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Journal of Applied Physics, College Park : American Institute of Physics - AIP, v. 110, n. 8, p.

083108-1-083108-5, Oct. 2011

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Citation: *J. Appl. Phys.* **110**, 083108 (2011); doi: 10.1063/1.3653272

View online: <http://dx.doi.org/10.1063/1.3653272>

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## Analysis of energy transfer processes in Yb<sup>3+</sup>-Tb<sup>3+</sup> co-doped, low-silica calcium aluminosilicate glasses

I. A. A. Terra,<sup>1,a)</sup> L. J. Borrero-González,<sup>1</sup> L. A. O Nunes,<sup>1</sup> M. P. Belançon,<sup>2</sup> J. H. Rohling,<sup>2</sup> M. L. Baesso,<sup>2</sup> and O. L. Malta<sup>3</sup>

<sup>1</sup>Instituto de Física de São Carlos, Universidade de São Paulo, CP 369, 13560-970 São Carlos, SP, Brazil

<sup>2</sup>Departamento de Física, Universidade Estadual de Maringá, Av. Colombo, 5790, 87020-900 Maringá, PR, Brazil

<sup>3</sup>Departamento de Química Fundamental, Universidade Federal de Pernambuco-CCEN, Cidade Universitária, Recife-PE 50670-901, Brazil

(Received 15 June 2011; accepted 13 September 2011; published online 24 October 2011)

Energy transfer processes in Yb<sup>3+</sup>-Tb<sup>3+</sup> co-doped, low-silica calcium aluminosilicate glasses were analyzed. Luminescence and time-resolved measurements were used to study upconversion processes, such as Yb-Tb cooperative sensitization, Yb-Yb cooperative luminescence, and Yb-Tb cross relaxation. The quantum cross relaxation efficiency was evaluated as a function on the Yb<sup>3+</sup> concentration, and the maximum estimated value was approximately 51%. In addition, the intensity of the upconversion luminescence from the Tb<sup>3+</sup>:<sup>5</sup>D<sub>4</sub> level decreased by two orders of magnitude comparing the value at room temperature with that at 123 K. As a consequence, Yb-Yb cooperative luminescence around 500 nm became comparable with the intensity of upconversion from the Tb<sup>3+</sup>:<sup>5</sup>D<sub>4</sub> level. Furthermore, a dependence of the upconversion kinetics luminescence on temperature was observed. The upconversion rise time was constant and equal to 65 μs for temperatures between 296 to 473 K and decreased from 65 to 19 μs, without variation in the decay part, when the temperature was lowered from 296 to 123 K. These results were explained by a phonon-assisted cooperative sensitization process for the population of the Tb<sup>3+</sup>:<sup>5</sup>D<sub>4</sub> level. © 2011 American Institute of Physics. [doi:10.1063/1.3653272]

### I. INTRODUCTION

Recently, extensive spectroscopy studies in different lanthanide or trivalent rare earth (RE<sup>3+</sup>) ion-doped materials have addressed the development of solid-state lasers and amplifiers that operate in the visible and infrared spectral region due to their possible applications as optical data storage, solid-state lasers, optical fiber amplifiers for optical telecommunications, and bioassays as well as for enhancing solar cell efficiency.<sup>1-4</sup> Among the various existent RE<sup>3+</sup> ion-doped materials, there is special interest in using low-silica calcium aluminosilicate (LSCAS) glass as a host for RE<sup>3+</sup> ions due to its set of optical, thermal, and chemical properties, such as a high transmission spectral window of 0.3 up to 6 μm, good optical quality, phonon energy (~800 cm<sup>-1</sup>), thermal diffusivity (~5 × 10<sup>-3</sup> cm<sup>2</sup>/s), thermal conductivity (~13 mW/cmK), and good chemical stability.<sup>5,6</sup> All of these properties indicate that this glass can be used as an alternative material for the development of lasers. For example, our group has demonstrated laser emission at 1077 nm in Nd<sup>3+</sup>-doped LSCAS glasses.<sup>7</sup>

The study of energy transfer processes in RE<sup>3+</sup> ion-doped glasses is fundamental to future applications. Several energy transfer processes are involved in optical excitation of RE<sup>3+</sup> ions. Particularly, the upconversion (UC) process has been studied extensively since the first proposition made by Auzel in 1966.<sup>8</sup> The UC process can occur in several ways: excited-state absorption (ESA), energy transfer upconversion

