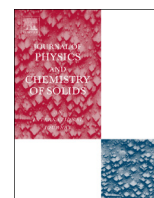




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journal homepage: [www.elsevier.com/locate/jpcs](http://www.elsevier.com/locate/jpcs)Spectroscopic properties of Nd<sup>3+</sup>-doped tungsten–tellurite glassesF.B. Costa<sup>a</sup>, K. Yukimitu<sup>a</sup>, L.A.O. Nunes<sup>b</sup>, M.S. Figueiredo<sup>c</sup>, L.H.C. Andrade<sup>d</sup>, S.M. Lima<sup>d</sup>, J.C.S. Moraes<sup>a,\*</sup><sup>a</sup> Faculdade de Engenharia, UNESP – Univ Estadual Paulista, Campus de Ilha Solteira, SP, Brazil<sup>b</sup> Laboratório de Laser e Aplicações, IFSC, São Carlos, SP, Brazil<sup>c</sup> UFGD, Dourados, MS, Brazil<sup>d</sup> Grupo de Espectroscopia Óptica e Fototérmica, UEMS, Dourados, MS, Brazil

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## ABSTRACT

In this work, we investigate the spectroscopy properties of neodymium doped tungsten–tellurite glasses prepared in ambient and O<sub>2</sub>-rich atmospheres. A conversion of TeO<sub>4</sub> to TeO<sub>3</sub> units was caused by the addition of Nd<sup>3+</sup> into the glass, which was confirmed by absorption spectra and by Judd–Ofelt parameter behavior. The relaxation of the <sup>4</sup>F<sub>3/2</sub> level is dominated by radiative decay and cross-relaxation between Nd<sup>3+</sup> and Nd<sup>3+</sup> ions. The energy transfer from Nd<sup>3+</sup> to the hydroxyl group is negligible when compared to the cross-relaxation. The luminescence quantum efficiency values of the <sup>4</sup>F<sub>3/2</sub> level decreases as the Nd<sup>3+</sup> concentration increases, independently if determined by the Judd–Ofelt method or by the thermal lens technique. The observed reduction in the IR absorption associated to OH groups was not effective to improve the luminescence quantum efficiency.

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## 1. Introduction

Several rare earth (RE) ions have been studied for laser application. Among them, the Nd<sup>3+</sup> ion is one of the most investigated, mainly due its large cross-sections of optical absorption near 800 nm (<sup>4</sup>I<sub>9/2</sub> → <sup>2</sup>H<sub>9/2</sub> + <sup>4</sup>F<sub>5/2</sub>), which turn easiest the excitation by diode laser, and the high quantum efficiency of the <sup>4</sup>F<sub>3/2</sub> → <sup>4</sup>I<sub>11/2</sub> emission near 1060 nm. Moreover, as the <sup>4</sup>I<sub>11/2</sub> energy level is ~2000 cm<sup>-1</sup> above the ground state, this turn the system as four level one, which it is well known to favor the population inversion avoiding the re-absorption effect. Lasing has been obtained in different bulk glasses doped with Nd<sup>3+</sup> ions [1–7], but the tellurite-based glasses have attracted special interest since Wang et al. were able to fabricate active tellurite glass fiber laser [1]. Tellurite glasses combine the attributes of reasonable thermal stability, high refractive index, high solubility of RE ions (some tellurite glasses may dissolve up to 25% of RE oxides [8]), larger absorption and emission cross-sections, and low phonon energy compared to the silicate, phosphate, and borate glasses [8,9], with a wide transmission window in the infrared region [9].

In particular, the RE doped tungsten–tellurite glasses have been shown to have excellent properties for applications such as planar

waveguides [10,11], amplifiers [12], lasers [4,5], single mode fiber lasers [13,14], and second harmonic generation devices [15]. However, tungsten–tellurite glasses have larger amounts of water when melted in air. The water is incorporated into the glass as hydroxyl (OH) groups, which have a strong and broad vibrational absorption band of between 2000 and 3600 cm<sup>-1</sup>, promoting the energy loss. The absorption losses due to OH groups are disadvantageous because they decrease the electronic population of the <sup>4</sup>F<sub>3/2</sub> excited level. This decreases luminescence quantum efficiency ( $\eta$ ), hindering the practical use of these glasses [16–18]. Zhang and Hu [19] studied the influence of the OH<sup>-</sup> content on IR emission of Nd<sup>3+</sup>, Yb<sup>3+</sup>, and Er<sup>3+</sup>-doped tetraphosphate glasses. They observed that OH<sup>-</sup> has a large effect on the IR emission of these RE ions and that the IR luminescence decay rate increases linearly with OH<sup>-</sup> concentration. Wang et al. [17] observed that, by reducing the OH<sup>-</sup> content in Yb<sup>3+</sup>-doped tellurite glasses, the lifetime luminescence increased from 0.7 to 1.22 ms, indicating an improvement of the optical gain.

