Photothermal spectroscopic characterization in tellurite glasses codoped with rare-earth ions

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ABSTRACT

Thermal Lens (TL) and spectroscopic characterizations were performed in $70TeO_2$-$19WO_3$-$7Na_2O$-$4Nb_2O_5$ (mol%) tellurite glasses. TL measurements were accomplished in Er^{3+} /Tm^{3+} co-doped tellurite glasses in function of the Tm_2O_3 concentration (0.4 -1.6 x10^{20} ions/cm^3). Fluorescence spectra at 488 nm showed that Er^{3+} /Tm^{3+} co-doped tellurite glasses present several emission bands between (500-1800) nm. However, the more intense emission bands correspond to the Er^{3+} and Tm^{3+} transitions ($^4I_{13/2} \rightarrow {}^4I_{15/2}$ and $^3F_4 \rightarrow {}^3H_6$), respectively. The absolute nonradiative quantum efficiency (φ) was determined by TL method. Higher values of φ were obtained with the increase of Tm_2O_3 concentration inside of the Er^{3+}/Tm^{3+} co-doped tellurite glasses. These results are corroborated by the Judd-Ofelt calculations.

Keyword: Er^{3+} /Tm^{3+} co-doped tellurite glasses, Thermal Lens, Spectroscopic properties, Judd-Ofeld

1. INTRODUCTION

Tellurite glasses are materials that present high rare earth ions solubility, large amplification bandwidth and higher refractive indices than the silicates and fluoride glasses, enhancing the radiative rate and emission cross-section [1-5]. In this way, these glasses have generated an increasing interest, becoming promising for applications as: optical amplifiers, optical recording, laser active media and infrared-to-visible converters [1-9]. Recently, energy transfers processes have been studied in rare earth doped and co-doped glasses using fluorescence spectroscopy [4-10]. The work is motivated by the interest in basic research phenomena and development of new solid state short-wavelength laser materials. In this way, it is very important the characterization of nonlinear optical and thermal-optical properties of the glasses, for optimization of the application of these materials.

Recently, several thermal studies have been made in different kind of glass host structures using Thermal Lens (TL) technique [11-16]. However, only Er^{3+}, Tm^{3+} or Yb^{3+} were embedded in fluoroindate, silica calcium aluminosilicate, chalcogenide and phosphate glasses. In this work, we studied the spectroscopic and thermooptics properties of Er^{3+}/Tm^{3+} co-doped tellurite glasses. The measurements were made in function of the Tm_2O_3 concentration (0.4 -1.6 x10^{20} ions/cm^3), with the purpose of producing multiphonon relaxation and determining the values of absolute nonradiative quantum efficiency (φ). Fluorescence spectra were obtained and the measures are in agreement with the results of Thermal Lens (TL) technique and Judd-Ofelt (JO) calculations.

2. THEORY

The TL effect is created when the excitation laser beam passes through the sample and the absorbed energy is converted into heat, changing the optical path length (s) and producing a lenslike optical element at the sample. The

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propagation of a probe laser beam (He-Ne laser) through the TL will results in either a spreading (ds/dT<0) or a focusing (ds/dT >0) of the beam, depending mainly on the sample temperature coefficients of electronic polarizability, stress and thermal expansion. TL effect can be treated through the calculation of the temporal evolution of the sample temperature profile $\Delta T(r,t)$ caused by a Gaussian intensity distribution of the excitation beam. The variation of probe beam on-axis intensity, I(t), can be calculated in *cw* excitation regime, in the form [11,17,18]:

$$I(t) = I(0)\left[1 - \frac{\theta}{2}\tan^{-1}\left(\frac{2mV}{[(1+2m)^2 + V^2]\tau_c/2t + 1 + 2m + V^2}\right)\right]^2 \quad (1)$$

