Luminescent and thermo-optical properties of germanate glasses

A.Iñiguez O. , J.D. Tapia-Takaki, R.P Duarte Zamorano, J.A. Duarte-Moller, E. Álvarez R.

Abstract

The visible photoluminescence of Tb^{3+} - doped germanate glass of composition (in mol%) $40GeO_2$-$20Na_2O$-$40SiO_2$ has been investigated for two Tb^{3+} concentrations. By using steady-state and pulsed laser spectroscopy. Concentration effects on luminescence are observed for Tb^{3+} concentration higher than 0.9 mol%. The thermo-optical characteristics were measured at room temperature under resonant conditions on the Tb^{3} ions. The thermo-optical properties of the glasses showed a dependence on the concentration of terbium ions. The effects of TL were also analyzed in terms of a theoretical model for CW laser induced thermal lensing under a Gaussian-beam approximation. Tb^{3+} concentration quenching effects on the dependence of thermo-optical properties are discussed.

Introduction

In the past years, a great deal of research work has been carried out to identify new optical glasses, having potential applications in technology. These materials are very attractive due to they could be prepared in different shapes and sizes and can to accept Rare Earth (RE) ions without inducing any crystallization. It was found that germinate glasses have smaller maximum vibrational frequencies than those shown by silicate, phosphate and borate glasses [1–5]. The reduced phonon energy increases the quantum efficiency of luminescence from excited states of RE ions in these matrices and provides the possibility to developed more efficient medium for optical lasers and fiber optical amplifiers [6,7]. However the thermo-optics effects have been not yet evaluated on these materials. In this regards, the areas of non-linear optics and laser physics deal with effects that occur when a material is subjected to an intense light source which also produces heating, due to the absorption of pump radiation by the matrix [8]. Furthermore, the temperature varies over the cross-section of the element because of the finite thermal conductivity and the non-uniformity of the pump radiation. This change in the local temperature may cause a change in the refractive index known as thermal lensing (TL, and the effects of TL on the divergence of laser light). Due to the importance of this effect, TL has been studied in a large number of optical glasses [9–13]. Trivalent terbium is an attractive optical activator to study the thermo-optical effect which offers the possibility of simultaneous, blue, green and red emission under UV and blue excitation; in consequence, the radiationless relaxations transfers their energy to the network of the host.

The aim of this work is to characterize the properties of the visible luminescence from Tb^{3+} Germanate glasses of composition $40GeO_2$-$20Na_2O.40SiO_2$ with different Tb^{3+} concentrations (0.0, 0.3, and 0.9 mol%) and their effects on the thermo-optical properties.

Experimental

Heavy germanate glasses doped with different terbium concentration have been prepared by using the highly pure (99.999%) chemical of SiO_2, GeO_2, Na_2O and Tb_2O_3. The chemical composition of the Tb^{3+}-doped glass is $40GeO_2$–$20Na_2O$–$(40\text{-}x)SiO_2$

(where *x* = 0, 0.3, 0.9 mol%). These glasses were prepared by melting appropriated quantities of the reactants in platinum crucibles. The mixtures of the constituent reactants were melting at 1400 °C during 6 h in the ambient atmosphere. By employing the quenching technique, the glass melts are quenched by pouring the liquid onto a stainless steel plate and pressed with another steel plate in the production of glass windows. Finally, the mixtures were annealed at 550 °C by one hour in order to obtain an homogeneous distribution of luminescent terbium ions in the glasses matrices investigated. The obtained samples were cut and polished into 1 × 1 × 0.2 cm blocks. The three samples were analyzed by X-ray diffraction and with a He–Ne laser in order to investigate their homogeneity, presenting a good optical quality with a low scattering and non-observed devitrification.

The photoluminescence measurements were obtained using a Jobin Ybon FluoroLog-3 Fluorometer. Lifetime data were obtained using a PTI GL300 and GL302 Dye nitrogen pulsed laser. This produces a pulse of about 600 ps in duration and 0.1 nm bandwidth at 337.1 nm. The resulting transient fluorescence signal was analyzed with a Jobin-Yvon monochromator Triax550 and detected with HORIBA-Jobin Yvon i-Spectrum Two ICCD.