In this paper, we investigate the behavior of the spectroscopic properties of the Nd<sup>3+</sup>-doped tungsten–tellurite glasses in function of the neodymium concentration with samples prepared in ambient and oxygen-rich atmospheres. Luminescence quantum efficiency was determined by applying the thermal lens (TL) technique in the samples, and the obtained results were confronted with those determined by the relationship between experimental luminescence lifetime and radiative lifetime calculated

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by the Judd–Ofelt (JO) theory.

## 2. Experimental

Two sets of tungsten–tellurite glass samples with nominal composition  $(100-x)(0.8\text{TeO}_2+0.2\text{WO}_3)+x\text{Nd}_2\text{O}_3$ , where  $x=0, 0.05, 0.5, 1, 2$ , and  $4$  mol%, were prepared by conventional melt-quenching method in ambient (Amb) or  $\text{O}_2$ -rich ( $\text{O}_2$ ) atmospheres. Table 1 shows the nominal composition (mol%) of the glasses. For the set prepared in the Amb atmosphere, grade reagents of the Sigma-Aldrich (with  $>99\%$  or higher purity) were weighed, mixed into an agate mortar, and melted in a platinum crucible at  $880^\circ\text{C}$  for 30 min. The melt was poured into a stainless-steel mold pre-heated near the glass transition temperature ( $T_g \sim 350^\circ\text{C}$ ). For the set prepared in an  $\text{O}_2$  atmosphere, the furnace was placed inside a sealed chamber, where a vacuum was created. This was followed by an injection of  $\text{O}_2$  (until the inner pressure reached 1 atm), and the same procedures were carried out. After their contents were poured, the glasses were returned to the other furnace for annealing in order to reduce mechanical stress. The annealing occurred for 2 h at  $T_g$  temperature, and then the sample was slowly cooled to room temperature. Finally, the produced glasses were cut and polished, reaching thicknesses of between 0.71 and 0.95 mm.

All of the samples exhibited good optical quality, without any scattering point or bubble, and the glassy state in these samples was confirmed by X-ray diffraction (XRD) analysis using  $\text{Cu K}\alpha$  radiation. The densities (Table 1) of the samples were determined by Archimedes' method, using distilled water as the immersion liquid.

Fourier transform infrared (FTIR) spectroscopy was performed using a Nicolet Nexus 670 FTIR spectrometer. The absorption spectra of the bulk samples were recorded in the range of  $2000\text{--}4000\text{ cm}^{-1}$  using 64 scans, a resolution of  $4\text{ cm}^{-1}$ , and a  $\text{N}_2$  purge. Raman measurements were carried out by exciting the samples under  $514.5\text{ nm}$  with an Ar+ laser (Innova 308C model, Coherent). Confocal lenses with 4 mm of focal length were used to focus the laser beam into the samples, and to detect the Raman signal. The scattering light was filtered by an edge filter and it was focused in an optical fiber coupled in a monochromator (iHR 320 model, Horiba Jobin Yvon) with CCD (Sygnature Hamamatsu S3903-1024Q PDA) for detection. The ground state absorption spectra of the glasses were obtained by using a Perkin Elmer Lambda 900 UV/VIS/NIR spectrophotometer in the range of  $400\text{--}925\text{ nm}$ .

The luminescence  ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_j$  ( $J=13/2, 11/2$  and  $9/2$ ) was measured by excitation at  $514.5\text{ nm}$  with an argon laser and corrected by  $\text{Nd}^{3+}$  nominal concentration values to ensure that all samples absorbed the same amount of photons. The luminescence lifetime measurements of the  ${}^4\text{F}_{3/2}$  level were obtained using  $808\text{ nm}$  wavelength radiation generated by an optical parametric oscillator (OPO) pumped by a 5 ns pulsed Nd:YAG laser ( $355\text{ nm}$ , 10 Hz).

The TL technique was used to measure the fraction of the

absorbed energy that was converted into heat by the samples. This result could be used to calculate the luminescence quantum efficiency. The TL setup was a two beam mode-mismatched configuration that used a Ti:Sapphire laser tuned at  $808\text{ nm}$  as the excitation source and a HeNe laser at  $632.8\text{ nm}$  to probe the TL effect. The experimental curves were fitted using the theoretical model proposed by Shen et al. [20]. The experimental geometrical parameters were  $m=8.4$  and  $V=1.8$ . Further details of the experimental arrangement can be found in the reference [21].

## 3. Results and discussion

Fig. 1 shows a comparison between spectra of the TW-1Nd glasses prepared in Amb and  $\text{O}_2$  atmospheres. The amplitude of the absorption bands centered at  $3160$  and  $\sim 2200\text{ cm}^{-1}$  were reduced on the average of 48% and 44%, respectively, when  $\text{O}_2$  atmosphere was used to prepare the samples. These bands have been ascribed to the stretching mode of the weakly and strongly hydrogen-bonded  $\text{Te-OH}\dots\text{O-Te}$  groups, respectively [22,23]. This result indicates that  $\text{O}_2$  atmosphere was efficient to reduce the OH ions content in the bulk.