where $m = (\omega_p/\omega_e)^2$, ω_p and ω_e are respectively the probe and excitation beam radius at the sample; $V = z_1/z_o$, z_1 is the distance between the sample and probe beam waist and z_o is the probe beam Rayleigh range; I(0) is the on-axis intensity when t, or θ, is zero. In the dual beam (excitation and probe beams), mode-mismatched configuration, the transient signal amplitude, θ, is approximately the phase difference of the probe beam at $r = 0$ and $r = \sqrt{2}\,\omega_e$ induced by the pump beam, given by: $\theta = \Theta P_e \alpha L_{eff}$. In this case, P_e(W) is the excitation power, α (cm^{-1}) the optical absorption coefficient at the excitation wavelength (λ_e), $L_{eff} = (1-e^{-\alpha L})/\alpha$ is the effective length and L(cm) is the sample thickness. The normalized phase shift, Θ, can be expressed as [17]:

$$\Theta = -\frac{1}{K\lambda_p}\frac{ds}{dT}\left[1 - \eta\frac{\lambda_e}{\langle\lambda_{em}\rangle}\right] \quad (2)$$

where K is the thermal conductivity (W/cmK), λ_p is the probe beam wavelength and ds/dT is the optical path temperature coefficient normalized by sample lengths (K^{-1}) and $\langle\lambda_{em}\rangle$ the average fluorescence wavelength. The term in parenthesis on the right-hand side of Eq. (2) is the fraction of absorbed energy converted into heat (φ) or absolute nonradiative quantum efficiency (the complementary part is converted into fluorescence). For direct excitation, η is defined as the ratio between the measured lifetime (τ_{exp}) and the radiative lifetime (τ_{rad}), $\eta = \tau_{exp}/\tau_{rad}$.
For other side, $\tau_c = \omega_e^2/4D$ is the characteristic heat diffusion time, where $D = K/\rho C$ is the thermal diffusivity (cm^2/s), ρ is the density (g/cm^3) and *C* is the specific heat (J/gK).

3. EXPERIMENTAL

Samples studied were prepared in the proportion $70TeO_2$-$19WO_3$-$7Na_2O$-$4Nb_2O_5$ (% mol). For Er^{3+}/Tm^{3+} co-doped tellurite glasses were added 1.2 x 10^{20} ions/cm^3 of Er_2O_3 and the concentration of Tm_2O_3 was varied between (0.4-1.6) x 10^{20} ions/cm^3. This raw material was melted and homogenized in platinum crucible at 800 ^{0}C during 30 minutes using a RF induction furnace. All absorbance spectra measurements were carried out with a Perkin Elmer Lambda 9 spectrophotometer at room temperature, with resolution of 1 nm. The fluorescence spectra were measured by a monochromator Spectral Energy connected to either a Silicon PIN or an InAs detector for measurements from (500-1100) nm or (1000-1800) nm, respectively. The samples were excited with an Ar^+ laser at λ_e = 488 nm.

The thermooptic properties of tellurite glasses were investigated by TL method [11,17]. TL transient measurements were performed using the mode-mismatched dual-beam (excitation and probe) configuration. A He-Ne laser (λ_p= 632.8 nm) was used as the probe beam and either an Ar^+ laser (λ_e= 488 nm) or a Ti-sapphire laser (λ_e= 785 nm) was used as the excitation beam. The absorption of the relatively intense excitation beam generates the TL heat profile and the induced phase shift, which is proportional to θ. For other side, θ is measured by the weak probe beam that counter propagates nearly collinear with the excitation beam. Details of the experimental setup can be found elsewhere [11,17,18]. The optical absorption coefficients (α) were determined applying the same experimental configuration used for realization of TL measurements. The reflections at the sample surface were considered in α calculus.

Lifetime (τ_{exp}) measurements of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition were done using a diode laser at λ_e= 980 nm (P_e ≈120 mW). The signal detected by a InGaAs fast response detector, after passing through a bandwidth centred at 1550 nm band pass filter, was acquired using a digital oscilloscope.

4. RESULTS AND DISCUSSIONS

4.1. Spectroscopic properties

The tellurite glasses studied in this paper are presented at Table 1. Absorbance spectra of Tm^{3+} (0.78 x 10^{20} ions/cm^3) doped tellurite and Er^{3+}/Tm^{3+} co-doped tellurite ($S_{1.2,0.4}$) glasses are showed in the Fig. 1 (a-b). The absorption bands of Er^{3+}/Tm^{3+} co-doped tellurite glasses (Fig. 1(b)) that do not appear in Fig. 1 (a) are characteristics of the Er^{3+} ion.

