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Broadband infrared emission from Er–Tm:Al₂O₃ thin films

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Thin films of amorphous aluminum oxide (Al₂O₃) co-doped with Er³⁺ and Tm³⁺ have been synthesized by alternate pulsed laser deposition. When pumped at 794 nm a broad emission band over 1400–1700 nm is observed. Two peaks related to the 1540 nm band from Er³⁺ and to the 1640 nm band from Tm³⁺ are clearly distinguished. The photoluminescence intensity ratio of the 1640–1540 nm emissions has been controlled by modifying the Tm concentration. A spectrum with a fairly flat profile and a full width at half maximum of 230 nm is obtained for an Er concentration of $7.2 \times 10^{19} \text{ cm}^{-3}$ and a [Tm]/[Er] concentration ratio of 3. It is found that the Er³⁺ to Tm³⁺ energy transfer processes play an important role in the definition of the luminescent response. The large width of the emission band and the excellent optical and thermomechanical properties of the Er–Tm co-doped Al₂O₃ signal this system as a potential candidate for the development of broadband integrated optical amplifiers. © 2005 American Institute of Physics. [DOI: 10.1063/1.2040005]

As a result of the rapid increase in information traffic there is a demand for broadband optical amplification beyond the conventional band of 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 fibers, the bands at 1440–1530 nm (S band) and 1625–1675 nm (U band) are being explored.^{1,2} Thulium is promising as a complement to Er³⁺ due to its emission bands around 1.4–1.5 μm and 1.6–1.8 μm.^{3,4} Therefore the Tm doping and Er–Tm co-doping have been studied for materials suitable both for fiber^{3–4} and thin film^{5,6} devices. However, silica and most silica based glasses are not as suitable for Tm-gain devices as they are for Er ones. This is due to the fact that the transition Tm³⁺:³H₄–³F₄ leading to the emission around 1.47 μm suffers appreciable multiphonon deexcitation because of the relative high maximum phonon energy (~1100 cm⁻¹) of these glasses.^{3,7} Therefore significant effort has been directed to the research of Tm-doped fluorides due to the low phonon energies of these materials (~580 cm⁻¹). But considering the rather poor chemical durability of most halide glasses, the development of more robust oxide glasses with sufficiently low maximum phonon energy is necessary. For this reason tellurite⁵ and more recently aluminate⁸ glasses have been explored.

The aim of this work is to demonstrate how a very broad and flat emission band in the spectral region 1400–1700 nm can be achieved from Er–Tm co-doped amorphous Al₂O₃ thin films by adequately controlling the Er and Tm concentration ratio. Amorphous aluminum oxide (Al₂O₃) is a promising material for thin film applications due to its high thermal conductivity, excellent mechanical properties, and a wide range of transparency. In addition, amorphous Al₂O₃ shows moderate maximum phonon energy (~870 cm⁻¹).⁹ In our previous works we have shown that alternate pulsed laser deposition (PLD) from the host

(Al₂O₃) and dopant rare earth (RE) targets can be used to obtain artificial structures in which the RE concentration and ion distribution are controlled.^{10,11}

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 Al₂O₃ and RE targets. The films were designed to have a 300 nm total thickness. They were deposited in a multilayer-like structure by alternating the growth of Al₂O₃ layers with the deposit of Er and Tm dopants, following the sequence [Er/(Al₂O₃/Tm) × n/Al₂O₃] 50 times, where **n** is the number of Tm-doped layers inserted between two Er-doped layers. Figure 1(a) shows schematically the structure

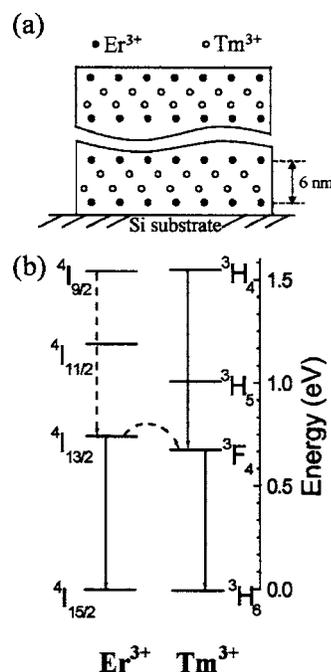


FIG. 1. (a) Schematic structure of the Er–Tm co-doped Al₂O₃ thin films with **n**=2 prepared by alternate PLD of Er, Tm, and Al₂O₃; (b) energy-level diagram of Er³⁺ and Tm³⁺ ions.

