Effects in the population inversion of $^3H_4$ level in Tm, Tm-Tb and Tm-Eu doped germanate glasses for amplifiers applications

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ABSTRACT

The population inversion of the Tm^{3+} in GLKZ glass involved in the 1470 nm emission ($^3H_4 \rightarrow {}^3F_4$) as a function of Tb (or Eu) concentration was calculated by computational simulation for a CW laser pumping at 792 nm. These calculations were performed using the experimental Tm→Tb an Tm→Eu transfer rates and the spectroscopic parameters of the Tm (0.1 mol %) system. The result shows that 0.2 mol % (Tb^{3+}) and 0.4 mol % of Eu^{3+} ions propitiate best population inversion of Tm^{3+} (0.1 mol %) maximizing the amplification coefficient of germanate (GLKZ) glass when operating as laser intensity amplification at 1470 nm. Besides the effective deactivation of the $^3F_4$ level, the presence of Tb^{3+} or Eu^{3+} ions introduce a depopulation of the $^3H_4$ emitting level by means of a cross relaxation process with Tm^{3+} ions. In spite of this, the whole effect is verified to be benefic for using Tm-doped GLKZ glass codoped with Tb^{3+} or Eu^{3+} as a suitable material for confectioning optical amplifiers that operates in the S-band for telecommunication.
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1. INTRODUCTION

Tellurite [1], chalcogenide [2] and heavy metal fluoride glasses [3] have been considered as key-materials for thulium doped fiber amplifier operation in the S-band (1450-1510 nm) mainly due to their low phonon energies (~580 cm^{-1}). Nevertheless, Tm:Ho doped lead cadmium fluorogermanate glass has been recently used as an alternative for developing material for fiber optical amplifier using Tm^{3+} emission at 1470 nm for telecommunication [4]. In this work we investigated the Tm^{3+} infrared emission properties in GeO_2 based glass due to its favorable optical properties such as a wide transmission window (typically 300-5000 nm), high linear (1.65) 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. It has been observed in the literature that thulium doped oxide and fluoride glasses show an intrinsic problem for the optical operation at ~1500 nm because the lower ($^3F_4$) excited state has longer lifetime then the upper excited level ($^3H_4$). A deactivation of $^3F_4$ state of Tm^{3+} is important. In view of these difficult, this article has the aim of studying the Tm, Tm:Tb, and Tm:Eu doped germanate glasses based on the composition GeO_2-Li_2O-K_2O-ZnO to characterize the energy transfer process and to discuss some relevant theoretical aspect of the $^3F_4$ deactivation of Tm^{3+} state by Tb^{3+} (or Eu^{3+}) ions in GLKZ glass.

2. EXPERIMENTAL PROCEDURE

Germanate glasses of GeO_2-Li_2O-K_2O-ZnO (GLKZ) family were prepared as single (Tm) and double-doped (Tm:Tb) and (Tm:Eu) 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:

$70GeO_2$-$10Li_2O$-$10K_2O$-$9.95ZnO$-$0.05Tm_2O_3$

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(*ii*) Tm:Tb (or Tm:Eu) codoped samples:

70GeO2-10Li_2O-10K_2O-(9.95-*y/2*)ZnO-0.05Tm_2O_3-(*y/2)*Re_2O_3 (*y* = 0.1, 0.2, 0.4 and 0.8 mol %) where Re=Tb or Eu.

Tm:GLKZ and Tm:Re:GLKZ glasses were produced by melting the starting materials at 1150°C for 30 minutes in a Pt-Au crucible. The liquids were poured into brass molds and annealed at 400°C for 4 h to remove the mechanical stresses. The samples were cut and polished into 15 x 10 x 5 mm pieces. Absorption spectra were obtained 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 luminescence to verify the Tm ($^3H_4$) decay and the Tm ($^3F_4$) →Re energy transfer. The lifetimes of Tm^{3+} excited states, $^3H_4$ and $^3F_4$, 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 $^3H_4$ and $^3F_4$ states of Tm^{3+}, respectively. The time-dependent luminescence of Tm^{3+} was detected by an InSb (77K) infrared detector (Judson model J10D) with a fast preamplifier (response time of 0.5 μs) 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 ~10^{-5}, were used to measure these luminescence signals.