Fig. 2 shows the absorption spectra of the  $\text{Nd}^{3+}$ -doped TW glasses prepared in the  $\text{O}_2$  atmosphere in the spectral range of  $400\text{--}925\text{ nm}$ . Each spectrum presents eight absorption bands located at  $514, 527, 585, 628, 682, 748, 808,$  and  $874\text{ nm}$ . The addition of  $\text{Nd}^{3+}$  caused an increase in the intensity of the absorption peaks and a blue-shift of the absorption edge. The inset of Fig. 2 shows the correlation between peak area ( $804\text{ nm}$ ) and  $\text{Nd}^{3+}$  concentration for glasses prepared in the Amb and  $\text{O}_2$  atmospheres, indicating that the incorporation of neodymium in the glass was effective. The same behavior was observed in the area of the other absorption peaks. The spectra of the samples prepared in the Amb and  $\text{O}_2$  atmospheres were similar in this spectral region.

The blue-shift of the absorption edge has been observed in previous studies [24–26], and it has been related to the changes in the glass structural units. Nazabal et al. [25] studied the  $\text{TeO}_2\text{-ZnO-ZnF}_2$  glass doped with erbium and attributed to the blue-shift the structural conversion from  $\text{TeO}_4$  (tbp=trigonal bipyramid) towards  $\text{TeO}_{3+1}$  and  $\text{TeO}_3$  (tp=trigonal pyramid) units. From Raman spectra of the samples, it was observed that the introduction of  $\text{Nd}^{3+}$  ions in the glass led to a similar variation in the glass network, for the two atmospheres in which the glasses were prepared. Fig. 3a shows the Raman spectra of the TW and TW-4Nd, both prepared in  $\text{O}_2$  atmosphere, in the  $1100\text{--}500\text{ cm}^{-1}$  range. The spectra shown a sharp scattering band located at  $930\text{ cm}^{-1}$  and a broad band around  $700\text{ cm}^{-1}$ . The first band correspond to the stretching vibrations of  $\text{W-O}^-$  and/or  $\text{W=O}$  in the  $\text{WO}_4$  and  $\text{WO}_6$  units [27,28], respectively. The observed decrease in the absorption band at  $930\text{ cm}^{-1}$  can be due to W ion coordination states changes from sixfold [ $\text{WO}_6$ ] to fourfold coordination [ $\text{WO}_4$ ] [28]. However, a more detailed study will be needed to confirm this change. The scattering extending from  $550$  to  $870\text{ cm}^{-1}$  is mainly due to the overlap of two strong bands:

**Table 1**

Nominal composition (mol%), density ( $\rho$ ), and molar volume ( $V_m$ ) of the  $\text{Nd}^{3+}$ -doped TW glasses in Amb and  $\text{O}_2$  atmospheres.

Sample	$\text{TeO}_2$ (mol%)	$\text{WO}_3$ (mol%)	$\text{Nd}_2\text{O}_3$ (mol%)	$\rho$ (Amb)* (g/cm <sup>3</sup> )	$V_m$ (Amb) (cm <sup>3</sup> /mol)	$\rho$ ( $\text{O}_2$ )* (g/cm <sup>3</sup> )	$V_m$ ( $\text{O}_2$ ) (cm <sup>3</sup> /mol)
TW	80	20	0	5.89	29.55	5.88	29.60
TW-0.05Nd	79.96	19.99	0.05	5.89	29.56	5.88	29.61
TW-0.5Nd	79.6	19.9	0.5	5.89	29.69	5.89	29.69
TW-1Nd	79.2	19.8	1.0	5.89	29.83	5.89	29.83
TW-2Nd	78.4	19.6	2.0	5.93	29.90	5.92	29.95
TW-4Nd	76.8	19.2	4.0	5.94	30.39	5.93	30.45

\* The density error is 0.02.

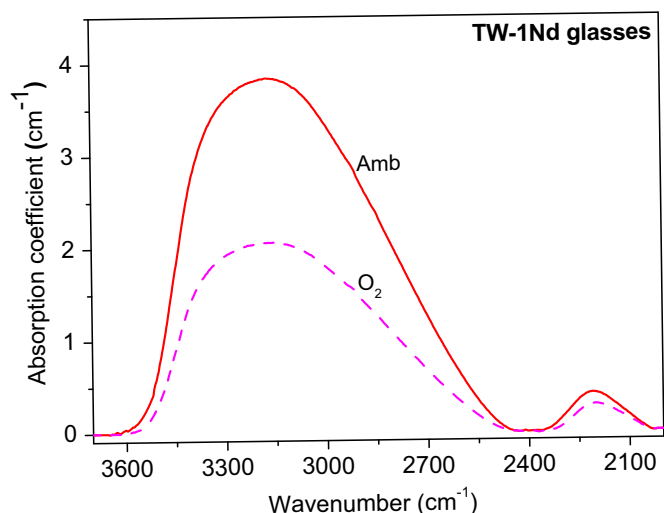


Fig. 1. IR absorption spectra of the TW-1Nd glasses prepared in Amb and  $O_2$  atmospheres.

