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Improving the photoluminescence response of Er-Tm: Al_2O_3 films by Yb codoping

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Abstract

Amorphous Al_2O_3 films doped with Er, Tm and Yb have been prepared by pulsed laser deposition. A broadband emission in the range 1400–1700 nm with two peaks around 1540 and 1640 nm has been observed, both in the Er-Tm and Er-Tm-Yb codoped films. The Tm-related photoluminescence (PL) intensity at 1640 nm is enhanced when codoping with Yb thus suggesting the existence of multiple energy transfer processes from Yb to Er and Er to Tm. The Er–Tm–Yb codoped film exhibits a broadband emission with a full-width half-maximum of 184 nm similar to that of the film codoped with Tm and Er but having higher Tm to Er concentration ratio and higher PL lifetime values.

Keywords: Broadband emission; Pulsed laser deposition; Energy transfer; Er–Tm–Yb; Al_2O_3

1. Introduction

As a result of the rapid increase in information traffic, there is a demand for broadband optical amplification beyond the conventional band in the range 1530–1600 nm (C + L-band) developed by erbium-doped amplifiers. In order to fully utilize the 1.4–1.7 μm low-loss band of silica-based optical fibres, bands at 1440–1530 nm (S band) and 1625–1675 nm (U-band) are being explored [1,2]. One possible approach is to exploit photoluminescence (PL) from more than one kind of rare-earth (RE) ion in a single device. Tm^{3+} has emission bands around 1.47 μm and 1.6–2.1 μm and thus is promising to complement Er^{3+} emission at 1.54 μm [3,4]. Significant effort is thus being invested to study Tm-doped materials for future near infrared light sources and amplifiers.

Recently, we have reported a broad emission band in the wavelength range of 1.4–1.7 μm from Er–Tm codoped amorphous Al_2O_3. It was found that the higher the Tm concentration the lower the intensity and lifetime of Er^{3+} related emission at 1540 nm as a result of energy transfer from Er^{3+} to Tm^{3+} [5]. The Yb to Er energy transfer has extensively been studied, and improvements of up two orders of magnitude in the Er-related emission of Er–Yb codoped films with respect to Er only doped films have been reported [6]. The aim of this work is to investigate Yb codoping as a means to improve Er- and Tm-related emission as well as to investigate possible multiple energy transfer processes among Yb^{3+}, Er^{3+} and Tm^{3+}.

2. Experimental

An ArF excimer laser ($\lambda = 193$ nm, $\tau = 20$ ns full-width half-maximum (FWHM), 2 J cm^{-2}) was used to ablate independently and sequentially the Al_2O_3 and RE targets. The films were designed to have a total thickness of 300 nm and consist of alternate "layers" of RE and host. The Er–Er in-depth separation was designed to be constant and equal to 6 nm for all studied films since it has been shown that this distance provides an optimum PL performance [7]. A reference film only doped with Tm and having Tm–Tm in-depth separation of 2 nm has also been

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produced. The Er–Tm codoped films have been produced by alternating the deposition of Er and Tm according to the sequence $[Er/(Al_2O_3/Tm) \times n/Al_2O_3]$ and repeating it 50 times, where n is the number of Tm layers inserted between two Er layers that was either 1 or 2. Further details on the deposition procedure can be found elsewhere [5]. The Er–Tm–Yb codoped film was produced by substituting one Tm layer in the Er–Tm codoped film with $n = 2$ by one Yb layer. The in-depth separation of Er–Tm, Er–Yb, Tm–Yb and Tm–Tm (for $n = 2$) is thus 2 nm in all cases.

The RE concentration and overall in-depth profile distribution have been measured by Rutherford back-scattering spectrometry (RBS) using a 2.0 MeV He^+ beam and a scattering angle of 165°. From the RBS analysis it is shown that the total projected Er areal density for the Er only doped film is $\sim 2.2 \times 10^{15}\,cm^{-2}$, which is also valid for all codoped films. The *average* Er concentration in all studied films has been determined from the measured areal density and the measured thickness, and resulted to be $7.2 \times 10^{19}\,cm^{-3}$. Er–Tm codoped films have an *average* Tm concentration of $7.2 \times 10^{19}\,cm^{-3}$ ($n = 1$) or $1.4 \times 10^{20}\,cm^{-3}$ ($n = 2$), corresponding to Tm to Er concentration ratios ([Tm]/[Er]) of 1 or 2. The Er–Tm–Yb codoped film has Er, Tm and Yb concentrations of $7.2 \times 10^{19}\,cm^{-3}$ and thus [Tm]/[Er] = 1.