3. EXPERIMENTAL RESULTS

3.1 Luminescence effect on the $^3H_4$ excited state of Tm^{3+}

Figure 1(a) shows the effect on the luminescence decay of the $^3H_4$ excited state of Tm^{3+} due to the Tm ($^3H_4$)→Tb ($^7F_{0,1,2}$) non-radiative energy transfer in (Tm:Tb) doped germanate glass. A strong decreasing of the 1470 nm luminescence is seen in Fig. 1(a) in Tb codoped samples. Figure 2 exhibits the Eu^{3+} effects on Tm^{3+} emissions for Tm:Eu:GLKZ glasses.

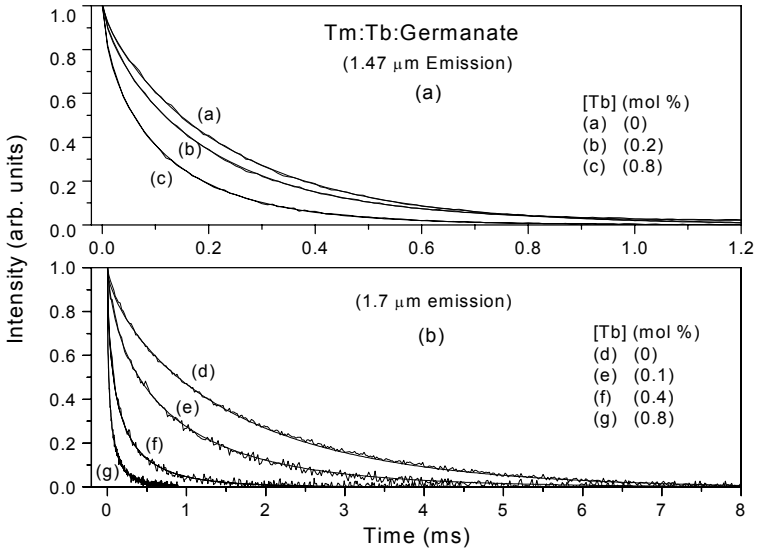

Figure 1(a). Tm^{3+} luminescence decay in Tm (0.1) and Tm (0.1): Tb(*y*): GLKZ glasses using several concentrations of Tb (*y* = 0, 0.1, 0.2, 0.4, and 0.8 mol %). Fig. 1(a) shows the 1470 nm luminescence decay of $^3H_4$ (Tm) state using a laser excitation at 776 nm with

time duration of 4 ns (10 Hz) and 10 mJ. Fig. 1(b) shows the 1700 nm luminescence decay of the $^3F_4$ (Tm) state using the laser excitation at 1671 nm of 4 ns of time duration (10 Hz) and 10 mJ.