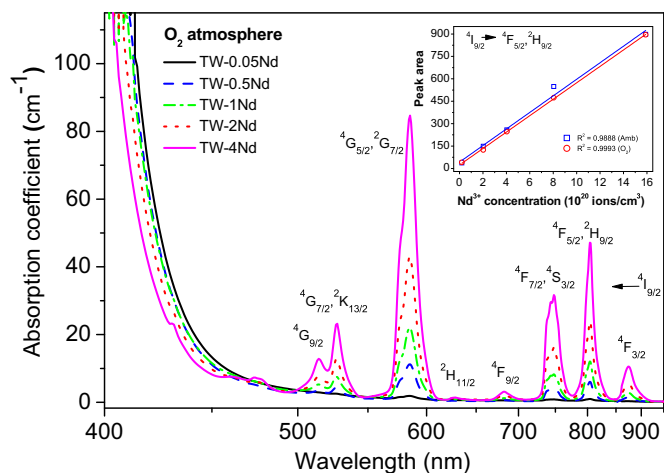


Fig. 2. VIS-NIR absorption spectra of the  $Nd^{3+}$ -doped TW samples prepared in an  $O_2$  atmosphere. The inset shows the linear dependence of the  ${}^4F_{5/2}$ ,  ${}^2H_{9/2}$  absorption area with  $Nd^{3+}$  ions concentration. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

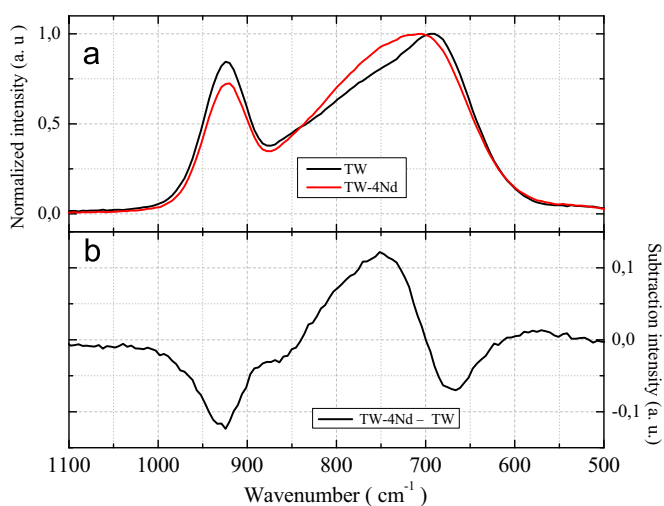


Fig. 3. (a) Raman absorption spectra of TW and TW-4Nd samples prepared in an  $O_2$  atmosphere and (b) the difference between the two spectra ( $I_{TW-4Nd} - I_{TW}$ ).

stretching vibrations of  $TeO_4$  units ( $\sim 670\text{ cm}^{-1}$ ) and stretching vibrations of  $TeO_{3+1}$  or  $TeO_3$  units ( $\sim 750\text{ cm}^{-1}$ ) [24,29,30]. In  $80TeO_2-20WO_3$  glasses these two bands are not well defined as observed in other TW composition [29], unlike observed in the Raman spectra of the  $Nd^{3+}$ -doped  $TeO_2-ZnO-Nb_2O_5$  (TZN) glass [24]. The addition of neodymium in TZN glass caused an inversion in the intensities of the peaks  $670$  and  $750\text{ cm}^{-1}$  and they are almost the same for TZN with 5 mol% of neodymium. In order to evidence the difference among our samples, the Raman spectrum for TW-4Nd was subtracted from TW spectrum (showed in Fig. 3b). The intensity at  $650\text{ cm}^{-1}$ , which is associated with Te-O bonds of  $TeO_4$  units, decreases compared with that associated with Te-O bonds of  $TeO_{3+1,3}$  units located at  $750\text{ cm}^{-1}$ . So, the absorption edge shift to low wavelength observed in our glasses occurred due to structural changes (from ttp to tp).

The Nd absorption bands (centered at  $\bar{\lambda}_{abs}$ ) in Fig. 2 were integrated to determine the area for JO calculation. In this model, parameters proportional to the oscillator strengths are measured ( $S_m$ ) and calculated ( $S_c$ ) for each absorption band (listed in Table. 2) [31]. In order to determine the  $\Omega_2$ ,  $\Omega_4$  and  $\Omega_6$  parameters, once  $Nd^{3+}$  transitions are assumed to be pure electric dipole,  $S_m$  and  $S_c$  are equal. All the obtained values are also exhibit in Table. 2. The  $\Omega$ 's obtained values are in good agreement to those reported in Ref. [4]. Furthermore, it was not observed any difference in the  $\Omega$ 's values among the group of studied samples (Amb and  $O_2$ ). As usually done, the  $\Omega$ 's parameters can be applied to calculate the line strengths corresponding to the transitions from  ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ ,  ${}^4I_{11/2}$ ,  ${}^4I_{13/2}$  and  ${}^4I_{15/2}$  of the  $Nd^{3+}$  ion, and with this, the radiative transition rates between two given levels  $A_{J'J''}$  were calculated, and consequently the radiative lifetime ( $\tau_{rad} \sim 154\text{ }\mu\text{s}$ ).