Tellurite	**Er^{3+} (10^{20} ions/cm^3)**	**Tm^{3+} (10^{20} ions/cm^3)**	**ξ**	η_{JO}
$S_{0,0}$	0	0	-	-
$S_{1.2,0}$	1.2	0	220	0.93
$S_{1.2,0.4}$	1.2	0.39	13	0.34
$S_{1.2,0.8}$	1.2	0.78	5	0.28
$S_{1.2,1.2}$	1.2	1.2	4	0.18
$S_{1.2,1.6}$	1.2	1.6	3	0.15

Table I- Composition of the analyzed tellurite glasses. ξ is the ratio between the fluorescence intensities of the T_{Er} and T_{Th} transitions. η_{JO} is the radiative quantum efficiency obtained by Judd-Ofelt method.

Figure 2 and 3 show the fluorescence spectra of the Er^{3+} and Er^{3+}/Tm^{3+} co-doped tellurite glasses. The measurements were made under low power laser $P_e \approx 10$ mW. The matrix of tellurite glass without rare earth ions presented no emission band with intensity comparable to those that measurements were performed. Tm^{3+} doped tellurite glass presented emission bands in ~ 804, 1470 and 1780 nm. For Er^{3+} doped tellurite glasses, the more intense emission band is centered at 1528 nm (Fig. 3 (a)). Er^{3+}/Tm^{3+} co-doped glasses presented suitable emission bands with those measured with the tellurite glass doped either with erbium or thulium (Fig. 2 e 3 (b-c)). In this case, it is possible to observe that are more intense, the emission bands correspondent to the transition of Er^{3+}: $^4I_{13/2} \rightarrow {}^4I_{15/2}$ (T_{Er}) and of Tm^{3+}: $^3F_4 \rightarrow {}^3H_6$ (T_{Th}), presented in the Fig. 3. The ratio of the fluorescence intensities (ξ) of the T_{Er} and T_{Th} transitions, are presented in the Table I. For Er^{3+}/Tm^{3+} co-doped tellurite glass with highest concentration of thulium ($S_{1.2,1.6}$) presents the emission intensity T_{Er} just 3 times larger than the emission of T_{Th} transition. In general form, for Er^{3+}/Tm^{3+} co-doped tellurite glasses, the emission bands between (500-800) nm and (850-1400) nm are respectively ~100 and 5 times less intense than the T_{Er} and T_{Th} emissions. In this form, the emission bands at wavelength < 1400 nm could be neglectful as a good approach.

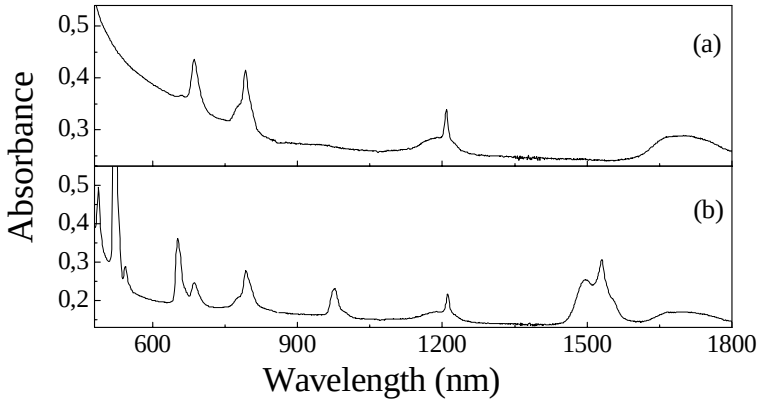

Figure 1- Absorbance (-ln(I/I_0)) for: (a) Tm^{3+} (0.78 x 10^{20} ions/cm^3) doped tellurite glass (L= (1.25 ± 0.03) mm) and (b) $S_{1.2,0.4}$ glass (L= (1.75 ± 0.03) mm).