Thermal lensing experiments were performed following an experimental procedure published elsewhere [13]. The excitation source was an argon laser model Melles Griot 35 LAP 431-220. The 488 nm line of the laser allowed performing experiments in resonance with an electronic transition of the Tb^{3+} in our glasses. A 10 W He–Ne laser was used as a probe to detect changes in the refractive index, induced by the excitation beam. The weak probe beam at this wavelength did not cause a perturbation of the refractive index.

The excitation and the probe laser beams were co-linear and focused inside the sample following previous experiments reported in the literature [13,14]. The transmitted excitation beam, was filtered out and the intensity *I(t)*, at the center of the probe beam, was monitored by using a pinhole and a Hamamatsu R928 photomultiplier tube. The signal was processed by using an EGG/PAR boxcar average and readout on a strip-chart recorder.

Results and discussion

The absorption spectra were obtained at room temperature for both samples in 350–600 nm range. As an example, Fig. 1 shows the optical absorption spectrum of the sample doped with 0.9 mol% of Tb3+ in the visible range. The spectrum consists of several bands corresponding to transitions between the $^7F_6$ ground state and the excited multiplets belonging to the $4f^8$ configuration of Tb^{3+} ions. The more intense absorption bands corresponds from $^7F_6$ ground state to $^5D_2$ (358 nm), $^5D_3$ (378 nm) and $^5D_4$ (488 nm) excited states transitions, of the Tb^{3+} ions present in the sample. The emission spectra of Tb^{3+} ions in germinate glasses were recorded at room temperature for both doped samples (0.3 and 0.9 mol%). In Fig. 2, the luminescence spectra of Tb3+ ions under excitation at 366 nm from $^5D_3 \rightarrow F_j$ and $^5D_4 \rightarrow {}^7Fj$ levels are shown. We can see from this figure Tb^{3+} concentration dependence of $^5D_3$ and 5D4 fluorescence intensities. At lower Tb^{3+} content, blue emissions at wavelength below 485 nm are observed, which can be attributed to the transitions from $^5D_3 \rightarrow {}^7F_J$. With an increase of

Tb^{3+} content, the transition $^5D_3 \rightarrow 7F_J$ decreases gradually, while the transition $^5D_4 \rightarrow {}^7F_J$ increases [15–17]. This can be explained by the cross-relaxation process present in our samples. The crossrelaxation induced by the resonance between the excited states and ground states of two Tb3+ ions as depicted [15,18]:

$$Tb^{3+}(^5D_3)+Tb^{3+}(^7F_0)\rightarrow Tb^{3+}(^5D_4)+Tb^{3+}(^7F_6)$$

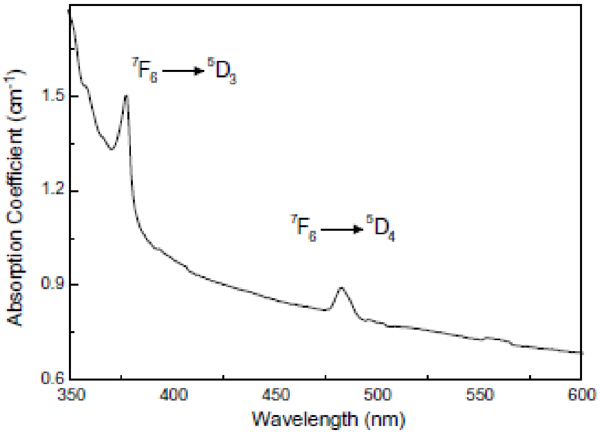

Fig. 1. Room temperature absorption spectrum of the SiO$_2$–GeO$_2$–Na$_2$O:Tb^{3+} (0.9 mol%) doped glass sample.

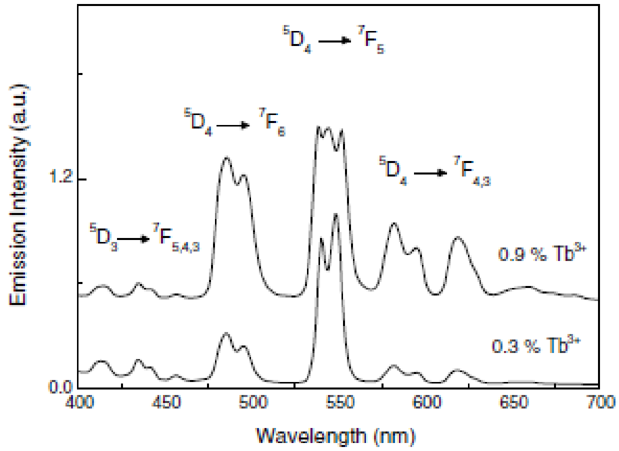

Fig. 2. The room temperature emission spectrum under continuous excitation at 378 nm.