After deposition, all films were annealed at 650 °C f or 1 h in air. PL measurements were performed at room temperature using a single grating monochromator (focal length 250 mm) with a wavelength resolution of 8 nm, a liquid-nitrogen-cooled Ge detector and standard lock-in techniques. The luminescence decay curves were averaged and recorded with a digital oscilloscope. Further details of the experimental set-up can be found elsewhere [6,7].

3. Results and discussion

Excitation spectroscopy has first been performed by using 800 mW of a Ti: sapphire laser. The highest PL efficiency in the 1400–1700 nm range has been achieved when pumping at 794 nm for the Er–Tm codoped films. This wavelength is thus selected for the PL studies presented from now on. Fig. 1 shows a schematic representation of the energy levels for Er^{3+}, Tm^{3+} and Yb^{3+}. Note that the levels for the Tm^{3+} are indicated following the notation of Carnall et al. [8], which means that the $^3H_4$ is the highest energy level. The 794 nm wavelength thus corresponds to the $^3H_6$ to $^3H_4$ and $^4I_{15/2}$ to $^4I_{9/2}$ transitions of Tm^{3+} and Er^{3+}, respectively, though it does not match the transition $^4F_{5/2}$ to $^4F_{7/2}$ of Yb^{3+} ions. The selected wavelength is thus optimum for efficiently pumping the PL of Tm^{3+} and Er^{3+}.

Fig. 2 shows the PL spectra of all studied films. The Er only doped film shows the characteristic Er^{3+} emission peaking at 1540 nm related to the $^4I_{13/2}$–$^4I_{15/2}$ transition from the first excited state to the ground state. The Tm only doped film exhibits two broad emission bands peaking

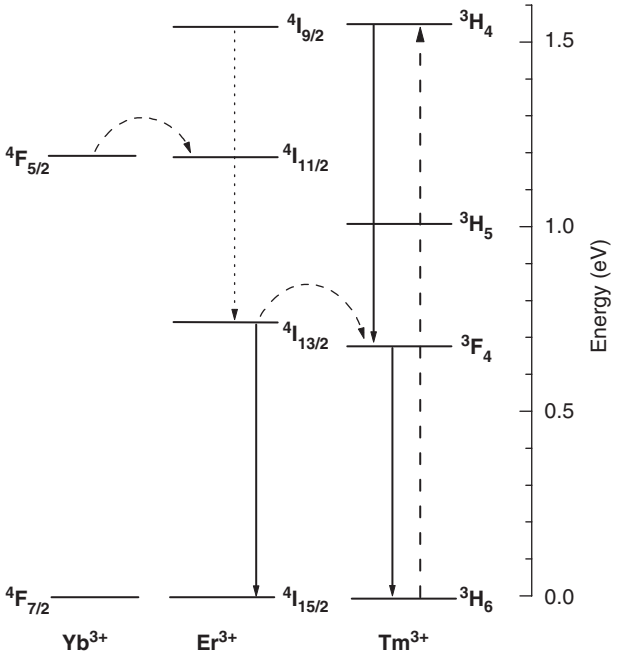

Fig. 1. Energy-level diagram of Er^{3+}, Tm^{3+} and Yb^{3+} ions.

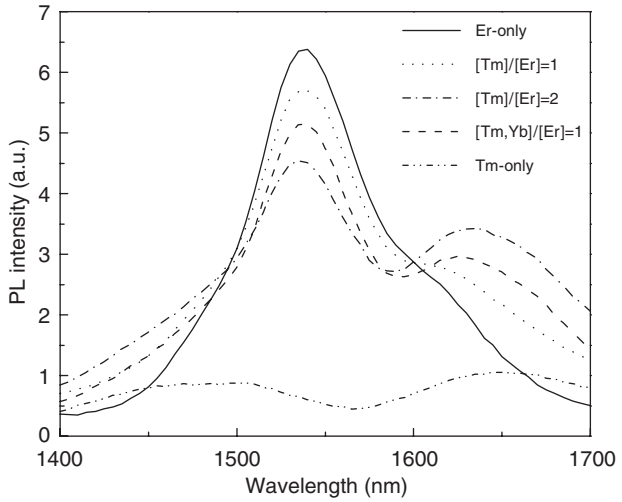

Fig. 2. PL spectra for amorphous Al_2O_3 films codoped with Er–Tm and Er–Tm–Yb. The spectra for Er and Tm only doped films are included for reference.