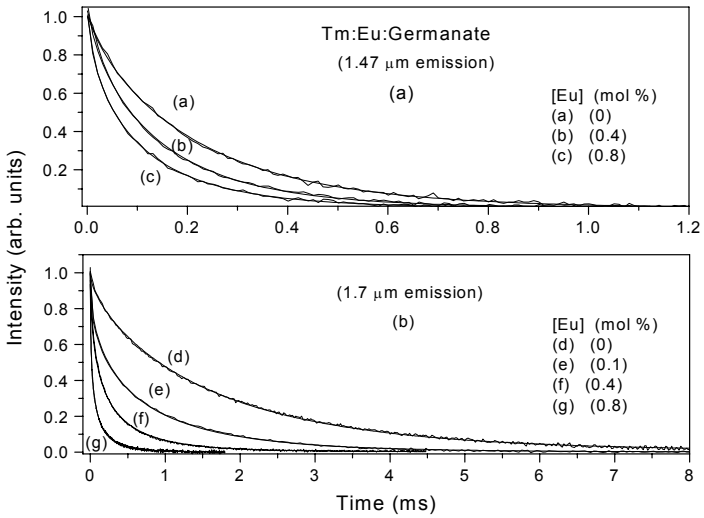

Figure 2. Tm^{3+} luminescence decay in Tm (0.1) and Tm (0.1): Eu(y): GLKZ glasses using several concentrations of Eu (y = 0, 0.1, 0.4, 0.4, and 0.8 mol %). Fig. 2(a) shows the 1470 nm luminescence decay of $^3H_4$ (Tm) state using a laser excitation at 776 nm with time duration of 4 ns (10 Hz) and 10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

Solid line of Figs. 1(a) and 2(a) represent the best fitting of 1470 nm luminescence decay obtained using the Burshtein model [5]. This model is given by Eq. (1), which includes the donor migration in the energy transfer process.

$$I = I_0 \, exp\left(- \frac{t}{\tau_D} - W\, t - \gamma_2 \sqrt{t} \right) \tag{1}$$

were τ_D is the intrinsic donor decay and γ_2 ($s^{-1/2}$) is the energy transfer parameter and W (s^{-1}) is the energy transfer rate due to the donor migration contribution by hopping. The total transfer rate (s^{-1}) and the total lifetime of $^3H_4$ (Tm) state were calculated using Eqs. (2) and (3), respectively.

$$W_2 = W + \gamma_2{}^2 - 16.8^2 \tag{2}$$

$$\tau_2{}^{-1} = W_{CR} + W_2 + \frac{1}{\tau_D} \tag{3}$$

τ_D is the intrinsic lifetime of $^3H_4$ (Tm), which is equal to 295 μs for [Tm] of 0.1 mol %. W_{CR} is the cross relaxation rate involving the $^3H_4$ excited and $^3H_6$ ground states of Tm^{3+} ions, which exists in Tm doped GLKZ glass at lower concentrations (0.1 mol %). W_{CR} = 281 s^{-1} according to the best fitting of the luminescence decay curves. Analogous results were encountered for Tm:Eu GLKZ glass. Table 1 gives the energy transfer parameters, the total luminescence lifetimes and luminescence efficiencies for the Tm ($^3H_4$) →Tb ($^7F_{0,1,2}$) and Tm($^3H_4$) →Eu($^7F_6$) systems.

Table 1. The energy transfer parameters γ_2 and W, the total lifetime and luminescence efficiency (η_ℓ) of the $^3H_4$ excited state of Tm^{3+} due to Tm ($^3H_4$) →Tb ($^7F_0$), Eu($^7F_6$) energy transfers are given in (Tm:Tb) and (Tm:Eu) doped GLKZ glasses.

$^3H_4$ (τ_D = 295 μs)					
[Tb]	γ_2 ($s^{-1/2}$)	W(s^{-1})	W_2(s^{-1})	τ_2 (μs)	η_ℓ
0	16.8	0	0	272	0.92
0.1	26.7	35	470	241	0.82
0.2	28.7	169	713	228	0.77
0.4	48.4	194	2259	169	0.57
0.8	62.6	709	4347	125	0.42
[Eu]					
0.1	40.0	0	1319	190	0.64
0.2	46.9	23	1937	170	0.58
0.4	47.8	727	2738	150	0.51
0.8	77.4	459	6174	99	0.33

W_{CR} = 281 s^{-1} ($^3H_4$:$^3H_6$ cross-relaxation)