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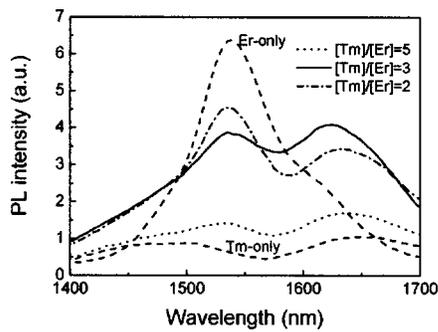


FIG. 2. PL spectra for Er-Tm co-doped Al_2O_3 films with $[\text{Tm}]/[\text{Er}]$ concentration ratios of 2, 3, and 5. As reference the spectra for Er-only and Tm-only doped films are shown. The spectra are not corrected for the detector response.

of the films. The Er-Er in-depth separation was designed to be constant and equal to 6 nm both for the Er-only doped film and the Er-Tm co-doped films. This Er-Er in-depth separation was chosen since in our earlier works we have shown that this distance allows an optimum photoluminescence (PL).¹¹ The number n of Tm-doped layers that were inserted between two Er-doped layers was varied from 1 to 5. In addition a Tm-only doped film was prepared with a Tm-Tm in-depth separation of 1.5 nm. Figure 1(b) shows a schematic representation of the energy levels for Er^{3+} and Tm^{3+} .¹²

The RE concentration and overall in-depth profile distribution were measured by Rutherford backscattering 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 $\sim 2.2 \times 10^{15} \text{ cm}^{-2}$, which is also valid for all the co-doped films. The average Er concentration in the film can be determined from the measured areal density and the measured thickness, and it is $7.2 \times 10^{19} \text{ cm}^{-3}$. By changing the number n of Tm-doped layers, the total areal density of Tm has been varied from 2.2×10^{15} to $1.1 \times 10^{16} \text{ cm}^{-2}$, corresponding to a Tm to Er concentration ratios ($[\text{Tm}]/[\text{Er}]$) of 1, 2, 3, and 5. The average Tm concentration in the Er-Tm co-doped films is between $7.2 \times 10^{19} \text{ cm}^{-3}$ ($n=1$) and $3.6 \times 10^{20} \text{ cm}^{-3}$ ($n=5$), and in the Tm-only doped film is $2.9 \times 10^{20} \text{ cm}^{-3}$.

After deposition the films were annealed at 650°C for 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. Excitation spectroscopy analysis was performed using a Ti:sapphire laser (power 800 mW), and the PL wavelength was fixed at 1480 nm, corresponding to the ${}^3\text{H}_4-{}^3\text{F}_4$ transition. Since the highest PL intensity was found for pumping at 794 nm in the following this wavelength was used for excitation. This result is consistent with earlier works on Tm-doped silica fibers.¹³ Note that this wavelength also overlaps with the absorption band of the Er^{3+} transition ${}^4\text{I}_{15/2}-{}^4\text{I}_{9/2}$ and therefore both Er^{3+} and Tm^{3+} can be pumped simultaneously at this wavelength.

Figure 2 shows the spectra for the Er-only doped, the Tm-only doped and three Er-Tm co-doped films. The spectrum for the Er-only doped film shows the characteristic Er^{3+} emission peak at 1540 nm due to the ${}^4\text{I}_{13/2}-{}^4\text{I}_{15/2}$ transition. The bandwidth is of 80 nm, slightly higher than that previ-