The emission spectra of the  $Nd^{3+}$ -doped glasses prepared in an  $O_2$  atmosphere are presented in Fig. 4. The  $514.5\text{ nm}$  radiation excites the  $Nd^{3+}$  ions to  ${}^4G_{9/2}$  level, and after fast non-radiative decays, these excited ions reach the  ${}^4F_{3/2}$  metastable state. The observed emission transitions occur from  ${}^4F_{3/2}$  emitting level to the following:  ${}^4I_{9/2}$  ( $\sim 907\text{ nm}$ ),  ${}^9I_{11/2}$  ( $1065\text{ nm}$ ), and  ${}^9I_{13/2}$  ( $1337\text{ nm}$ ). The inset of Fig. 4 shows that the intensity of emission transition at  $1065\text{ nm}$  decreases as the  $Nd^{3+}$  concentration is increased. This decrease indicates that the total decay rate ( $W$ ) increased due to the non-radiative decay rate ( $W_{NR}$ ) meaning that the fraction of absorbed energy converted into heat ( $\varphi$ ) increased.

Fig. 5 shows the fluorescence decay curves for  ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$  transition of the  $Nd^{3+}$ -doped TW samples prepared under  $O_2$  atmosphere, and similar curves were also obtained for the samples prepared in Amb atmosphere. The measured lifetime ( $\tau_{exp}$ ) of  ${}^4F_{3/2}$  level for each doped sample was determined fitting the experimental fluorescence decay curve with a single exponential dependence (Table. 3). The total decay rate for  ${}^4F_{3/2}$  ( $Nd^{3+}$ ) level was evaluated by the reciprocal of the measured lifetime, which is given by  $W = \tau_{exp}^{-1} = W_R + W_{NR}$ , where  $W_R$  is the sum of all radiative decay rates originating from the  ${}^4F_{3/2}$  level. The obtained values are also presented in Table. 3.  $W_R = 1/\tau_{rad}$  was obtained by the JO $\Omega$ 's parameters and, as a consequence, the  $W_{NR}$  can be evaluated as follows:

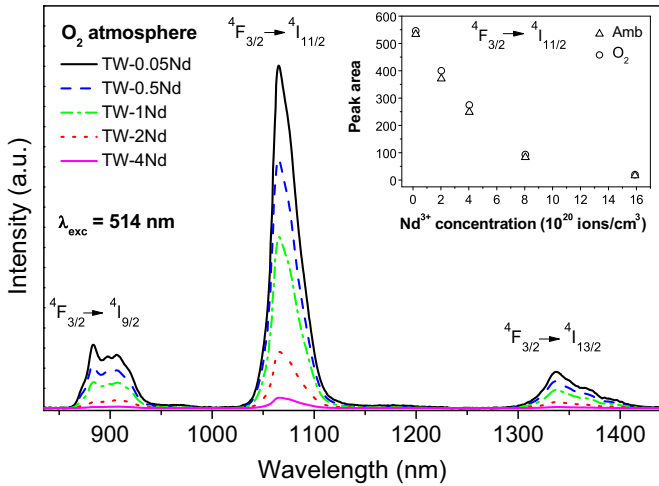
$$W_{NR} = \frac{1}{\tau_{exp}} - \frac{1}{\tau_{rad}} \quad (1)$$

For the lowest  $Nd^{3+}$  concentration sample, the measured and the calculated radiative lifetime values are similar, for both atmosphere, indicating a very small energy loss by nonradiative process. They also are in agreement to those reported in other studies using  $Nd^{3+}$ -doped tungsten-tellurite glasses [4]. As can be seen,  $W_{NR}$  increases greatly with the increase of the  $Nd^{3+}$  concentration, which is the sum of the following non-radiative processes: cross-relaxation between  $Nd^{3+}$  ions ( $W_{CR}$ ) ( ${}^4F_{3/2} \rightarrow {}^4I_{15/2}$ :

**Table 2**

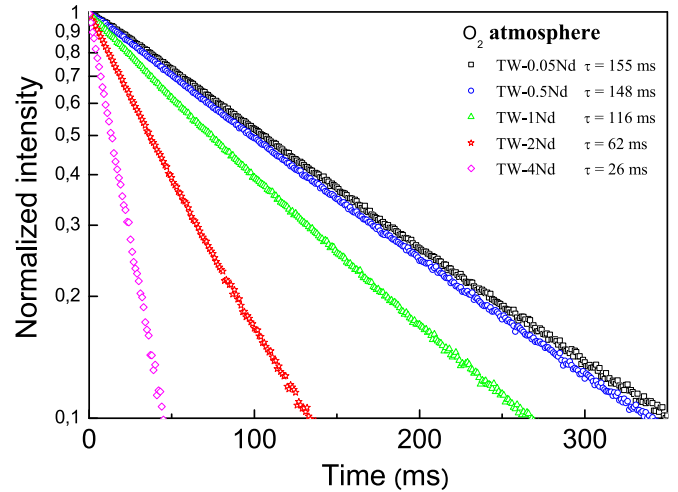
Absorption and emission parameters and JO intensity parameters of TW-1Nd glasses prepared in O<sub>2</sub> atmosphere. The Ω's values obtained for the other samples are similar, including those prepared in Amb atmosphere.