(ETU), cooperative sensitization (CS), cross relaxation (CR), and cooperative luminescence (CL) among others.<sup>1-9,11</sup> Some RE<sup>3+</sup> ions are favorable for UC with strong emission in the visible region, for instance: Er<sup>3+</sup> (550 nm), Tb<sup>3+</sup> (544 nm), and Tm<sup>3+</sup> (470 nm). The sensitization of these ions can be achieved directly or through sensitizer ions in co-doped glasses. The latter is a well-known method to increase the optical pumping efficiency. Usually, Yb<sup>3+</sup> ions are used as sensitizers due to the high absorption cross-section and simplified energy level diagram, allowing efficient sensitization of the energy transfer process.<sup>12</sup> In the last decades, UC luminescence in Yb<sup>3+</sup>-Tb<sup>3+</sup> co-doped in various materials has been widely studied, specifically in relation to CS processes. High energy-transfer efficiency from Yb<sup>3+</sup> to Tb<sup>3+</sup>, on the order of 60%, was reported by Yamashita *et al.*<sup>13</sup> in borosilicate glass, indicating that this system could be used in compact fiber lasers, amplifiers operating in the visible spectral region, displays and optical data storage.<sup>14</sup> In addition, infrared quantum cutting has been demonstrated to enhance silicon solar cell efficiency.<sup>2,3</sup> Therefore, Tb<sup>3+</sup>-Yb<sup>3+</sup> co-doped materials seems to be a suitable system because the Tb<sup>3+</sup> ion presents an absorption band localized at approximately 488 nm assigned to the <sup>7</sup>F<sub>6</sub>→<sup>5</sup>D<sub>4</sub> electronic transition and close to the wavelength corresponding to the maximum intensity of the solar spectrum. Additionally, Yb<sup>3+</sup> ion emission through cooperative downconversion energy transfer from Tb<sup>3+</sup> is situated in the range between 980 and 1100 nm, which is just above the band edge of crystalline silicon and where silicon solar cells exhibit their greatest spectral response.<sup>3,15</sup>

<sup>a)</sup>Author to whom correspondence should be addressed. Electronic mail: idelma@ifsc.usp.br.

UC luminescence studies reported by Salley *et al.*<sup>16,17</sup> in  $\text{SrCl}_2:\text{Yb}, \text{Tb}$  showed that the  $\text{Tb}^{3+}:^5\text{D}_4 \rightarrow ^7\text{F}_5$  UC luminescence intensity follows a Boltzmann distribution with  $\Delta E$  on the order of the energy difference between  $\text{Tb}^{3+}:^7\text{F}_6 \rightarrow ^5\text{D}_4$  and  $2\text{Yb}^{3+}:^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ , indicating a temperature-dependent, phonon-assisted,  $\text{Tb}^{3+}:^5\text{D}_4 \rightarrow ^7\text{F}_5$  UC process. A great deal has been devoted to understanding  $\text{Tb}^{3+}$  UC kinetic processes.<sup>17</sup> Therefore, understanding the pathways involved in energy transfer processes is fundamental to technological applications of this material.

The purpose of the present study was to analyze energy transfer processes in two sets of samples of  $\text{Yb}^{3+}\text{-Tb}^{3+}$  codoped, LSCAS glasses, prepared under vacuum conditions in order to eliminate the presence of  $\text{OH}^-$  radicals. Visible luminescence spectra were recorded as a function of the concentration of  $\text{Tb}^{3+}$  ions with a fixed concentration of  $\text{Yb}^{3+}$  ions (set of sample A). Measurements of room-temperature  $\text{Tb}^{3+}$  UC emission allowed identification of the cooperative sensitization process ( $\text{Yb}^{3+} \rightarrow \text{Tb}^{3+}$ ), and at low temperature (123 K), cooperative luminescence ( $\text{Yb}^{3+}\text{-Yb}^{3+}$ ) was observed. In addition,  $\text{Tb}^{3+}:^5\text{D}_4 \rightarrow ^7\text{F}_5$  UC kinetic measurements at different temperatures enabled estimation of the rise and decay times. The  $\text{Tb}^{3+}:^5\text{D}_4 \rightarrow ^7\text{F}_5$  UC rise times permitted evaluation of the time scale of the energy transfer process. Furthermore, the  $\text{Tb}^{3+}:^5\text{D}_4 \rightarrow ^7\text{F}_5$  UC decay times recorded at room temperature allowed determination of the quantum cross relaxation efficiency between  $\text{Tb}^{3+}$  and  $\text{Yb}^{3+}$  ions as a function on the  $\text{Yb}^{3+}$  concentration (set of sample B). For both sets of samples, the downconversion process (DC) could not be observed for the range of ion concentrations used here, indicating the inefficiency of this process.