The $^5D_3 \rightarrow {}^7F_J$ emissions of Tb^{3+} tends to vanish with higher concentration of Terbium in many oxides hosts [15, 18, 19]. Generally, it is difficult to observe the emission from $^5D_3 \rightarrow {}^7F_J$ transitions of Tb^{3+}, because the relaxation of $^5D_3 \rightarrow 5D_4$ is very fast [16,20]. However, at low concentration of Tb^{3+}, the distance between neighboring ions is large, resulting in an inefficient transfer process and enabling the $^5D_4 \rightarrow {}^7F_J$ transitions [16].

Decay-time measurements were performed at room temperature for $^5D_4$ levels by monitoring the $^5D_4 \rightarrow {}^7F_5$ transitions. Lifetime measurements revealed that decay scheme of $^5D_4$ florescence consists of pure exponential decay for both Tb^{3+} concentration glasses and lifetime constants showed small fluorescence quenching effects in the concentration range, τ varies from 3.12 ms (0.3% Tb^{3+}) to 2.81 ms (0.9% Tb^{3+}). The effects of the experimental findings described above on the thermo-optical properties of our glass sample will be discussed below.

For thermo-optical studies, the 488 nm line was used to excite resonantly the $^7F_6 \rightarrow {}^5D_4$ to Terbium ion absorption, and attenuated 10 mW red He–Ne laser was used as a probe-beam to detect changes in the refractive index, induced by the excitation beam. The temporal variation of the intensity of probe-beam pattern provides useful information for understanding the mechanism of the laser-induced refractive index changes. When the samples placed just before the beam-waist of the probe beam, we observed an expansion of the transmitted probe beam profile when the excitation beam was turned on. This indicates that the excitation beam causes that the sample acts like a positive lens [13,21].

Also, for the three glasses, was observed that if the excitation beam is turned off after the equilibrium point, the signal returns to its original level. This suggests the creation of a non-permanent change in the refractive index. The general characteristics and the response time observed in our experiments indicate that thermal lensing is the dominating mechanism of the laser induced refractive index changes at medium power levels (10^2–10^3 W cm^{-2}) [13]. Also, for our experimental configuration, the relative change in the intensity at the center of the transmitted probe beam can be determined from ray analysis by using transfer matrices under a Gaussian-beam approximation [13,21]. According to this model the ratio $I_0/I(t)$ is given by:

$$I_0/I(t) = 1 - \theta\{1 + \tau_c/2t\}^{-1} + \theta^2\{4(1 + \tau_c/2t)^2\}^{-1} \qquad (1)$$

where $\tau_c = \omega^2/4D$, ω is the excitation beam radius inside the sample and D is the thermal diffusivity in units of $cm^2\ s^{-1}$. The parameter θ is a dimensionless collection of variables and can be viewed as characterizing the strength of the thermal lens [13]. A computer fit to the experimental data using Eq. (1) was obtained by treating θ and τ_c as adjustable parameters. Fig. 3 displays the results of such fits. Good agreement is obtained between the theory and the experimental results; the values obtained for the adjustable parameters are depicted in Table 1.

The thermo-optical parameter shows a dependence on the doping Tb ions concentration, i.e. variation of θ and τ_c values result as a function of the Tb concentration. Since the excitation power is remained constant for the three samples, the variation of parameter θ can be associated to Tb concentration effects on the samples optical absorption coefficient at 488 nm. The conversion of electromagnetic energy to thermal energy is due to non radiative transitions. Thus, in the doped samples, under laser excitation at 488 nm, the fluorescence measurements show that the emission occurs mainly at 545 nm, from the $^5D_4 \rightarrow {}^7F_5$ transition. Non-radiative relaxation then occurs from $^7F_4$ state to $^7F_6$. In RE ground state glasses radiationless relaxation transitions have been showed to be multiphonon emission processes that generate high energy phonons [13,22].