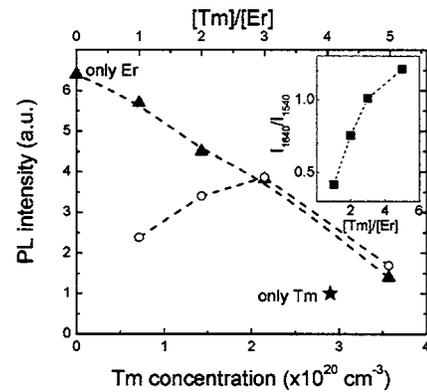


FIG. 3. PL intensity at 1540 nm (\blacktriangle) and 1640 nm (\circ) for the Er-Tm co-doped Al_2O_3 films as a function of the Tm concentration (bottom axis) and as a function of the $[\text{Tm}]/[\text{Er}]$ concentration ratio (top axis). The PL intensity at 1640 nm for the Tm-only doped film (\star) is included for reference. The inset shows the 1640 to 1540 nm PL intensity ratio as a function of the $[\text{Tm}]/[\text{Er}]$ concentration ratio.

ously reported for Er-doped Al_2O_3 .¹⁴ This is in part due to the lower resolution used for these measurements, and in part to the lower annealing temperature used for this study that yields to a broadening of the transition. The spectrum for the Tm-only doped film shows two broad emission bands centered at 1480 and 1640 nm. The 1480 nm peak, as discussed before, is originated from the ${}^3\text{H}_4-{}^3\text{F}_4$ transition. At this point it is interesting to note that for Tm^{3+} due to the presence of the intervening ${}^3\text{H}_5$ level that has an energy gap with the upper ${}^3\text{H}_4$ level of only about 4400 cm^{-1} and the desired ${}^3\text{H}_4-{}^3\text{F}_4$ transition suffers appreciable multiphonon deexcitation when Tm is doped into glasses with high maximum phonon energy.⁸ A glass host with maximum phonon energy of 880 cm^{-1} , corresponding to the exchange of five phonons, is expected to be suited for high luminescence quantum efficiency.^{4,6,8} In the case of amorphous Al_2O_3 a phonon energy spectrum has been reported with maximum phonon energy value of 870 cm^{-1} ,¹⁰ which is consistent with the clear observation of the 1480 nm emission in Fig. 2. The 1640 nm emission can be assigned to the short wavelength band edge emission of the transition from the ${}^3\text{F}_4$ multiplet to the ${}^3\text{H}_6$ multiplet [Fig. 1(b)]. The emission at this wavelength has been observed in both crystalline and amorphous hosts.^{13,15,16} Note that the peak emission for this band is around 1800 nm, which is out of the range of this study.

The Er-Tm co-doped films show a broad PL band in the $1.4-1.7 \mu\text{m}$ region (Fig. 2), with two peaks centered at around 1540 and 1640 nm. This broadband is the result of the simultaneous emission of both Er^{3+} and Tm^{3+} . For the co-doped films the typical Er^{3+} spectrum has been modified first by an intensity enhancement in the region of 1400–1500 nm, and second by the emergence of a peak at 1640 nm. For the film with $[\text{Tm}]/[\text{Er}]$ ratio of 3 the spectrum is fairly flat over all the emission range FWHM of 230 nm. This value is quite high compared to the 90 nm bandwidth recently reported for an Er-Tm co-doped silica fiber.¹⁷

Figure 3 shows the evolution of the PL intensity of the two peaks as a function of the Tm concentration in the films. The PL intensity at 1540 nm measured for the Er-only doped film is shown on the left axis, corresponding to $[\text{Tm}]=0$. The PL intensity at 1640 nm measured for the Tm-only doped film is shown with a star. It can be seen that for all the Er-Tm co-doped films the PL intensity at 1540 nm is re-

duced with respect to that of the Er-only doped film. The decrease of the 1540 nm PL intensity is nearly linear with the increase of Tm concentration. However, the Tm^{3+} PL intensity at 1640 nm for all the Er–Tm co-doped films is always higher than that of the Tm-only doped film, and it increases when the Tm concentration increases up to $2.2 \times 10^{20} \text{ cm}^{-3}$, and then decreases for the highest studied concentration $[\text{Tm}]/[\text{Er}]=5$, and $3.6 \times 10^{20} \text{ cm}^{-3}$. In Fig. 2 for this high Tm concentration there is also a reduction of the PL intensity for the emission around 1480 nm. This PL intensity decrease is most likely due to concentration quenching originated from energy transfer between Tm^{3+} ions.¹⁸ The inset in Fig. 3 shows that the PL intensity ratio of the 1640 nm to the 1540 emission increases as the $[\text{Tm}]/[\text{Er}]$ ratio increases.

