Critical separation for efficient Tm^{3+} – Tm^{3+} energy transfer evidenced in nanostructured $\text{Tm}^{3+}:\text{Al}_2\text{O}_3$ thin films

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Received November 19, 2007; revised December 28, 2007; accepted February 7, 2008; posted February 20, 2008 (Doc. ID 89694); published March 14, 2008

Nanostructured amorphous Al oxide ($\alpha\text{-Al}_2\text{O}_3$) thin films doped with Tm^{3+} were synthesized by alternate pulsed laser deposition. The Tm^{3+} ions have been deposited in layers with in-depth separation ranging from 0.75 to 6 nm. The films show two broad emission bands originated from the $\text{Tm}^{3+} {}^3\text{H}_4 \rightarrow {}^3\text{F}_4$ and ${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$ transitions. Their intensity increases at a similar rate and the lifetimes are not modified as the layer separation decreases down to 1.5 nm, suggesting that there is no concentration quenching. At the critical value of 1.5 nm the onset of Tm^{3+} – Tm^{3+} energy transfer is evidenced by a sharp decrease of the emission intensity and lifetime. Below this critical value, the rate at which the intensity increases for the ${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$ transition is much higher than that for the ${}^3\text{H}_4 \rightarrow {}^3\text{F}_4$ transition, evidencing quenching of the ${}^3\text{H}_4 \rightarrow {}^3\text{F}_4$ transition through a cross-relaxation mechanism. The control of the Tm^{3+} ions in the nanometer scale allows evidencing the onset of energy transfer processes among ions and offers a route to optimize compact photonic gain integrated devices. © 2008 Optical Society of America
OCIS codes: 160.5690, 130.3130, 300.6280, 250.5230.

Tm -doped thin films are of great interest for the development of lasers and optical amplifiers in planar waveguide devices [1–3]. The $\text{Tm}^{3+} {}^3\text{H}_4 \rightarrow {}^3\text{F}_4$ and ${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$ transitions give rise to the 1.46–1.48 and 1.6–2.1 μm luminescent bands that are currently being investigated for extending the conventional band (1530–1600 nm) developed by Er-doped amplifiers [4]. Nevertheless, it has been found that the ${}^3\text{H}_4$ level of Tm^{3+} is easily quenched in a high-phonon-energy host material such as silica glass ($\sim 1100 \text{ cm}^{-1}$) [5,6]. This problem can be circumvented by using low-phonon-energy materials such as fluoride glass ($\sim 580 \text{ cm}^{-1}$) or some multicomponent glasses [7,8]. However, these materials present some disadvantages as usually their mechanical and thermal properties are far from those offered by silica-based glasses [9,10]. Besides the host material an important factor to be considered is the Tm^{3+} – Tm^{3+} interaction that leads to energy transfer among ions due to cross-relaxation processes [7,11–13]. Those effects become critical when developing integrated waveguide devices with dimensions in the micrometer scale.

In this work, we investigate the Tm^{3+} – Tm^{3+} energy transfer in nanostructured amorphous Al oxide ($\text{Tm}^{3+}:\text{Al}_2\text{O}_3$) films in which the dopant ions are distributed in layers whose in-depth separation has been accurately controlled in the nanoscale. The amorphous Al oxide ($\alpha\text{-Al}_2\text{O}_3$) has been chosen as host because it is a material with high potential to develop active integrated waveguide devices owing to its high refractive index contrast with respect to SiO_2 (~ 0.2) and its excellent mechanical and thermal properties [14,15]. Moreover, $\alpha\text{-Al}_2\text{O}_3$ has a maxi-

mum phonon energy of 870 cm^{-1} , which makes it suitable for Tm^{3+} doping [16].