## II. MATERIALS AND METHODS

Two sets of LSCAS glass samples were prepared: (A) with a nominal composition of 41.7%  $\text{CaO} + (40.2-x)\%$   $\text{Al}_2\text{O}_3 + 7\%$   $\text{SiO}_2 + 4.1\%$   $\text{MgO} + 5\%$  ( $6.00 \times 10^{20}$  ions/ $\text{cm}^3$ )  $\text{Yb}_2\text{O}_3 + x\%$   $\text{Tb}_4\text{O}_7$ , where  $x = 0.0, 0.5, 1.0,$  and  $2.0$  of  $\text{Tb}_4\text{O}_7$  (in wt. %) and (B) with a nominal composition of 41.7%  $\text{CaO} + (40.2-x)\%$   $\text{Al}_2\text{O}_3 + 7\%$   $\text{SiO}_2 + 4.1\%$   $\text{MgO} + 2\%$  ( $2.53 \times 10^{20}$  ions/ $\text{cm}^3$ )  $\text{Tb}_4\text{O}_7 + x\%$   $\text{Yb}_2\text{O}_3$ , where  $x = 0.2, 1.0, 2.0,$  and  $5.0$  wt% of  $\text{Yb}_2\text{O}_3$ . The reagent quantities were homogeneously mixed in a ball mill for 12 h. Afterwards, the sets of samples were melted at  $1500^\circ\text{C}$  under vacuum conditions ( $10^{-3}$  mbar) in graphite crucibles for 2 h to eliminate the presence of  $\text{OH}^-$  radicals.<sup>7</sup> Thereafter, annealing was performed by returning the crucible to the melting position, where the temperature was approximately  $600^\circ\text{C}$ , and allowing it to cool to room temperature. Finally, the samples were cut and polished into a plate shape with dimensions of  $3 \times 5 \times 10$  mm. For optical measurements, the 325 nm line of a HeCd laser (Kimmon/IK5652R-G) was used to pump the  $\text{Tb}^{3+}$  ions, and the luminescence spectra were collected at different  $\text{Tb}^{3+}$  ion concentrations. The UC luminescence spectra were obtained using a diode laser (InGaAs) at 980 nm as the excitation source and were taken at different temperatures (123 and 296 K). The luminescence signals were dispersed by a monochromator (0.3 m, Thermo Jarrel Ash/82497) coupled to a photomultiplier tube (PMT) (Hamamatsu/R928) and

amplified by a Lock-In amplifier. Lifetime and UC kinetic measurements were performed using an optical parametrical oscillator (OPO) (Surelite/Continuum) pumped by the third harmonic (355 nm) of a Nd-YAG laser (Surelite II/Continuum, 10 Hz, 5 ns) to provide 488 and 980 nm wavelengths, using the same monochromator and PMT. Luminescence decay curves were recorded in a digital oscilloscope (Tektronix/TDS380).  $\text{Tb}^{3+}:^5\text{D}_4 \rightarrow ^7\text{F}_5$  UC kinetic responses were registered at different temperatures from 123 to 475 K, and the rise and decay times of the  $\text{Tb}^{3+}:^5\text{D}_4 \rightarrow ^7\text{F}_5$  UC kinetic were estimated.

## III. RESULTS AND DISCUSSIONS

Figure 1 shows a partial energy diagram of the  $\text{Yb}^{3+}$  and  $\text{Tb}^{3+}$  ions with the relevant optical transitions for analysis. Also, essential features of the kinetics of the  $\text{Tb}^{3+}\text{-Yb}^{3+}$  energy transfer are illustrated by considering the energy level system. The four main processes involved are depicted: CS, CL, ESA, and the CR process. The energy transfer processes are indicated by dashed lines, whereas excitation and emission transitions are indicated by solid lines.

### A. Visible luminescence spectra

The visible luminescence spectra of  $\text{Yb}^{3+}\text{-Tb}^{3+}$  codoped LSCAS glasses were obtained at room temperature under an excitation of 325 nm, i.e., pumping the  $^5\text{D}_1$  level of the  $\text{Tb}^{3+}$  ions. Figure 2 shows the visible luminescence spectrum of a LSCAS sample co-doped with 5.0% Yb and 2.0% Tb. In this spectrum, eight distinct emission bands are clearly observed, originating from the  $^5\text{D}_3$  and  $^5\text{D}_4$  emitter levels of  $\text{Tb}^{3+}$  ions. The emission bands corresponding to  $^5\text{D}_3 \rightarrow ^7\text{F}_j$  transitions at 380 nm ( $^5\text{D}_3 \rightarrow ^7\text{F}_6$ ), 417 nm ( $^5\text{D}_3 \rightarrow ^7\text{F}_5$ ), 438 nm ( $^5\text{D}_3 \rightarrow ^7\text{F}_4$ ), and 460 nm ( $^5\text{D}_3 \rightarrow ^7\text{F}_3$ ) can be observed, as well as  $^5\text{D}_4 \rightarrow ^7\text{F}_j$  transitions at 488 nm ( $^5\text{D}_4 \rightarrow ^7\text{F}_6$ ), 544 nm ( $^5\text{D}_4 \rightarrow ^7\text{F}_5$ ), 587 nm ( $^5\text{D}_4 \rightarrow ^7\text{F}_4$ ), and 623 nm ( $^5\text{D}_4 \rightarrow ^7\text{F}_3$ ). The  $^5\text{D}_3 \rightarrow ^7\text{F}_j$  emission bands were clearly observed at the same intensity as the  $^5\text{D}_4 \rightarrow ^7\text{F}_j$  emissions due to the absence of  $\text{OH}^-$  and cross relaxation between  $\text{Tb}^{3+}$  pairs. The  $\text{Tb}^{3+}:^5\text{D}_4 \rightarrow ^7\text{F}_j$  emission intensity increased linearly with the increase in the concentration of  $\text{Tb}^{3+}$  ions (up to 2 wt. %) for the (A) samples.