3.2 Luminescence effects on the $^3F_4$ excited state of Tm^{3+}

Figures 1(b) shows the luminescence decay of the $^3F_4$ excited state of Tm^{3+} observed at 1700 nm, due to the Tm ($^3F_4$)→Tb($^7F_0$) non-radiative energy transfer in Tb codoped germanate glasses. Figure 2(b) exhibits the Eu^{3+} effects on Tm^{3+} emissions for Tm:Eu:GLKZ glasses. The $^3F_4$ luminescence decay could be best fitted applying Bursthein model using Eq. (1) resulting the transfer parameters W negligible and γ with a significant value, so indicating that the Inokuti-Hirayama model [6] is more appropriated in the Tm ($^3F_4$):Tb and Tm($^3F_4$):Eu systems exhibited in Eq. (4) for a dipole-dipole interaction Best fitting of the $^3F_4$ luminescence decay was done using Eq. (4), which sure does not involve donor migration among $^3F_4$ (Tm) excited state.

$$I = I_0 \, exp\left(- \frac{t}{\tau_D} - \gamma_1 \sqrt{t} \right) \tag{4}$$

where γ_1 ($s^{-1/2}$) is the energy transfer parameter. In this case, the energy transfer rate W_1 (s^{-1}) was calculated using Eq. (5).

$$W_1 = \gamma_1^{\,2} - 10.8^2 \tag{5}$$

According to the luminescence fitting, the intrinsic lifetime of $^3F_4$ excited state is 2.45 ms. It was observed that the γ_1 parameter is equal to 10.8 $s^{-1/2}$ for the best fitting of the $^3F_4$ luminescence decay for the single doped glass with Tm (0.1 %). This suggests that an unknown quenching effect is present in this sample, with a probability rate named W_{other} equals to 117 s^{-1}. This non-radiative rate (W_{other}) (or luminescence quenching) will be used in the calculation of population distribution in Tm(0.1), Tm(0.1):Tb(y) and Tm(0.1):Eu(y) systems). The total lifetime (τ_1) of the $^3F_4$ state of Tm^{3+} can be calculated by

$$\tau_1^{-1} = W_{other} + W_1 + \frac{1}{\tau_D} \tag{6}$$

The energy transfer parameters and the total lifetime and luminescence efficiency (η_ℓ) due to Tm ($^3F_4$) → Tb ($^7F_{0,1,2}$) and Tm ($^3F_4$) → Tb ($^7F_6$) interactions are given in Table 2.

Table 2. The energy transfer parameter γ_1, the total lifetime and luminescence efficiency (η_ℓ) of the $^3F_4$ excited state of Tm^{3+} due to Tm ($^3F_4$) →Tb ($^7F_0$), Eu($^7F_6$) interaction are given in (Tm:Tb) and (Tm:Eu) doped GLKZ glasses.

$^3F_4$ (τ_D = 2.45 ms)				
[Tb]	γ_1 ($s^{-1/2}$)	W_1(s^{-1})	τ_1 (μs)	η_ℓ
0	10.8	0	1900	0.78
0.1	30.4	805	752	0.31
0.2	64.1	3991	221	0.09
0.4	86.2	7321	128	0.05
0.8	164.7	27000	36	0.01
[Eu]				
0.1	35.8	1163	553.6	0.23
0.2	49.2	2310	339.5	0.14
0.4	74.5	5430	164.6	0.07
0.8	147.3	21581	45	0.02

W_{other} = 116.6 s^{-1} (unknown quenching of $^3F_4$ state).

We have seen that W_1 has a quadratic dependence on Tb^{3+} concentration that is compatible with the Inokuti-Hirayama model for the Tm→Tb energy transfer. This result indicates that Tb^{3+} acceptor ions does not saturate by the Tm→ Tb transfer at least in the concentration scale used in this work, in opposite to that has been observed in the case of Tm ($^3F_4$) →Ho ($^5I_7$) transfer in ZBLAN glass [7] .

4. DISCUSSION

4.1 Rate equations for the Tm:Tb and Tm:Eu GLKZ glasses

Figure 3 shows the schematic energy levels diagram used for the Tm:Tb system considered for continuous laser pumping at 792 nm, which also represents approximately the diagram used for Tm:Eu systems.