To understand the observed results it is necessary to assume that an energy transfer process takes place between Er^{3+} and Tm^{3+} . From the energy-level diagram of Er^{3+} and Tm^{3+} ions in Fig. 1(b) it can be observed that the Er^{3+} level $^4I_{13/2}$ has a small energy mismatch ($\sim 0.1 \text{ eV} \equiv 806 \text{ cm}^{-1}$) with the Tm^{3+} level 3F_4 thus allowing a phonon assisted energy transfer. This implies that once the Er^{3+} ions are excited to the $^4I_{9/2}$ they decay nonradiatively to the $^4I_{13/2}$ and they can transfer the energy to the 3F_4 level of a neighboring Tm^{3+} , which then can decay radiatively giving rise to an enhancement of the 1640 nm PL intensity. Note that this Er^{3+} to Tm^{3+} energy transfer process seems to dominate even for high Tm concentrations, since for $[\text{Tm}]/[\text{Er}]=5$ the PL intensity of Tm^{3+} at 1640 nm keeps increasing at the expense of the PL intensity of Er^{3+} at 1540 nm. For Er–Tm co-doped silica materials another energy transfer process has been reported, namely the energy transfer from the Er^{3+} $^4I_{13/2}$ level to the Tm^{3+} 3H_4 level, after which either Tm^{3+} ions decay radiatively to 3F_4 resulting in an enhancement of the 1480 nm emission or Tm^{3+} ions decay nonradiatively because of the strong multiphonon effects in high phonon energy materials.⁷ In our present experiments the overlapping of the 1480 nm band with the high intensity of the Er^{3+} -related 1540 nm peak prevents a quantitative assessment of a possible 1480 nm intensity enhancement. Finally, regarding the nature of the energy exchange between Er^{3+} and Tm^{3+} , it is expected to be of dipolar nature, and therefore to follow a R^{-6} dependence, where R is the ions distance. At present, with the samples designed for this work, it is not straightforward to clearly separate the role played by the Er–Tm distance from the concentration effects. Work to design samples in which the $[\text{Tm}]/[\text{Er}]$ concentration is constant and only changes the Er–Tm layer separation is under way.

Further evidence of the Er^{3+} to Tm^{3+} energy transfer from the Er^{3+} $^4I_{13/2}$ level to the Tm^{3+} 3F_4 level is found when comparing the lifetimes measured for these films. The PL lifetime for the Er–Tm co-doped film with $[\text{Tm}]/[\text{Er}]=3$ at 1540 nm is 0.72 ms and at 1640 nm is 0.54 ms. For the Er-only doped film the PL lifetime at 1540 nm is 3.42 ms, and for the Tm-only doped film the PL lifetime at 1640 nm is 0.29 ms. Therefore in the co-doped film the lifetime of the

Tm^{3+} related transition has increased by almost a factor of 2, whereas that of the Er^{3+} has been reduced by almost a factor of 5 as a result of the Er^{3+} to Tm^{3+} energy transfer process. Therefore Er^{3+} is acting as a sensitizer for Tm^{3+} as well as a light emitter itself.

In conclusion, we have prepared Er–Tm co-doped amorphous Al_2O_3 thin films by PLD that under 794 nm excitation show a broad emission band for the wavelength range of 1.4–1.7 μm . It is shown that for a $[\text{Tm}]/[\text{Er}]$ ratio of 3 a fairly flat band with a FWHM of 230 nm is obtained. The band is composed of the 1480 and 1640 nm emissions from Tm^{3+} , and the 1540 nm emission from Er^{3+} . The results evidence energy transfer from Er^{3+} to Tm^{3+} which can be used to tailor the PL response. Further studies are necessary to optimize the concentration and distribution of the dopants in order to tune the energy exchange interaction between ions and to obtain higher PL efficiencies. The obtained results suggest that the Er–Tm: Al_2O_3 system is a potential candidate for the development of integrated waveguide broad gain devices.

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