$\lambda_{abs}$ (nm)	$S_m (\times 10^{-20} \text{ cm}^2)$	$S_c (\times 10^{-20} \text{ cm}^2)$	$ S_m - S_c  (\times 10^{-20} \text{ cm}^2)$
526	1.6	1.5	0.1
585	6.56	6.57	0.01
682	0.16	0.17	0.01
748	2.39	2.46	0.07
804	2.73	2.65	0.08
874	0.8	1.0	0.2
<hr/>			
$\Omega_2 (\times 10^{-20} \text{ cm}^2)$	$\Omega_4 (\times 10^{-20} \text{ cm}^2)$	$\Omega_6 (\times 10^{-20} \text{ cm}^2)$	
4.6	3.3	3.5	
RMS = $4.6 \times 10^{-21}$			
<hr/>			
Transition from $^4F_{3/2}$ to	$\bar{\lambda}$ (nm)	$A_{JF}$ (s <sup>-1</sup> )	$\tau_{rad}$ (μs)
$^4I_{15/2}$	1900	30.3	154 ± 4
$^4I_{13/2}$	1337	669.9	
$^4I_{11/2}$	1065	3138.4	
$^4I_{9/2}$	907	2695.3	



**Fig. 4.** Emission spectra of Nd<sup>3+</sup>-doped TW glasses in the O<sub>2</sub> atmosphere. The inset shows the intensity behavior of the  $^4F_{3/2} \rightarrow ^4I_{11/2}$  transition.

$^4I_{9/2} \rightarrow ^4I_{15/2}$ ), energy transfer rate from Nd<sup>3+</sup> to OH<sup>-</sup> ions ( $W_{OH}$ ), and multiphonon relaxation rate ( $W_{MP}$ ). The latter rate depends on the temperature, the energy gap between the  $^4F_{3/2}$  and  $^4I_{15/2}$  levels, and the phonon energy of the host glass [32,33]. In a room temperature environment,  $W_{MP}$  is very low ( $\sim 2 \times 10^{-3} \text{ s}^{-1}$ ) for all present Nd<sup>3+</sup>-doped tellurite glasses independent of the environmental conditions in which they have been prepared. Therefore, it can be disregarded. Furthermore,  $W_{MP}$  is the same for all samples because the maximum phonon energy is practically independent (around 940 cm<sup>-1</sup>) with the increase of Nd<sup>3+</sup> concentration.



**Fig. 5.** Luminescence decay from  $^4F_{3/2}$  level of the Nd<sup>3+</sup>-doped TW glasses prepared under O<sub>2</sub> atmosphere.

$W_{OH}$  is proportional to the donor (Nd<sup>3+</sup>) and acceptor (OH<sup>-</sup>) concentrations and the absorption coefficient of the OH<sup>-</sup> free ( $\alpha_{OH}$ ), which can be defined as follows [19,33,34]:

$$W_{OH} = K_{Nd-OH} N_{Nd} \alpha_{OH} \quad (2)$$

where  $K_{Nd-OH}$  is a constant determined by the force of interactions between Nd<sup>3+</sup> and OH<sup>-</sup> ions and is independent of the concentration of these ions. The value of this constant for interaction between Er<sup>3+</sup> and OH<sup>-</sup> ions is practically the same in tetraphosphate ( $15 \times 10^{-19} \text{ cm}^4 \text{ s}^{-1}$ ) [19] and tellurite ( $14 \times 10^{-19} \text{ cm}^4 \text{ s}^{-1}$ ) [33] glasses. Thus, taking the  $K_{Nd-OH}$  value equal to that

**Table 3**  
Experimental lifetime ( $\tau_{exp}$ ), reciprocal of the experimental lifetimes ( $W$ ), non-radiative rate ( $W_{NR}$ ), energy transfer rate between  $Nd^{3+}$  and  $OH^-$  ions ( $W_{OH}$ ), and cross-relaxation rate ( $W_{CR}$ ) for  $Nd^{3+}$ -doped TW glasses prepared in the Amb and  $O_2$  atmospheres.