An ArF excimer laser [$\lambda=193 \text{ nm}$, $\tau=20 \text{ ns}$ full width at half-maximum (FWHM), 2 J cm^{-2}] was used to ablate independently the ceramic Al_2O_3 and metal Tm targets. The deposition sequence involves the production of one $\alpha\text{-Al}_2\text{O}_3$ layer followed by the ablation of the Tm target with a single pulse to form a Tm^{3+} -doped layer. The thickness of the spacing $\alpha\text{-Al}_2\text{O}_3$ layers was controlled by varying the number of pulses on the ceramic Al_2O_3 target [17]. The Tm^{3+} – Tm^{3+} in-depth separation (s) was changed, with $s=0.75, 1, 1.5, 2, 4$, and 6 nm , by increasing the number of Tm^{3+} -doped layers in the films from 50 ($s=6 \text{ nm}$) to 400 ($s=0.75 \text{ nm}$) while keeping a constant film thickness of $\sim 300 \text{ nm}$. Therefore as s decreases, the Tm^{3+} content increases. After deposition, all films were step annealed up to 800°C for 1 h in air [17].

The Tm^{3+} concentration ($[\text{Tm}^{3+}]$) was measured by Rutherford backscattering spectrometry (RBS) using a 2.0 MeV He^+ beam and a scattering angle of 165° . It was checked that the annealing did not cause any significant change in the measured Tm^{3+} profile distribution of the films. The results show that the total Tm^{3+} areal density has been varied in the range from 2.1×10^{15} to $1.7 \times 10^{16} \text{ cm}^{-2}$, and the Tm^{3+} areal density in a single doped layer is of $4.2 \times 10^{13} \text{ cm}^{-2}$. The average $[\text{Tm}^{3+}]$ has been calculated as the areal density divided by the film thickness, and thus it is in the range from $7.0 \times 10^{19} \text{ cm}^{-3}$ to $5.7 \times 10^{20} \text{ cm}^{-3}$.

Photoluminescence (PL) was excited at room temperature with a Ti:sapphire laser at 794 nm and detected by a cooled Ge detector in the wavelength

range of 1400–1700 nm with a time resolution of 0.05 ms. The luminescence decay curves were averaged and recorded with a digital oscilloscope. Further details of the setup can be found elsewhere [18]. Figure 1 shows the PL spectra corresponding to films having four different separations of the Tm^{3+} -doped layers at 200 mW pump intensity. It has been checked that the shapes of the PL spectra do not depend on the pump intensity in the range from 100 to 800 mW. Two broad emission bands are observed for all films, whose maximum position and bandwidth do not change with the Tm^{3+} layer separation. However, the PL intensities change significantly. The 1480 nm band with a FWHM of 113 nm is originated from the $^3\text{H}_4 \rightarrow ^3\text{F}_4$ transition (see inset). Usually, the strong multiphonon relaxation effect in high-phonon-energy materials such as silica glasses ($\sim 1100 \text{ cm}^{-1}$) is known to result in a nonradiative transition of $\text{Tm}^{3+}: ^3\text{H}_4 \rightarrow ^3\text{H}_5$ at a rate much faster than the radiative decay rate owing to a small energy gap between the $^3\text{H}_4$ and $^3\text{H}_5$ levels. The presence of 1480 nm emission band in the $\alpha\text{-Al}_2\text{O}_3$ is consistent with the low phonon energy values of 870 cm^{-1} reported for this material [16]. The 1640 nm band with a FWHM of 82 nm corresponds to the higher energy side of the $^3\text{F}_4 \rightarrow ^3\text{H}_6$ transition (see inset), which has been observed in both crystalline and amorphous hosts [4,11,12,16]. Its maximum emission is usually found $\sim 1.7\text{--}2.1 \mu\text{m}$, which is out of the range of this study owing to the upper detection limit of our system.