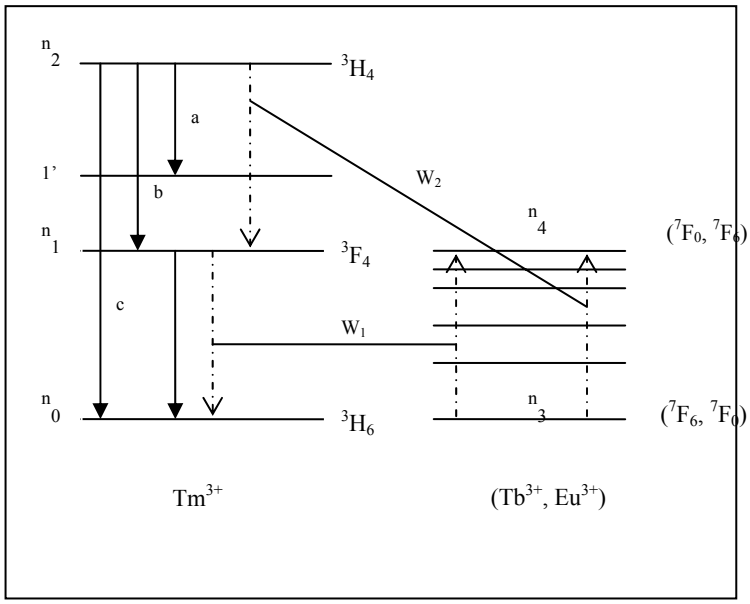

Figure 3. A schematic energy levels diagram used for the (Tm:Tb) and Tm:Eu systems considered for continuous laser pumping at 792 nm. n_0, n_1, n_2 are the population of the Tm^{3+} and the n_3 and n_4 are the population of Tb^{3+} or Eu^{3+} ions.

The following rate equations were also derived for this system and the equilibrium populations were derived from the numerical solutions obtained using the Runge-Kutta numerical method (4^{th} order). We have assumed that n_4 population is negligible for both systems ions (Tm:Tb and Tm:Eu) because the acceptor levels $^7F_0$(Tb) and $^7F_6$(Eu) are strongly depopulated by an effective intrinsic multiphonon decay to the next lower level $^7F_{3,4}$ for Tb^{3+} and $^7F_5(Eu^{3+})$. The small energy difference (~ 500 cm^{-1}) existing in these systems strongly competes with the radiative transition. As a consequence the luminescences from these levels are not observed. By this arguments, we have considered n_3 equal to the Tb (or Eu) concentration or $n_3 = y$ (mol %).

$$\frac{dn_0}{dt} = -\sigma_{12}\, n_0\, I_P + \frac{n_1}{\tau_1} + \frac{B_{20}}{\tau_2} n_2 - W_{CR}\, n_0\, n_2 + W_1\, n_1\, y + W_{other}\, n_1 \tag{7}$$

$$\frac{dn_1}{dt} = 2W_{CR}\, n_0\, n_2 + \frac{B_{21}'}{\tau_2} n_2 + \frac{B_{21}}{\tau_2} n_2 - \frac{n_1}{\tau_1} - W_1\, n_1\, y + W_2\, n_2\, y - W_{other}\, n_1 \tag{8}$$

$$\frac{dn_2}{dt} = \sigma_{12}\, n_0\, I_P - \frac{n_2}{\tau_2} - W_{CR}\, n_0 n_2 - W_2\, n_2\, y \tag{9}$$

Calculations were performed for single Tm (0.1) doped and Tm (0.1): Re(y) double-doped germanate glasses (y = 0, 0.1, 0.2, 0.4 and 0.8) using Scilab software (free software available in the web).
The $n_i(t)$ populations evolute to equilibrium values after switching the pumping (CW) laser (792 nm) ON at t = 0, and therefore they were considered to evaluate the stationary population inversion and gain of the system.
Figure 5 shows the population difference Δn = (n_2-n_1) obtained from rate equations as a function of Tb (or Eu) concentration for several pumping rates Rp = 10, 50 and 80 s^{-1}. The $^3H_6 \rightarrow {}^3H_4$ absorption cross-section of Tm^{3+} at 792 nm used in the calculation was equal to $\sigma_{12} = 7\text{x}10^{-21}$ cm^2. Fig. 5 shows Δn positive for Tm:Tb and Tm:Eu GLKZ with maximum inversion attained for 0.2 % of Tb (or 0.4 mol % for Eu), according to our computational simulation.