Since the thermal diffusion in oxide glasses is typically slow, the phonons generated by the radiationless processes remain localized, creating a high level of vibrational energy around each rare earth ion. This can produce a high effective local temperature and high value for the strength of the TL effect. For the 0.3% and 0.9% Terbium doped glasses, the temperature increases through radiationless relaxation processes that transfer their energy to the network of the host. For non doped sample excitation, the observed thermal lensing is due to the absorption of light by the network of the glass host and the time evolution is governed by the thermal properties of the bulk sample.

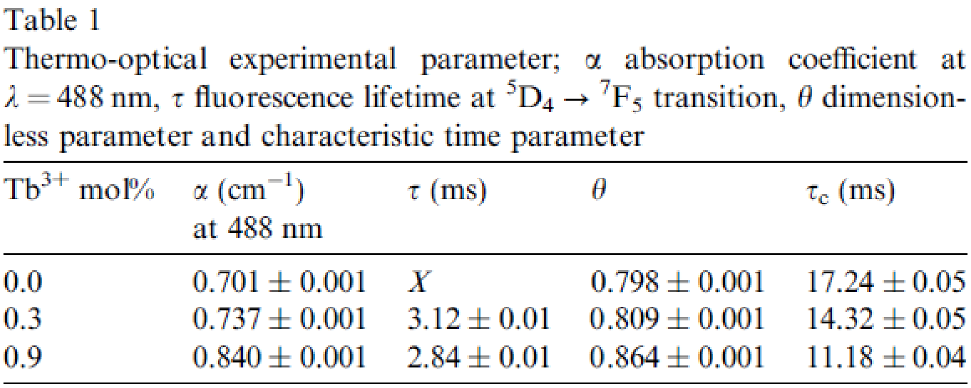

Table 1

Thermo-optical experimental parameter; α absorption coefficient at $\lambda = 488$ nm, τ fluorescence lifetime at $^5D_4 \rightarrow {}^7F_5$ transition, θ dimensionless parameter and characteristic time parameter

Tb^{3+} mol%	α (cm^{-1}) at 488 nm	τ (ms)	θ	τ_c (ms)
0.0	0.701 ± 0.001	X	0.798 ± 0.001	17.24 ± 0.05
0.3	0.737 ± 0.001	3.12 ± 0.01	0.809 ± 0.001	14.32 ± 0.05
0.9	0.840 ± 0.001	2.84 ± 0.01	0.864 ± 0.001	11.18 ± 0.04

While changes of τ_c as function of Tb ions concentration can be explained in terms that a quenching luminescence process is present in Tb^{3+} doped samples, the quenching process involves energy transfer to quenching center such as impurities or defects. This results are agree with the mechanism of generating the thermal effect for Tb^{3+} concentration is responsible for difference in the time constant τ_c and in the strength of the thermal lens θ. For the 0.3% and 0.9% Terbium doped glasses, the temperature increases through radiationless relaxation processes that transfer their energy to the network of the host. These facts are in agreement with previous results that have been reported for other oxides rare earth doped glasses, in which an interaction RE–RE ions is observed [14].

The dependence of TL parameters, as a function of the Tb^{3+} doping, combined with previous observations allows speculate about the possibility that the Tb^{3+} ions are incorporated like formers of network in the glass [9,14,23].

Conclusion

Experimental data on optical and thermo-optical properties of doped germanate glasses for two Tb^{3+} concentrations have been presented. From spectroscopic results, cross-relaxation had to be considered to account for the $^5D_3$ emission spectra. Decay times were founded to be a small quenching effects and exponential behavior in the concentration range studied. The thermo-optical results provided quantitative information on thermal lens effects in heavy germanate glasses Tb^{3+} doped. The influence of rare earth doping on the thermo-optical parameter θ and D pointed in the same direction: its increase with concentration on Tb^{3+}. These results can be interpreted as that the Tb^{3+} ions can act as network former similar to the cases reported for other oxide glasses.

The optical and thermo-optical properties has been employed to get a better understanding on the effects of that are induced by doped with lanthanides ions on the properties of the network.

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