Figure 2 shows the PL maximum intensity of the $^3\text{H}_4 \rightarrow ^3\text{F}_4$ and $^3\text{F}_4 \rightarrow ^3\text{H}_6$ emission bands as a function of both the $[\text{Tm}^{3+}]$ (bottom axis) and $\text{Tm}^{3+}\text{--Tm}^{3+}$ separation (top axis). Two concentration regions can be identified: a low $[\text{Tm}^{3+}]$ region for concentrations lower than $2.8 \times 10^{20} \text{ cm}^{-3}$ and a high $[\text{Tm}^{3+}]$ region for concentrations higher or equal to $2.8 \times 10^{20} \text{ cm}^{-3}$. In the low $[\text{Tm}^{3+}]$ region the PL intensities of both emission bands tend to increase as $[\text{Tm}^{3+}]$ increases, and the maximum is reached for the film with

Fig. 1. PL spectra of $\text{Tm}^{3+}:\text{Al}_2\text{O}_3$ films for different $\text{Tm}^{3+}\text{--Tm}^{3+}$ layer separations (s) in nanometers: 0.75, 1.5, 2, and 6. The inset (a) shows schematically the energy-level diagram of Tm^{3+} and the (b) process of cross relaxation.

Fig. 2. PL intensity at 1480 nm ($\blacktriangle$) and 1640 nm ($\bullet$) of $\text{Tm}^{3+}:\text{Al}_2\text{O}_3$ films as a function of $[\text{Tm}^{3+}]$ (bottom axis) and as a function of $\text{Tm}^{3+}\text{--Tm}^{3+}$ in-depth separation (top axis). The dashed lines are linear fits of the experimental data.

$[\text{Tm}^{3+}] = 2.2 \times 10^{20} \text{ cm}^{-3}$ ($s = 2 \text{ nm}$). In this low $[\text{Tm}^{3+}]$ region the ratio of the emission intensity of transition $^3\text{H}_4 \rightarrow ^3\text{F}_4$ to that of transition $^3\text{F}_4 \rightarrow ^3\text{H}_6$ is nearly constant with increasing $[\text{Tm}^{3+}]$. Instead, for a $[\text{Tm}^{3+}] = 2.8 \times 10^{20} \text{ cm}^{-3}$ ($s = 1.5 \text{ nm}$) there is a sharp decrease of the emission intensity of both bands thus marking the beginning of the high $[\text{Tm}^{3+}]$ region. In this region the intensities of both bands also tend to increase with the $[\text{Tm}^{3+}]$; nevertheless the ratio of the emission intensity of transition $^3\text{H}_4 \rightarrow ^3\text{F}_4$ to that of transition $^3\text{F}_4 \rightarrow ^3\text{H}_6$ now decreases as $[\text{Tm}^{3+}]$ increases. This is due to the fact that the $^3\text{F}_4 \rightarrow ^3\text{H}_6$ emission increases at a faster rate as a function of $[\text{Tm}^{3+}]$ in this region (see Fig. 2). It has been determined that the slope of the $^3\text{F}_4 \rightarrow ^3\text{H}_6$ emission as a function of $[\text{Tm}^{3+}]$ is 0.4 and 0.8 for the low and high $[\text{Tm}^{3+}]$ regions.

The sharp discontinuity of the evolution of the PL response with the $[\text{Tm}^{3+}]$ occurs for a $\text{Tm}^{3+}\text{--Tm}^{3+}$ separation of $s = 1.5 \text{ nm}$. Note that within the low concentration region, the $\text{Tm}^{3+}\text{--Tm}^{3+}$ layers are separated up to $s = 6 \text{ nm}$; thus it is expected that the interaction between ions in different layers will be very weak and that the concentration quenching is limited by the in-plane concentration, similar to what has been found for Er-doped $\alpha\text{-Al}_2\text{O}_3$ films [15]. For all the films the areal density of Tm^{3+} per layer is maintained constant at $4.2 \times 10^{13} \text{ cm}^{-2}$, which corresponds to an average $\text{Tm}^{3+}\text{--Tm}^{3+}$ in-plane separation of 1.74 nm. As long as the $\text{Tm}^{3+}\text{--Tm}^{3+}$ in-depth separation is larger than this value, the effect of the energy transfer between ions in different layers is not significant. This allows obtaining relatively high values simultaneously for the $^3\text{H}_4 \rightarrow ^3\text{F}_4$ and $^3\text{F}_4 \rightarrow ^3\text{H}_6$ emissions. Nevertheless, once the layers are at a separation s below the in-plane separation (i.e., $\leq 1.5 \text{ nm}$) the intensity of both emissions decreases, and the relative intensity of the $^3\text{F}_4 \rightarrow ^3\text{H}_6$ emission