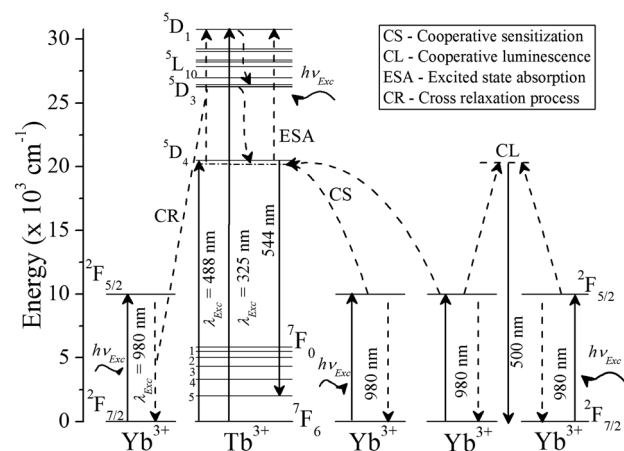


FIG. 1. Partial energy level diagram of  $\text{Yb}^{3+}$  and  $\text{Tb}^{3+}$  ions. The energy transfer processes are indicated by dashed lines and excitation and emission transitions are indicated by solid lines.

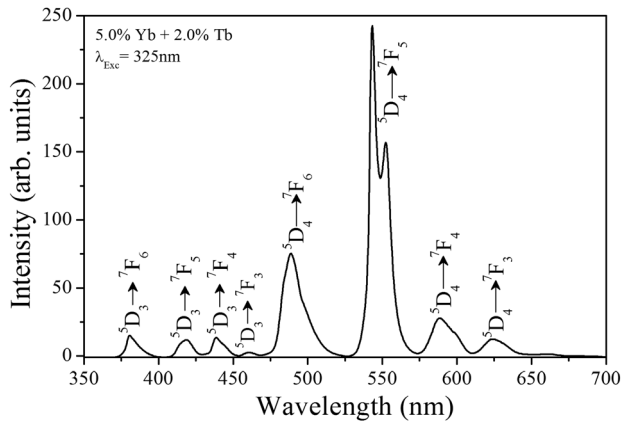


FIG. 2. Room-temperature visible luminescence spectrum of the 5.0% Yb + 2.0% Tb codoped LSCAS glass, under excitation at 325 nm.

However, for the (B) samples, the  $\text{Tb}^{3+}:^5\text{D}_4 \rightarrow ^7\text{F}_j$  emission intensity was constant by varying the concentration of  $\text{Yb}^{3+}$  ions (results not shown here), probably due to a low efficiency of the DC process. Furthermore, the emission intensities of the  $\text{Tb}^{3+}:^5\text{D}_4$  level when pumping with 488 nm for the (B) samples were also constants. Moreover, with excitation at 488 nm, the luminescence decay curves of the  $\text{Tb}^{3+}:^5\text{D}_4$  emitter level were nearly the same, and the radiative lifetime was estimated to be 1.69 ms for the (A) samples, due to the large energy gap between the  $^5\text{D}_4$  and  $^7\text{F}_0$  levels ( $\approx 16000 \text{ cm}^{-1}$ ). However, the radiative lifetime for the (B) samples was similar to the (A) samples, but a maximum percentage variation of approximately 10% was observed with  $\text{Yb}^{3+}$  concentration (Figure 4) due to the DC process.

Also, weak Near Infrared (NIR) emission for both sets of (A) and (B) samples were detected between 950 and 1100 nm when pumping at 488 nm, which is associated with the  $\text{Yb}^{3+}:^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$  emitter level. The above results confirm the low efficiency of the DC process, at least for the concentration of ions used here. The radiative lifetime of the  $\text{Yb}^{3+}:^2\text{F}_{5/2}$  emitter level for the sample with the lowest  $\text{Yb}^{3+}$  concentration (2.0% Tb + 0.2% Yb) was 0.80 ms with an

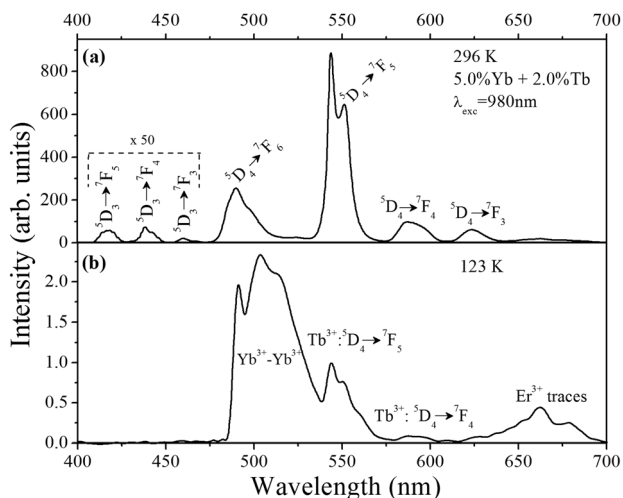


FIG. 3. (a) Room-temperature UC emission spectrum for 5.0% Yb + 2.0% Tb codoped LSCAS glass, under excitation at 980 nm. (b) UC emission spectrum at 123 K.