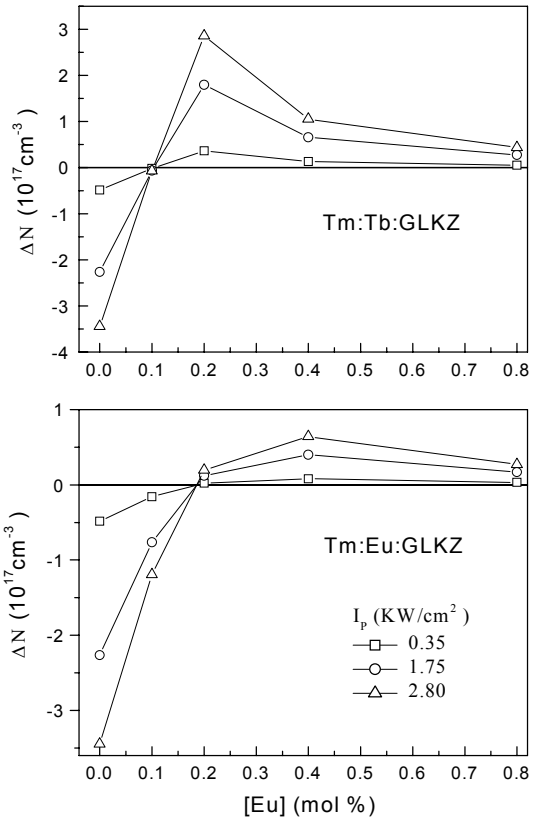

Figure 5. This figure shows the population difference $\Delta n=(n_2-n_1)$ obtained from rate equations as a function of Tb and Eu concentrations for several pumping rates Rp = 10, 50 and 80 s^{-1}. These pumping rates are consistent the following pumping intensities I_P equals to 358, 1430 and 2860 W/cm^2, respectively, considering that the absorption cross-section of Tm^{3+} at 792 nm is equal to σ_{12} = $7x10^{-21}$ cm^2.

Figure 6 shows the population difference Δn (given in ions/cm^3) obtained from the numerical solutions for the steady state regime as a function of the (CW) laser pumping intensity at 792nm for Tm(0.1) and Tm(0.1):Tb(0.2):GLKZ glasses. Open circles of Fig. 6(a) exhibits the maximum Δn got if one solves the rate equation system taking W_2 transfer rate equal to zero for comparison. Fig. 6(b) shows that the population of the $^3F_4$ excited state of Tm^{3+} is higher than the $^3H_4$, the upper excited state in Tm (0.1):GLKZ.