to the ${}^3\text{H}_4 \rightarrow {}^3\text{F}_4$ emission increases. This behavior has been previously reported for Tm^{3+} -doped glasses and was attributed to cross relaxation between Tm^{3+} ions. In this process part of the energy of an ion in the ${}^3\text{H}_4$ level is transferred to another ion in the ground state, thus ending with two ions in the ${}^3\text{F}_4$ level (${}^3\text{H}_4, {}^3\text{H}_6 \rightarrow {}^3\text{F}_4, {}^3\text{F}_4$), as it is represented in the inset of Fig. 1. As a result, the efficiency of the ${}^3\text{H}_4 \rightarrow {}^3\text{F}_4$ emission is reduced in favor of the ${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$ emission. In the case of Tm^{3+} -doped glasses this cross-relaxation process has been shown to be due to a dipole-dipole quenching mechanism in the framework of a limited-diffusion regime. In this regime a critical radius for energy transfer can be defined as the distance at which the probability of the cross-relaxation process becomes equal to the intrinsic decay rate of the metastable ${}^3\text{H}_4$ level; i.e., energy transfer can take place among ions located within this distance. The values for this radius reported for Tm^{3+} -doped systems are 0.73 nm for chalcogenide glasses [12], 1.79 nm for tellurites [13], 0.94 nm for lead niobium germanate glasses [7], and ~ 1.0 nm for LuAG crystals [19]. Therefore, these values are in good agreement with the 1.5 nm critical separation deduced from Fig. 2. The lifetime values for the ${}^3\text{H}_4 \rightarrow {}^3\text{F}_4$ emission have been determined to be $\sim 0.10 \pm 0.05$ ms for the whole range of concentration, that are similar to those reported for Tm^{3+} -doped bulk glasses with similar concentrations [7,8,13].

Concerning the ${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$ emission the observed PL intensity decrease at $s=1.5$ nm ($2.8 \times 10^{20} \text{ cm}^{-3}$) cannot be due to cross relaxation between various excited states. Its lifetime decreases from 0.25 ± 0.05 ms for the low $[\text{Tm}^{3+}]$ region to 0.17 ± 0.05 ms for the high $[\text{Tm}^{3+}]$ region. This suggest that there is a self-concentration quenching owing to nonradiative energy transfer processes that has been attributed to energy diffusion toward impurities and defects in the matrix [7,20]. For germanate glasses the critical concentration for self-quenching has been reported to be $2.88 \times 10^{20} \text{ cm}^{-3}$, which is in good agreement with the value observed in our case (see Fig. 2).

In conclusion, the fact that both the ${}^3\text{H}_4 \rightarrow {}^3\text{F}_4$ and ${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$ emissions have clearly been observed in the $\alpha\text{-Al}_2\text{O}_3$ matrix suggests that $\text{Tm}^{3+}:\text{Al}_2\text{O}_3$ is a very promising material for the development of optical waveguide amplifiers in the range of 1.4–1.7 μm . However, it is necessary to control the concentration quenching due to cross relaxation and energy diffusion to impurities. The present results indicate that such control can be achieved by the choice of a suitable Tm^{3+} – Tm^{3+} layer separation with an appropriate in-plane concentration. For $\alpha\text{-Al}_2\text{O}_3$ the structuring should be designed to have the highest $[\text{Tm}^{3+}]$

while keeping the Tm^{3+} – Tm^{3+} layer separation ≥ 1.5 nm. Nanostructuring the dopant distribution is thus suggested as a promising route toward the development of efficient optical waveguide amplifiers.