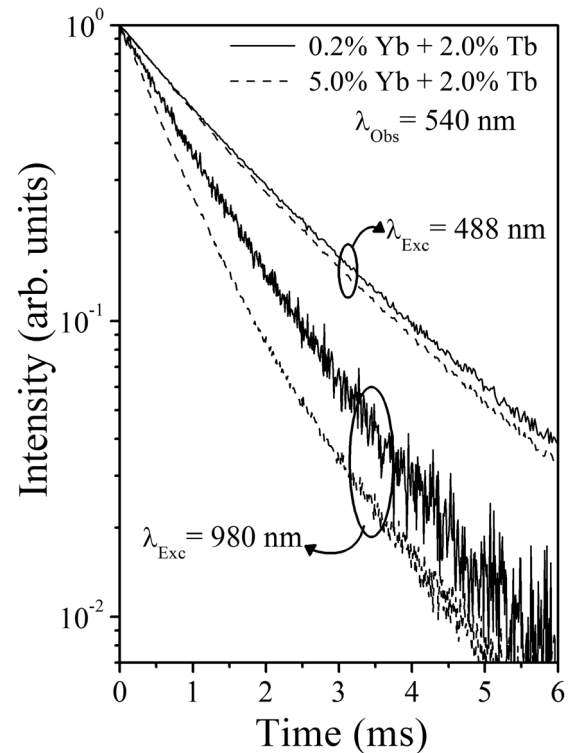


FIG. 4. Luminescence decay curves of  $\text{Tb}^{3+}$  ions at 544 nm for the 2.0% Tb + 0.2% Yb and 2.0% Tb + 5.0% Yb co-doped LSCAS glasses, with excitations at 488 and 980 nm using a pulsed laser.

excitation at 532 nm, and this value increased with  $\text{Yb}^{3+}$  concentration up to 1.08 ms for 5.0%  $\text{Yb}^{3+}$ . This result could be explained by the energy migration process among  $\text{Yb}^{3+}$  ions.

## B. Upconversion

Figure 3(a) shows the room-temperature UC emission spectrum for the sample co-doped with 5.0%  $\text{Yb}^{3+}$  and 2.0%  $\text{Tb}^{3+}$  (the UC emission associated with the other concentrations are not shown here). This spectrum was obtained by pumping at 980 nm from the electronic transition of the  $\text{Yb}^{3+}$  ions, according to the diagram shown in Figure 1. The emission bands corresponding to the optical transitions of  $\text{Tb}^{3+}$  ions attributed to the  $^5\text{D}_4 \rightarrow ^7\text{F}_j$  energy levels at 623 nm ( $^5\text{D}_4 \rightarrow ^7\text{F}_3$ ), 587 nm ( $^5\text{D}_4 \rightarrow ^7\text{F}_4$ ), 544 nm ( $^5\text{D}_4 \rightarrow ^7\text{F}_5$ ), and 488 nm ( $^5\text{D}_4 \rightarrow ^7\text{F}_6$ ) are indicated. In addition, the emission bands at 417 nm ( $^5\text{D}_3 \rightarrow ^7\text{F}_5$ ), 438 nm ( $^5\text{D}_3 \rightarrow ^7\text{F}_4$ ), and 460 nm ( $^5\text{D}_3 \rightarrow ^7\text{F}_3$ ) were multiplied by 50 to facilitate visualization. The intensity evolution of  $\text{Tb}^{3+}$  UC emission, integrated at 544 nm ( $^5\text{D}_4 \rightarrow ^7\text{F}_5$ ), rises linearly with increasing concentrations of  $\text{Tb}^{3+}$  and  $\text{Yb}^{3+}$  ions, for samples (A) and (B), respectively, and the spectra are similar, i.e., without changing the position and the spectral profiles of the emission bands.

To elucidate the origin of the processes involved in the UC emissions, pumping power measurements were performed in a 5.0% Yb + 2.0% Tb co-doped LSCAS glass. A  $P^n$  power law was found for an n-photon process, in which n is the slope of the double-logarithmic plots of the intensity emission versus pump power. A slope of  $n = 2.1$  of the green emission (544 nm) from the  $^5\text{D}_4$  level was obtained, indicating that emission occurs through 2-photon absorption, representing

the 2-photon nature of the CS process ( $2\text{Yb}^{3+}:^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ ;  $\text{Tb}^{3+}:^7\text{F}_6 \rightarrow ^5\text{D}_4$ ). That is, two excited  $\text{Yb}^{3+}$  ions (sensitizer) simultaneously transfer their excitation energies from the  $^2\text{F}_{5/2}$  level to the  $^5\text{D}_4$  level of  $\text{Tb}^{3+}$  (activator), as shown in Figure 1. However, the pump power dependence of the emission from the  $^5\text{D}_3$  level exhibits a slope of  $n = 2.9$ , which indicates a 3-photon process. This 3-photon process is thought to be due to two distinct processes, as depicted in Figure 1: CS followed by CR, in which two excited  $\text{Yb}^{3+}$  ions simultaneously transfer their energies to a  $\text{Tb}^{3+}$  ion ( $^5\text{D}_4$  level), plus energy transfer from a third  $\text{Yb}^{3+}$  ion not participating in the CS [ $(2\text{Yb}^{3+}:^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}; \text{Tb}^{3+}:^7\text{F}_6 \rightarrow ^5\text{D}_4) + (\text{Yb}^{3+}:^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}; \text{Tb}^{3+}:^5\text{D}_4 \rightarrow ^5\text{D}_3)$ ]; and by ESA through absorption of pumping photons ( $h\nu_{\text{EXC}}$ ) in the  $\text{Tb}^{3+}:^5\text{D}_4$  level.