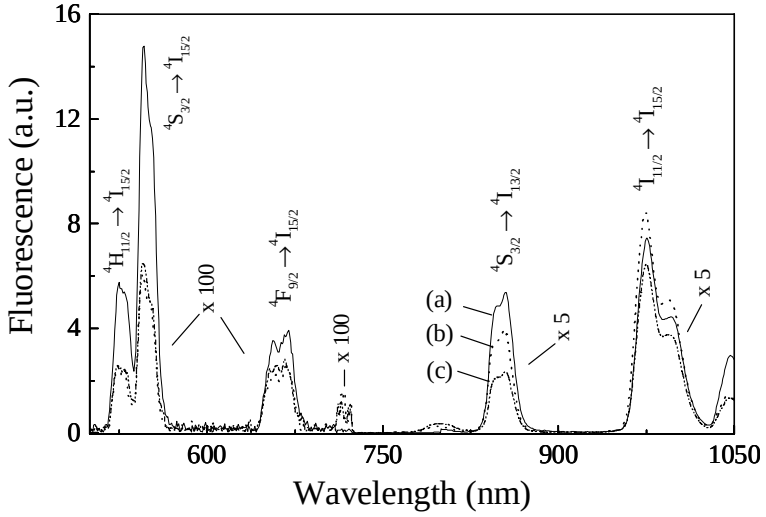

Figure 2- Fluorescence spectra between (500-1050) nm for (a) $S_{1.2,0}$; (b) $S_{1.2,0.4}$ and (c) $S_{1.2,1.6}$ at λ_e= 488 nm ($P_e \approx$ 10 mW).

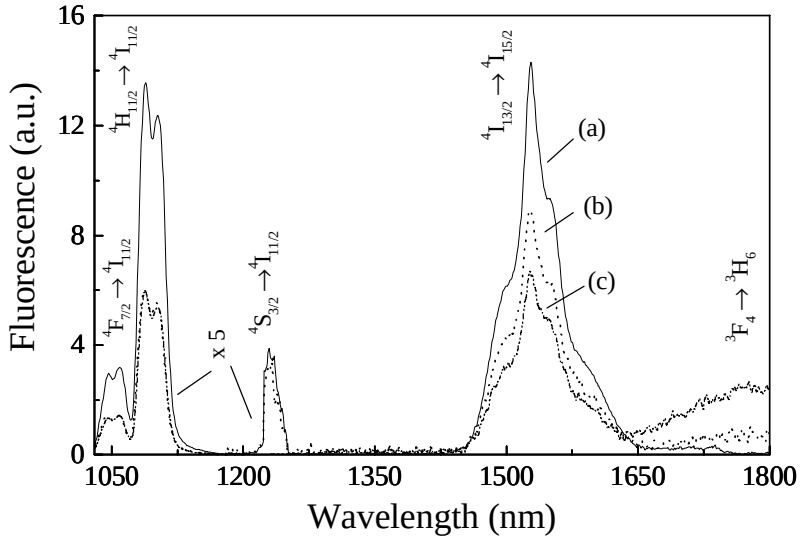

Figure 3- Fluorescence spectra between (1050-1800) nm for (a) $S_{1.2,0}$; (b) $S_{1.2,0.4}$ and (c) $S_{1.2,1.6}$ at λ_e= 488 nm ($P_e \approx$ 10 mW).

4.2. Thermal lens measurements

Figure 4 shows typical TL transient signals for the Er^{3+} doped, Tm^{3+} doped and Er^{3+}/Tm^{3+} co-doped tellurite glasses. The curve behaviors of the Fig. 4 indicate that ds/dT is positive, i.e., the created TL focalize the probe beam in the far field. Fitting the experimental data of Fig. 4 by Eq. (1), θ and τ_c were obtained. From $D = w_e^2/4\tau_c$ and using the measured value $w_e = 2.6\times10^{-3}$ cm, the thermal diffusivity was determined. The pattern sample, whose thermal properties are well known, has been used to test the calibration of our optical system.