This work was supported by Comisión Interministerial de Ciencia y Tecnología (CICYT) (Spain) under project TEC2006-04538-MIC, and by the National Natural Science Foundation of China (grant 10604003), and Beijing Nova Program (grant 2006B15) from Beijing Municipal Science and Technology Commission. We thank I. Vickridge and the collaborative structure around Systeme d'analys por faisceau d'ions rapides (SAFIR) (CNRS and French Ministry of National Education Research and Technology, France) for RBS measurements.

References

1. H. Ennen, J. Schneider, G. Pomrenke, and A. Axmann, *Appl. Phys. Lett.* **43**, 943 (1983).
2. A. Polman, *J. Appl. Phys.* **82**, 1 (1997).
3. W. J. Miniscalco, *J. Lightwave Technol.* **9**, 234 (1991).
4. T. Tsuboi, *J. Electrochem. Soc.* **147**, 1997 (2000).
5. E. R. Taylor, L. N. Ng, N. P. Sessions, and H. Buerger, *J. Appl. Phys.* **92**, 112 (2002).
6. S. Y. Seo, J. H. Shin, B. S. Bae, N. Park, J. J. Penninkhof, and A. Polman, *Appl. Phys. Lett.* **82**, 3445 (2003).
7. R. Balda, J. Fernandez, M. A. Arriandiaga, L. M. Lacha, and J. M. Fernandez-Navarro, *Opt. Mater.* **28**, 1253 (2006).
8. B. G. Aitken, M. J. Dejneka, and M. L. Powley, *J. Non-Cryst. Solids* **349**, 115 (2004).
9. T. Komukai, T. Yamamoto, T. Sugawa, and Y. Miyajima, *IEEE J. Quantum Electron.* **31**, 1880 (1995).
10. M. Naftaly, S. Shen, and A. Jha, *Appl. Opt.* **39**, 4979 (2000).
11. Y. S. Han, J. Heo, and Y. B. Shin, *J. Non-Cryst. Solids* **316**, 302 (2003).
12. A. Sennaroglu, A. Kurt, and G. Ozen, *J. Phys.: Condens. Matter* **16**, 2471 (2004).
13. S. L. Oliveira, S. M. Lima, T. Catunda, L. A. O. Nunes, J. H. Rohling, A. C. Bento, and M. L. Baeso, *Appl. Phys. Lett.* **84**, 359 (2004).
14. G. N. van den Hoven, E. Snoeks, A. Polman, J. W. M. van Uffelen, Y. S. Oei, and M. K. Smit, *Appl. Phys. Lett.* **62**, 3065 (1993).
15. S. K. Lazarouk, A. V. Mudryi, and V. E. Borisenko, *Appl. Phys. Lett.* **73**, 2272 (1998).
16. M. B. Lee, J. H. Lee, B. G. Frederick, and N. V. Richardson, *Surf. Sci.* **448**, L207 (2000).
17. R. Serna, M. J. de Castro, J. A. Chaos, A. Suarez-Garcia, C. N. Afonso, M. Fernandez, and I. Vickridge, *J. Appl. Phys.* **90**, 5120 (2001).
18. Z. Xiao, R. Serna, C. N. Afonso, and I. Vickridge, *Appl. Phys. Lett.* **87**, 111103 (2005).
19. H. Kalaycioglu, A. Sennaroglu, A. Kurt, and G. Ozen, *J. Phys.: Condens. Matter* **19**, 036208 (2007).
20. F. Auzel, G. Baldachini, L. Laversene, and G. Boulon, *Opt. Mater.* **24**, 1003 (2003).