Sample	$\tau_{exp}$ ( $\mu s$ )		$W=1/\tau_{exp}$ ( $10^3 s^{-1}$ )		$W_{NR}=\tau_{exp}^{-1}\tau_{rad}^{-1}$ ( $10^3 s^{-1}$ )		$W_{OH}$ ( $10^3 s^{-1}$ )		$W_{CR}=W_{NR}-W_{HO}$ ( $10^3 s^{-1}$ )	
	Amb	$O_2$	Amb	$O_2$	Amb	$O_2$	Amb	$O_2$	Amb	$O_2$
TW-0.05Nd	152 ± 1	155 ± 1	6.58 ± 0.04	6.45 ± 0.04	–	–	–	–	–	–
TW-0.5Nd	141 ± 1	148 ± 1	7.09 ± 0.05	6.76 ± 0.05	0.6 ± 0.2	0.3 ± 0.2	0.6 ± 0.1	0.4 ± 0.1	–	–
TW-1Nd	115 ± 1	116 ± 1	8.70 ± 0.08	8.62 ± 0.08	2.2 ± 0.3	2.2 ± 0.3	1.0 ± 0.1	0.5 ± 0.1	1.2 ± 0.4	1.7 ± 0.4
TW-2Nd	58 ± 1	62 ± 1	17.2 ± 0.3	16.1 ± 0.3	10.7 ± 0.5	9.7 ± 0.5	1.6 ± 0.2	0.7 ± 0.1	9.1 ± 0.7	9.0 ± 0.6
TW-4Nd	22 ± 1	26 ± 1	45 ± 2	38 ± 1	39 ± 2	32 ± 1	2.9 ± 0.2	1.6 ± 0.2	36 ± 2	30 ± 1

obtained in tetraphosphate glasses ( $6.2 \times 10^{-19} cm^4 s^{-1}$ ), it was possible to estimate the value of  $W_{OH}$  for each sample and, consequently, the value of  $W_{CR}$ . Although  $\alpha_{OH}$  decreases with increasing  $Nd^{3+}$  concentration, the product of  $N_{Nd}$  and  $\alpha_{OH}$  increased and, consequently,  $W_{OH}$  is also increased. It is interesting to note that the  $W_{OH}$  values for the  $Nd^{3+}$ -doped samples prepared in  $O_2$  atmosphere are lower than the values for the samples prepared in Amb.

The subtracting among  $W_{NR}$  and  $W_{OH}$ ,  $W_{CR}$  was calculated and the values are also listed in Table 3. Unlike  $W_{OH}$ ,  $W_{CR}$  values increase greatly with the  $Nd^{3+}$  concentration mainly because of  $W_{NR}$  values ( $W_{OH}$  contributes to  $W_{CR}$  with less than 10%). Furthermore, for TW-4Nd sample prepared in  $O_2$  atmosphere the  $W_{CR}$  value is approximately 20% lower than those prepared in Amb. It was not possible to note difference among  $W_{NR}$  and  $W_{OH}$  for samples prepared with lowest  $Nd^{3+}$  concentration, indicating that both equally contribute to  $W_{CR}$ .

The findings discussed so far suggest that when  $Nd^{3+}$  ions were added in the sample, the luminescence quantum efficiency ( $\eta$ ) of the  ${}^4F_{3/2}$  level decreased (due to the noted increment in  $W_{NR}$ ). As a consequence, the fraction of energy absorbed by the sample and converted into heat ( $\phi$ ) should increase.  $\eta$  can be evaluated using the radiative and experimental lifetimes ( $\eta = \tau_{exp}/\tau_{rad}$ ). In the context of our work, this term will be referenced as luminescence quantum efficiency from JO ( $\eta_{JO}$ ). On the other hand, the TL technique allows us to evaluate  $\eta$  as well as  $\phi$ , which can be determined using this equation [20–21]:

$$\phi C = -\frac{\theta}{\alpha L_{eff} P_e} = \Theta \quad (3)$$

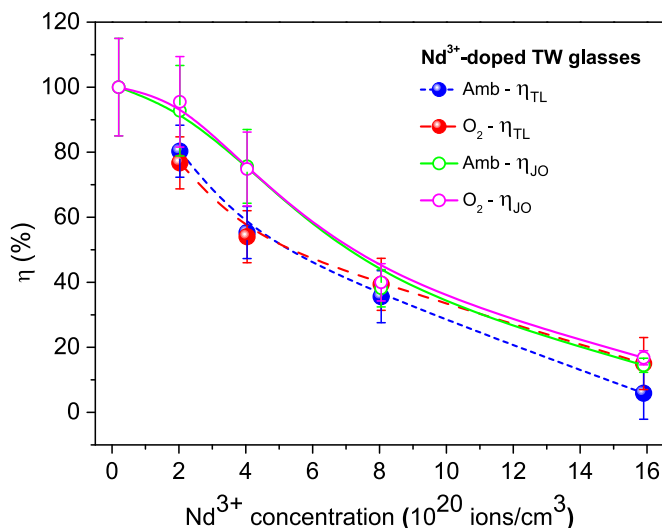
where  $\theta$  is the TL signal amplitude obtained by fitting the experimental curves,  $\alpha$  is the absorption coefficient,  $L_{eff} = (1 - e^{-\alpha L})/\alpha$  is the effective thickness of the sample,  $L$  is the thickness,  $P_e$  is the excitation power, and  $C = (ds/dT)/K\lambda_p$  is the intrinsic parameters for the matrix. In this parameter,  $K$  is the thermal conductivity,  $ds/dT$  is the temperature coefficient of the optical path length, and  $\lambda_p$  is the probe beam wavelength.