The medium value of D obtained for Er^{3+}/Tm^{3+} co-doped tellurite samples in function of thulium concentration, at λ_e= 488 nm and 785 nm, is D = (3.1 ± 0.2)×10^{-3} cm^2/s. This result of D is similar to the values obtained for us to Er^{3+} doped tellurite glass (D = (3.1 ± 0.2)×10^{-3} cm^2/s), Tm^{3+} doped tellurite glass (D = (3.2 ± 0.4) × 10^{-3} cm^2/s), and for others glasses obtained in literature, as: ZBLAN, YABC, PGIZCa, ISZn and InSBZnGdN [11,19].

In order to calculate φ, we supposed a negligible fluorescence to the tellurite glass without earth rare ion ($S_{0,0}$), where all absorbed energy is converted into heat by the sample, i.e., $\varphi_{S0,0}$ = 1 ($\eta_{S0,0}$ = 0). $\Theta_{S0,0}$ value was determined through transient thermal lens measurements. However, normalizing the thermal parameters of erbium (E) and thulium (T) co-doped tellurite samples ($S_{E,T}$), i.e. $\Theta_{SE,T}$ by $\Theta_{S0,0}$ value for the undoped tellurite matrix, we obtain:

$$\varphi = 1 - \eta\left(\frac{\lambda_e}{<\lambda_{em}>}\right) = \frac{\Theta_{s_{E,T}}}{\Theta_{s_{0,0}}} \tag{3}$$

where $\Theta_{SE,T} = \theta_{SE,T} / P_e \alpha L_{eff}$ and $\theta_{SE,T}$ is the amplitude of TL signal for Er^{3+}/Tm^{3+} co-doped tellurite glass. In this case, $\Theta_{SE,T}$ was changed by $\Theta_{S1.2,0}$, $\Theta_{S1.2,0.4}$, $\Theta_{S1.2,0.8}$, $\Theta_{S1.2,1.2}$ or $\Theta_{S1.2,1.6}$, that correspond the samples $S_{1.2,0}$, $S_{1.2,0.4}$, $S_{1.2,0.8}$, $S_{1.2,1.2}$ and $S_{1.2,1.6}$, respectively (Table I) . φ results obtained by TL method are presented in Fig. 5.

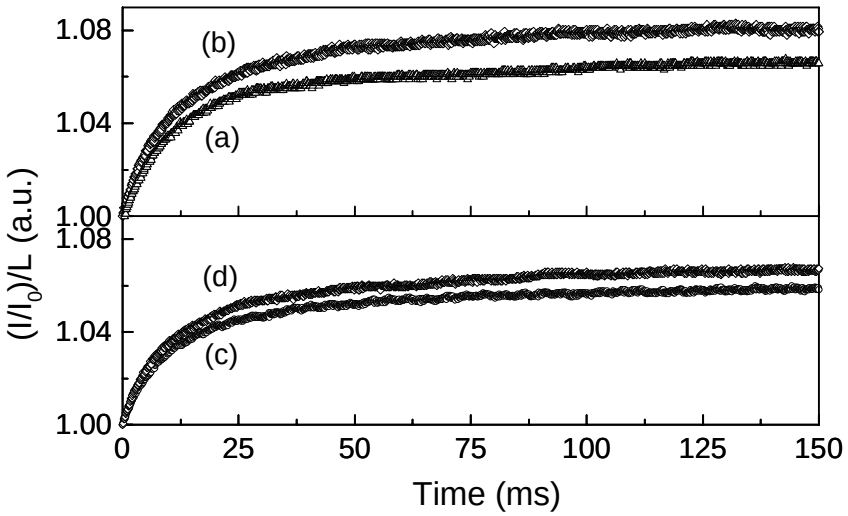

Figure 4- TL transient signal normalized by L versus time for Er^{3+}/Tm^{3+} co-doped tellurite glasses: (a) $S_{0,0}$, (b) Tm^{3+} (0.78x10 ^{20} ions/cm^3) doped tellurite glass, (c) $S_{1.2,0}$ and (d) $S_{1.2,0.4}$, respectively. The samples were excited with an Ar^+ laser at 488 nm with P_e = 20 mW and probe laser beam at λ_p= 632.8 nm.