at 1480 and 1640 nm. The former is most likely originated from the $^3H_4$–$^3F_4$ transition, which is usually quenched in high phonon energy host materials such as silica glass ($\sim 1100\,cm^{-1}$) due to its small energy gap with the lower level $^3H_5$ (see energy level diagram in Fig. 1) [9]. The presence of the 1480 nm emission thus evidences the relatively low phonon energy ($< 870\,cm^{-1}$) of the Al_2O_3 host used in this work [10]. The band peaking at 1640 nm is most likely related to the high energy side of the $^3F_4$–$^3H_6$ transition. This transition usually results in a broad emission band that peaks around 1800 nm, the specific wavelength being dependent on the specific host material.

Recently, emission at wavelength as short as 1630 nm has been reported for a Tm doped fluorine crystal [11]. The observation of emission at relatively shorter wavelengths is consistent with the fact that Tm^{3+} has a strong coupling to its surroundings, resulting in transitions that have a particularly large inhomogeneous broadening.

The spectra in Fig. 2 corresponding to the Er–Tm and Er–Tm–Yb codoped films show a broadband emission with two peaks at 1540 nm and 1640 nm, most likely related to Er and Tm emissions, respectively. In addition, the codoped films show an enhancement of the PL intensity in the region 1400–1500 nm with respect to that of the film only doped with Er. Fig. 3 shows the evolution of the PL intensity at the two peaks observed in the codoped films as a function of the Tm to Er concentration ratio. Whereas the Er related PL intensity at 1540 nm decreases with the increase of the Tm to Er concentration ratio, the Tm related PL intensity at 1640 nm increases. The Er–Tm–Yb codoped film that has [Tm]/[Er] = 1 exhibits a PL intensity at 1540 nm lower than that of the Er only doped film and the Er–Tm co-doped film with the same Tm to Er concentration ratio. The opposite behaviour is seen for the Tm-related PL intensity at 1640 nm that is higher than in the films with no Yb. When the PL intensity of the Er–Tm–Yb film is compared to that of the Er–Tm film with the highest Tm to Er concentration ratio ([Tm]/[Er] = 2), the situation is reversed since the intensity of the Er related and Tm-related PL becomes lower and higher, respectively, in the Er–Tm–Yb film.

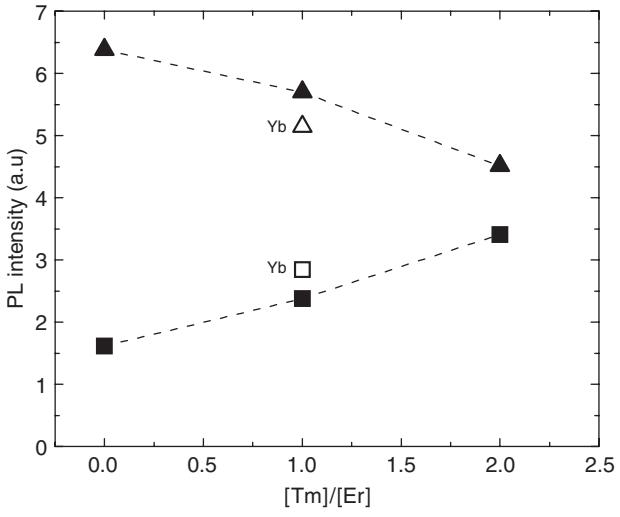

Fig. 3. PL intensity at 1540 nm (△, ▲) and 1640 nm (□, ■) for Er–Tm (▲, ■) and Er–Tm–Yb (△ ,□) codoped films as a function of Tm to Er concentration ratio. The data at [Tm]/[Er] = 0 refer to (▲) Er and (■) Tm only doped films.