As the undoped samples present no fluorescence,  $\phi=1$  and in this case  $C$  is equal to  $\Theta$ , whose measured value ( $\Theta=37 W^{-1}$ ) is close to that obtained for TLT glasses ( $34 W^{-1}$ ) [35]. Therefore, the value of  $\phi$  for the doped samples was determined by comparing the data of doped samples ( $\Theta_d$ ) with those of the undoped ones ( $\Theta_{und}$ ) ( $\phi = \Theta_d/\Theta_{und}$ ), as is usually done in the  $\eta$  determination by TL technique [21]. When the  $Nd^{3+}$  concentration increased from 0.5 to 4 mol%, the fraction of absorption energy converted in heat increased from 0.39 to 0.95 and from 0.41 to 0.88, respectively, for samples prepared in Amb and  $O_2$  atmospheres.

Having the  $\phi$  values, it was possible to evaluate  $\eta$  using the relationship [21]:

$$\phi = 1 - \eta \frac{\langle \nu_{em} \rangle}{\nu_{ex}} \quad (4)$$

where  $\nu_{ex}$  and  $\langle \nu_{em} \rangle$  are the excitation and the average emission



**Fig. 6.** Luminescence quantum efficiency calculated by the Judd–Ofelt theory and measured by TL technique for the  $Nd^{3+}$ -doped TW glasses in the Amb and  $O_2$  atmospheres.

wavenumber, respectively. For our studied  $Nd^{3+}$ -doped samples,  $\langle \nu_{em} \rangle = 9381 cm^{-1}$  and for our experimental setup,  $\nu_{ex} = 12,318 cm^{-1}$ . Fig. 6 shows a comparison between luminescence quantum efficiencies obtained by the JO method ( $\eta_{JO}$ ) and by the TL technique ( $\eta_{TL}$ ) for both of the sample sets. The observed difference between the  $\eta$  values is within the margin of error of both of the methods used. The same behavior was observed in other works: Suzuki et al. [36] observed that the quantum efficiency of the  $Nd^{3+}$ -doped  $TeO_2-K_2O$  glass varied from 86% at 0.05 mol% of  $Nd_2O_3$  to 18% at 2 mol% and concluded that this decrease was due to concentration quenching. Jaba et al. [37] concluded that the decrease from 166  $\mu s$  at 0.2 mol% to 62  $\mu s$  at 62% was due solely to energy transfer between  $Nd^{3+}$  ions. Rajeswari et al. [38] concluded that the observed decrease in the fluorescence (from 93% to 33%) accompanied by an increase in the  $Nd_2O_3$  concentration was due to cross-relaxation among  $Nd^{3+}-Nd^{3+}$  ions. They found the multiphonon relaxation rate from  ${}^4F_{3/2}$  level to be negligible.

#### 4. Conclusion

TW glasses doped with various concentrations of  $Nd^{3+}$  ions were prepared in air and  $O_2$ -rich atmospheres in order to obtain glasses with better spectroscopic properties. Measurements of the optical absorption, luminescence, and lifetime were performed. From the TL data, it was possible to determine the heat absorbed by the glass samples and consequently, the luminescence quantum efficiency. We can conclude from this investigation that: (1) in each sample set, the increase of  $Nd^{3+}$  ions into the  $80TeO_2-20WO_3$

matrix caused structural changes ( $\text{TeO}_4 \rightarrow \text{TeO}_3$ ) causing a blue-shift of the absorption edge; (2) the cross-relaxation was the main loss mechanism in fluorescence for  $\text{Nd}^{3+}$  ions concentrations greater than 1%; (3) the quantum efficiencies evaluated by JO and TL are in agreement, and the small observed differences are within their margin of error; (4) the luminescence quantum efficiency for lowest concentration of  $\text{Nd}^{3+}$  is close to unity; and (5) the  $\text{OH}^-$  ions reduction into the  $\text{Nd}^{3+}$ -doped TW glass slightly increase the  ${}^4\text{F}_{3/2}$  level lifetime value, but the improvement in the luminescence quantum efficiency was not determined by TL measurements because it is within the experimental error. Important to mention that, although it was observed a reduction in  $W_{\text{OH}}$  from Amb to  $\text{O}_2$  synthesis procedure, all the calculated values for  $W_{\text{OH}}$  are lower than the  $W_{\text{NR}}$  values, mainly for higher  $\text{Nd}^{3+}$  concentration. This suggests that  $W_{\text{NR}}$  is dominant in heating the sample, so that some improvement in the optical quality sample due  $W_{\text{OH}}$  is difficult to be measured by TL technique.

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