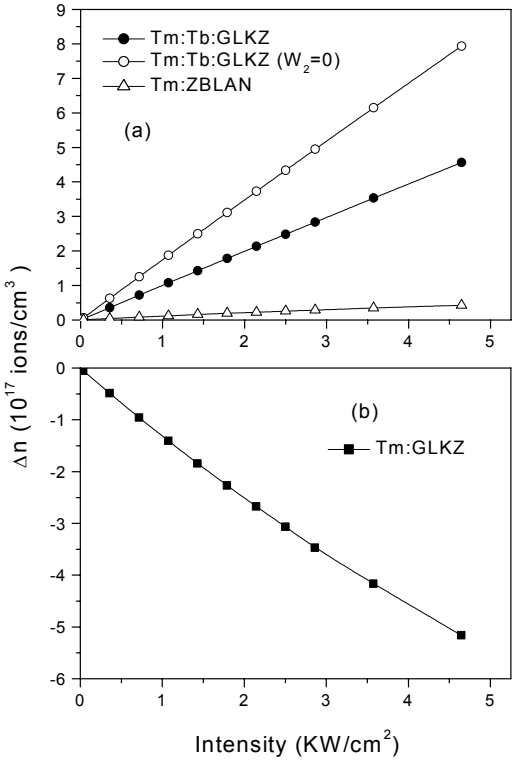

Figure 6. This figure shows the population difference Δn obtained for the steady state regime as a function of the laser pumping intensity at 792nm. Tm(0.1) and Tm(0.1):Tb(0.2) codoped GLKZ and Tm(0.1):ZBLAN glasses were used. Open circles in Fig.6(a) exhibits the maximum Δn got if the W_2 transfer rate would be taken as zero in the rate equations, for comparison. Fig. 6(b) shows that the population of the $^3F_4$ excited state of Tm^{3+} is higher than the $^3H_4$, the upper excited state in Tm(0.1):GLKZ.

4.2 The linear gain coefficient g(cm^{-1})

If a small volume of (Tm:Tb) doped germanate 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 $^3H_4 \rightarrow {}^3F_4$ 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 Eq. (10).

$$I = I_0 \left(e^{-\sigma_{abs}\, n_1\, N_0\, z}\right)\left(e^{\sigma_{emis}\ \ n_2\, N_0\, z}\right) = I_0\, e^{\,\sigma_{emis}\,(\Delta n)\, z} \tag{10}$$

considering that $\sigma_{abs.} \sim \sigma_{emiss} = \sigma$ (6×10^{-22} cm^2) and z the gain length. Using the Tm concentration of 0.1 mol% and the glass density of 3.95 g/cm^3 of GLKZ, we calculate N_0 equals to 2.53×10^{19} ions of Tm^{3+} per cubic centimeters. Eq. (10) shows that the probe laser beam will be absorbed or amplified if Δn would be negative or positive, respectively. Δn positive means that the $^3H_4$ excited state population exceeds the $^3F_4$ state population when the system gets a steady state

regime. The linear gain of the medium g(cm^{-1}) is estimated by the difference between the stimulation coefficient β(cm^{-1}) with the absorption coefficient α(cm^{-1}) as follows

$$g = \beta - \alpha = \sigma_{emis}\, n_2 - \sigma_{abs}\, n_1 \approx \sigma\, \Delta n \tag{11}$$

The linear gain coefficient is proportional to Δn. If Δn is positive the probe intensity at 1470 nm will be amplified, otherwise it will be attenuated. Contrary to the behavior of Tm(0.1):GLKZ, ZBLAN glass already exhibits small amplification effect for 1470 nm probe beam when doped with Tm(0.1 mol %), as seen in Fig. 6(a).

5. CONCLUSIONS

In this work, we investigated the amplification properties of the germanate glasses operating for 1470 nm wavelength. Despite the lower absorption coefficient produced by the use of low Tm concentration (0.1 mol %) to minimize the cross-relaxation effect on $^3H_4$ luminescent level, the Tb codoped GLKZ glass showed capability for laser radiation amplification in the S-band because $\beta > \alpha$. Best Tb^{3+} concentration was found be in the order of 0.2 mol % and 0.4 mol % in the case of Tm:Eu. Our result showed that Tm(0.1):Tb(0.2):GLKZ has an amplification coefficient about 18 times higher than one estimate for Tm(0.1):ZBLAN glass for an typical intensity of 2 KW/cm^2. On the other hand, the single doped Tm:GLKZ might exhibit an attenuation of a laser radiation of 1470 nm because it was observed that $\beta < \alpha$. Tb^{3+} ion works better than Eu^{3+} as deactivator of the $^3F_4$ lowest excited level of Tm^{3+} doped GLKZ glass. The amplification gain of (Tm:Tb) and (Tm:Eu) germanate glasses justifies the use of this material in the development of Tm based optical amplifiers to operate in S-band for telecommunication applications.

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