Figure 3(b) shows the UC emission spectrum at 123 K under excitation at 980 nm. Four distinct emission bands are depicted in this spectrum: the band around 500 nm is readily assigned due to the well-known CL of two  $\text{Yb}^{3+}$  ions<sup>18</sup> (Fig. 1), the bands at 544 and 587 nm attributed to  $\text{Tb}^{3+}:^5\text{D}_4 \rightarrow ^7\text{F}_5$  and  $\text{Tb}^{3+}:^5\text{D}_4 \rightarrow ^7\text{F}_4$  transitions due to the CS process and a band located at 630–700 nm assigned to  $\text{Er}^{3+}$  traces. At this temperature, quenching of UC emission from  $\text{Tb}^{3+}:^5\text{D}_4$  level was observed because this process is non-resonant (Fig. 1), and the emission intensity became comparable to the Yb-Yb cooperative luminescence centered around 500 nm.

The cooperative energy from two  $\text{Yb}^{3+}$  ions ( $2\text{Yb}^{3+}:^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ ) is not enough to reach the lowest Stark sub-level of  $\text{Tb}^{3+}:^5\text{D}_4$ . Therefore, a phonon-assisted process is required. The  $\text{Tb}^{3+}:^5\text{D}_4 \rightarrow ^7\text{F}_5$  UC emission intensity at 544 nm recorded at 123 K was almost 800 times weaker than the corresponding intensity at 300 K, which means that the temperature dependence of the  $\text{Tb}^{3+}:^5\text{D}_4 \rightarrow ^7\text{F}_5$  UC emission intensity follows a Boltzmann distribution. The phonon-assisted  $\text{Tb}^{3+}:^5\text{D}_4 \rightarrow ^7\text{F}_5$  (Ref. 16) UC process will be better discussed in the next section. We also observed that the emission band around 500 nm had a lifetime on the order of the half of the lifetime of the  $\text{Yb}^{3+}:^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$  transition, in agreement with similar results reported in the literature.<sup>18</sup> A rise time around 10 ns was further observed for this CL ( $2\text{Yb}^{3+}:^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ ) process, indicating an electronic origin.

### C. Upconversion kinetic response

Most studies have assigned the  $\text{Tb}^{3+}:^5\text{D}_4 \rightarrow ^7\text{F}_5$  UC in the  $\text{Yb}^{3+}\text{-Tb}^{3+}$  system to the cooperative sensitization process, which was first proposed in 1969.<sup>16–18</sup> Recently, a temperature-dependent study demonstrated that in many  $\text{Yb}^{3+}\text{-Tb}^{3+}$  systems, this process must be mediated by phonons to bridge the electronic energy gap between the  $\text{Tb}^{3+}:^5\text{D}_4$  level and two times the lowest crystal field level of  $\text{Yb}^{3+}:^2\text{F}_{5/2}$ .<sup>17</sup> However, the  $\text{Tb}^{3+}$  UC kinetic response dependence on temperature is not well studied yet. In this section,  $\text{Tb}^{3+}$  UC kinetic measurements and the influence on temperature were investigated. In addition, the quantum cross relaxation ( $\text{Yb}^{3+}\text{-Tb}^{3+}$ ) efficiency was evaluated as a function on  $\text{Yb}^{3+}$  ion concentrations. Also, a dependence of the  $\text{Tb}^{3+}:^5\text{D}_4 \rightarrow ^7\text{F}_5$  UC rise time on temperature was obtained. These measurements enable a description of the  $\text{Tb}^{3+}$  UC processes.

Figure 4 shows the normalized  $\text{Tb}^{3+}:^5\text{D}_4$  luminescence decay curves for LSCAS glasses codoped with 0.2%  $\text{Yb} + 2.0\%$   $\text{Tb}$  (solid line) and 5.0%  $\text{Yb} + 2.0\%$   $\text{Tb}$  (dashed line).  $\text{Tb}^{3+}$  luminescence was excited directly (488 nm) and by UC (980 nm) with a 5 ns pulsed laser. As previously mentioned (luminescence section), the  $\text{Tb}^{3+}:^5\text{D}_4$  level decay curves are very similar for both samples when exciting at 488 nm due to the low efficiency of the DC process. However, for the excitation at 980 nm, the  $\text{Tb}^{3+}:^5\text{D}_4 \rightarrow ^7\text{F}_5$  UC decay was faster and the effect of varying the  $\text{Yb}^{3+}$  ion concentration was more evident than exciting at 488 nm (the decay times derived from the  $\text{Tb}^{3+}:^5\text{D}_4 \rightarrow ^7\text{F}_5$  UC experiment are summarized in Table I). Furthermore, an increase in  $^5\text{D}_3 \rightarrow ^7\text{F}_J$  emissions and a decrease in  $^5\text{D}_4 \rightarrow ^7\text{F}_J$  emissions with increasing concentration of  $\text{Yb}^{3+}$  ions were observed. These results are due to the cross relaxation process between  $\text{Yb}^{3+}\text{-Tb}^{3+}$  ions ( $\text{Yb}^{3+}:^7\text{F}_{5/2} \rightarrow ^7\text{F}_{7/2}$ ;  $\text{Tb}^{3+}:^5\text{D}_4 \rightarrow ^5\text{D}_1$ ) (this process was called a second step of upconversion by Noginov *et al.*<sup>20</sup>).