4.3. Judd-Ofelt (JO) results

The quantum efficiencies for Er^{3+}/Tm^{3+} co-doped tellurite glasses were determined through the Judd-Ofelt (JO) model [5,20,21]. The radiative lifetime value (τ_{rad}) was calculated as being 5.6 ms and using the experimental measurements of lifetime τ_{exp} at 980 nm, the fluorescence quantum efficiency was estimated by $\eta_{JO=} \tau_{exp}/\tau_{rad}$ for $^4I_{13/2} \rightarrow {}^4I_{15/2}$ (Table I). Then using the Eq. (3) considering λ_e= 980 nm, we calculated φ_{JO} values. The results of φ_{JO} in function of thulium concentration for Er^{3+}/Tm^{3+} co-doped glasses are presented in the Fig. 5. There are good agreement between both TL and JO methods for φ. For Er^{3+} -doped tellurite glass, the difference of the results should be due to resonance at 980 nm with $^4I_{15/2} \rightarrow {}^4I_{11/2}$ transition and consequently a decreasing of cross-relaxation process and lose of energy by phonons.

Finally, Table I shows, by JO theory, an increase of radiative quantum efficiency ~ 6 for the $S_{1.2,0}$ glass with relation to the $S_{1.2,1.6}$ sample. Then, the presence of thulium ($1.6x10^{20}$ ions/cm^{-3}) inside of the tellurite matrix co-doped with Er^{3+}/Tm^{3+}, corroborate with the lost of energy by phonons, producing an increase of the fraction of energy turned into heat, and consequently the quantum efficiency approaches zero.

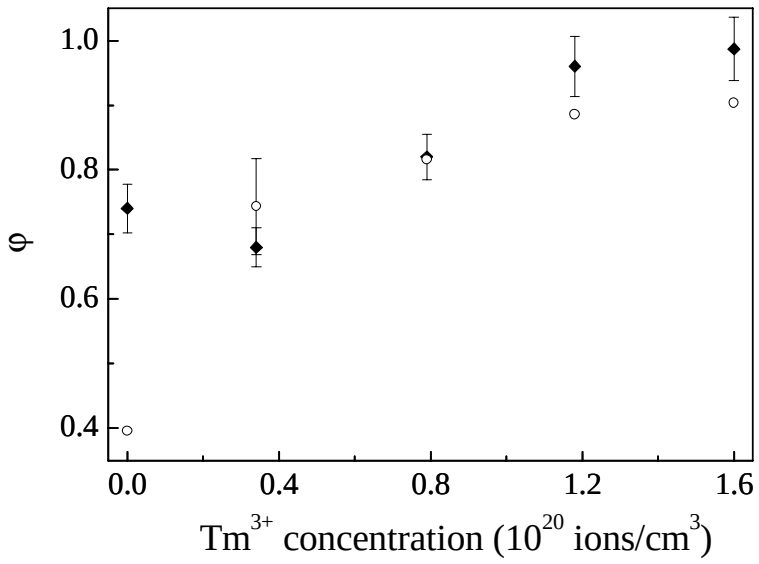

Figure 5- φ versus thulium concentration for Er^{3+}/Tm^{3+} co-doped tellurite glasses, obtained by TL and JO (open circle) methods.

5. CONCLUSIONS

Spectroscopic characterizations of the Er^{3+}/Tm^{3+} co-doped tellurite glasses were performed using Thermal Lens (TL) and fluorescence techniques at visible wavelength (488 and 785 nm). The behavior of the nonradiative quantum efficiency (φ) was determined in $70TeO_2$-$19WO_3$-$7Na_2O$-$4Nb_2O_5$ (% mol) tellurite matrix. The measurements were made in function of the TmO_3 concentration in Er^{3+}/Tm^{3+} co-doped tellurite glasses and φ values are in agreement with the results obtained by Judd-Ofelt theory.

6. ACKNOWLEGMENTS

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