped with 0.2 mol% of terbium has highest gain for light amplification at 1470 nm and can be used in optical

amplifier development based on Tm^{3+} -doped materials for optical telecommunications operating in the S-band.

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