The cross relaxation efficiency ( $\eta_{\text{CR}}$ ) can be evaluated using the following expression:

$$\eta_{\text{CR}} = 1 - (\tau_{\text{Tb-Yb}} / \tau_{\text{Tb}}^{\text{rad}}), \quad (1)$$

where,  $\tau_{\text{Tb-Yb}}$  is the decay time of  $^5\text{D}_4$  emitter level (544 nm) of the  $\text{Tb}^{3+}$  ion in the presence of  $\text{Yb}^{3+}$  ion and  $\tau_{\text{Tb}}^{\text{rad}} = 1.69$  ms is the radiative lifetime of  $\text{Tb}^{3+}$  ions.  $\eta_{\text{CR}}$  increased with the concentration of  $\text{Yb}^{3+}$  ions, and the results are shown in Table 1 with the corresponding  $\text{Tb}^{3+}:^5\text{D}_4$  level decay time.

To further investigate the origin of the UC emission processes, the influence of the temperature on the  $\text{Tb}^{3+}:^5\text{D}_4 \rightarrow ^7\text{F}_5$  UC kinetics was studied. Figure 5(a) shows the normalized UC kinetic response,  $\text{Tb}^{3+}:^5\text{D}_4 \rightarrow ^7\text{F}_5$  (544 nm) luminescence at different temperatures for the 5.0%  $\text{Yb} + 2.0\%$   $\text{Tb}$  codoped LSCAS glass. The sample was excited at 980 nm (5 ns laser pulse). As can be observed, the intensity of the  $\text{Tb}^{3+}:^5\text{D}_4 \rightarrow ^7\text{F}_5$  UC luminescence rose from zero counts slowly after the pulse. In addition, the slow decay part was similar for all transients. Following Salley *et al.*,<sup>16</sup> the transients can be fitted using the following equation,

$$I(t) = A \left[ e^{-\frac{t}{\tau_1}} - e^{-\frac{t}{\tau_2}} \right],$$

where  $\tau_1$  and  $\tau_2$  represent the decay and rise times of the transient, respectively. The inset in Figure 5(a) shows the dependence of  $\tau_2$  on temperature.  $\tau_2$  was equal to 65  $\mu\text{s}$  and presented no variation when the temperature increased from

TABLE I.  $\text{Tb}^{3+}:^5\text{D}_4$  decay time in  $\text{Yb}^{3+}\text{-Tb}^{3+}$  co-doped LCAS glasses and cross relaxation efficiency as a function of the concentration of  $\text{Yb}^{3+}$  ions. The excitation wavelength was  $\lambda_{\text{exc}} = 980$  nm from a 5 ns pulsed laser.

Concentration of $\text{Tb}^{3+}$	Concentration of $\text{Yb}^{3+}$	$\text{Tb}^{3+}:^5\text{D}_4 \rightarrow ^7\text{F}_5$ decay time (ms)	$\eta_{\text{CR}}(\%)$
2.0	0.2	1.11	34.32
2.0	1.0	1.07	36.69
2.0	2.0	1.00	40.83
2.0	5.0	0.83	50.89

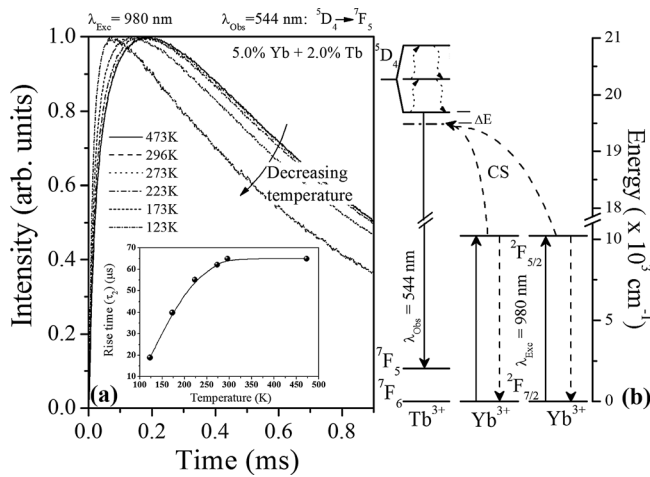


FIG. 5. (a) Kinetic response of Tb<sup>3+</sup> UC luminescence for the 5.0% Yb + 2.0% Tb co-doped LSCAS glass monitored at 544 nm under excitation at 980 nm (5 ns) at different temperatures. The inset shows the rise times, obtained using Eq. (2). (b) Energy level diagram of Tb<sup>3+</sup> and Yb<sup>3+</sup> ions. The Tb<sup>3+</sup>:<sup>5</sup>D<sub>4</sub> Stark levels are shown.