To understand these results it is necessary to review the possible energy transfer processes among ions that can be taking place. The comparison of results for the Er only doped film and the Er–Tm codoped films clearly evidences the existence of energy transfer from Er^{3+} to Tm^{3+}. The energy-level diagram of Er^{3+} and Tm^{3+} in Fig. 1 shows that the $^4I_{13/2}$ level of Er^{3+} has a small energy mismatch ($\sim$0.1 eV$\equiv$806 cm^{-1}) with the $^3F_4$ level of Tm^{3+} thus making possible a phonon-assisted energy transfer. This implies that once Er^{3+} is excited to the $^4I_{9/2}$, they decay nonradiatively to the $^4I_{13/2}$ level. From this level, Er^{3+} can decay radiatively or transfer their energy to the $^3F_4$ level of neighbouring Tm^{3+}. If the latter occurs, Tm^{3+} can then decay radiatively giving rise to an enhancement of the 1640 nm PL intensity. This process necessarily involves a reduction of Er^{3+}- related emission at 1540 nm and an increase of Tm^{3+}-related emission at 1640 nm as is indeed observed in Figs. 2 and 3.

It is well known that energy transfer between Yb^{3+} and Er^{3+} is very efficient since the $^2F_{5/2}$ level of Yb^{3+} is resonant in energy with the $^4I_{11/2}$ level of Er^{3+}. In the present study the Er^{3+}-related emission at 1540 nm of the Er–Tm–Yb codoped film is smaller than that of the Er-Tm codoped film having the same Tm to Er concentration ratio while the Tm^{3+}-related emission at 1640 nm is higher. These results suggest the existence of multiple energy transfer processes involving the transfer from Yb^{3+} to Er^{3+}, as well as the transfer from Er^{3+} to Tm^{3+}. From the spectra of Fig. 2, it seems that the energy transfer efficiency between Er^{3+} and Tm^{3+} has been enhanced by the presence of Yb^{3+} at the expense of the Er^{3+} radiative decay at 1540 nm, although the mechanism is not completely clear.

Table 1 includes lifetime values at the peak wavelengths and FWHM of the PL emission bands of all the studied films. It is seen that PL lifetimes of the Er–Tm–Yb codoped film are higher than those of the films having the highest Tm to Er concentration ratio ([Tm]/[Er] = 2), but shorter than the films having the same concentration ratio ([Tm]/[Er] = 1). Since multiple energy transfer processes are involved, the understanding of this result is not straightforward and a more detailed analysis of the decay time as a function of the relative RE ion concentration is necessary.

Table 1
Tm to Er concentration ratio ([Tm]/[Er]), PL lifetime τ for the Er^{3+} (1540 nm) and Tm^{3+} (1640 nm) related emissions and FWHM of the PL for amorphous Al_2O_3 films doped only with Er or Tm, and codoped with Er–Tm and Er–Tm–Yb codoped thin films

Type of film	Er/Tm-only	Er–Tm codoped	Er–Tm codoped	Er–Tm–Yb codoped ([Yb]/[Er] = 1)
[Tm]/[Er]	—	1	2	1
τ[1540 nm] (ms)	3.42	2.62	1.22	1.55
τ[1640 nm] (ms)	0.29	1.65	0.85	1.02
FWHM (nm)	—	125	186	184

The FWHM is seen to increase both as the Tm to Er concentration ratio increases or upon co-doping to Yb while keeping the Tm to Er concentration ratio low. This result is very promising for achieving an optimized PL in a broad range with high pumping efficiencies.

4. Conclusions

Single or multiply Er, Tm or Yb amorphous Al_2O_3 doped films have successfully been prepared by pulsed laser deposition. A broadband emission in the range 1400–1700 nm is obtained when codoping with Er–Tm and Er–Tm–Yb that is related to energy transfer processes from Er^{3+} to Tm^{3+} ions. In the Er–Tm codoped films this energy transfer is responsible for the increase of the Tm^{3+}-related emission at the expense of the Er^{3+}-related emission. This situation is improved by Yb codoping since higher lifetime values are achieved while keeping PL intensity and FWHM values around optimum values. These results provide evidence for the existence of multiple energy transfer mechanisms among Er^{3+}, Tm^{3+} and Yb^{3+}. The results also show that Yb codoping is a potential method to improve the broadband emission properties related to Er^{3+} and Tm^{3+} in amorphous Al_2O_3 hosts.

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