296 to 473 K, and the Tb<sup>3+</sup>:<sup>5</sup>D<sub>4</sub>→<sup>7</sup>F<sub>5</sub> intensity was practically the same. However, τ<sub>2</sub> strongly diminished (65 to 19 μs) when the temperature decreased from 296 to 123 K, whereas the Tb<sup>3+</sup>:<sup>5</sup>D<sub>4</sub>→<sup>7</sup>F<sub>5</sub> intensity decreased. In addition, for all temperatures, τ<sub>1</sub> was constant and equal to 0.83 ms.

The rise time after a short pulse is a well-known fingerprint of an energy transfer process that needs no light to proceed and, therefore, continues after the laser pulse.<sup>17</sup> Furthermore, for the Yb:Tb system, the rise time is expected to be related to half of the Yb<sup>3+</sup> lifetime, and the decay should be related to the Tb<sup>3+</sup> lifetime. τ<sub>1</sub> = 0.83 ms was shorter than the Tb<sup>3+</sup>:<sup>5</sup>D<sub>4</sub> lifetime, 1.69 ms, obtained under direct excitation, and this could be due to CR and ESA processes.

To explain these results, we must discuss the energy levels involved in the CS process. From the energy of the lowest excited state of Yb<sup>3+</sup>, 9800 cm<sup>-1</sup>, cooperative sensitization cannot populate the lowest Tb<sup>3+</sup>:<sup>5</sup>D<sub>4</sub> Stark level, which would require an energy of about 19700 cm<sup>-1</sup>. Then, there is a gap in energy at approximately 100 cm<sup>-1</sup>. Salley *et al.*<sup>17</sup> have estimated a similar energy gap ΔE = 150 cm<sup>-1</sup> for the activation energy of the Tb<sup>3+</sup>:<sup>5</sup>D<sub>4</sub>→<sup>7</sup>F<sub>5</sub> UC luminescence by using the Arrhenius equation. This is the main reason for the observed temperature dependence of the Tb<sup>3+</sup>:<sup>5</sup>D<sub>4</sub>→<sup>7</sup>F<sub>5</sub> UC luminescence rise time (inset in Figure 5(a)) and intensity (Figure 3). This energy gap is close to the energy mismatch between the lowest level of Tb<sup>3+</sup>:<sup>5</sup>D<sub>4</sub> at 19700 cm<sup>-1</sup> and twice the lowest Yb<sup>3+</sup>:<sup>2</sup>F<sub>5/2</sub> level. From this analysis, it is clear that the CS process is facilitated only at higher temperatures, where host phonons can contribute to the energy of the UC-active ions, and the rise time is longer due to multiphonon population and thermalization mechanisms into the Tb<sup>3+</sup>:<sup>5</sup>D<sub>4</sub> Stark levels (see Figure 5(b)). At higher temperatures, vibronic <sup>2</sup>F<sub>5/2</sub> levels of the Yb<sup>3+</sup> ions are thermally populated, from which the energy transfer can occur. These results indicate that cooperative energy transfer is assisted by phonons, as was suggested by Salley *et al.*<sup>17</sup>

## IV. CONCLUSION

In conclusion, in this work, we investigated the energy transfer process in Yb<sup>3+</sup>-Tb<sup>3+</sup> co-doped, low-silica calcium aluminosilicate glasses. Luminescence and time-resolved measurements data showed the occurrence of upconversion processes, such as Yb-Tb cooperative sensitization, Yb-Yb cooperative luminescence, and Yb-Tb cross relaxation. The quantum cross relaxation efficiency was evaluated as a function of the Yb<sup>3+</sup> ion concentrations, and the maximum estimated value was approximately 51%. In addition, the Tb<sup>3+</sup>:<sup>5</sup>D<sub>4</sub>→<sup>7</sup>F<sub>5</sub> UC luminescence intensity decreased by two orders of magnitude comparing the value at room temperature with that at 123 K. As a consequence, Yb-Yb cooperative luminescence at approximately 500 nm becomes comparable. Furthermore, a dependence of the Tb<sup>3+</sup>:<sup>5</sup>D<sub>4</sub>→<sup>7</sup>F<sub>5</sub> UC kinetics luminescence on temperature was observed. The Tb<sup>3+</sup>:<sup>5</sup>D<sub>4</sub>→<sup>7</sup>F<sub>5</sub> UC rise time was constant and equal to 65 μs for temperatures between 296 to 473 K and decreased from 65 to 19 μs when the temperature decreased from 296 to 123 K, without variation in the decay part. These results were explained by a phonon-assisted cooperative sensitization process for population of the Tb<sup>3+</sup>:<sup>5</sup>D<sub>4</sub> level.

## ACKNOWLEDGMENTS

This work was supported by Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) and Instituto Nacional de Nanotecnologia para Marcadores Integrados (INAMI) (Brazil). The authors are especially thankful to Professor Maria Cristina Terrile for valuable discussions.

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