



Up-conversion fluorescence spectroscopy in $\text{Er}^{3+}:\text{TiO}_2$ planar waveguides prepared by a sol–gel process

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Abstract

The up-conversion of infrared radiation into blue, green and red fluorescences has been investigated for erbium-doped titanium dioxide (TiO_2) optical planar waveguides. These waveguides have been prepared by a sol–gel process and a dip-coating technique. The lifetime measurements of the $^4\text{S}_{3/2}$ level (green fluorescence) were performed using a pulsed excimer-pumped dye laser operating at 650 nm. They were found to depend strongly on the Er^{3+} ion concentration.

1. Introduction

The production of visible and UV light via ‘frequency up-conversion’ phenomena of rare earth ions in solids, pumped with near infrared radiation is currently an active research area. Furthermore, the use of planar waveguides structures may lead to the achievement of compact and reliable all solid-state laser sources across the visible and near UV spectrum for integrated-optics. Up to now, visible up-conversion lasing at room temperature has already been achieved in bulk crystals doped with rare-earth ions such as $\text{Tm}^{3+}:\text{BaYbF}_8$ [1], $\text{Er}^{3+}:\text{YLF}$ [2], $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ [3] and in various rare-earth doped fluorozirconate fibers [4,5].

Recently, we have reported on the fluorescence around 1.53 μm of $\text{Er}^{3+}:\text{TiO}_2$ waveguides [6]. In this paper, we report on the first observation of blue, green and red up-conversion fluorescences in $\text{Er}^{3+}:\text{TiO}_2$ optical planar waveguides prepared by a sol–gel process and a dip-coating technique. Section 2 describes the sol–gel process employed to prepare $\text{Er}^{3+}:\text{TiO}_2$ waveguides. The experimental results are presented in Section 3.

2. Experiment

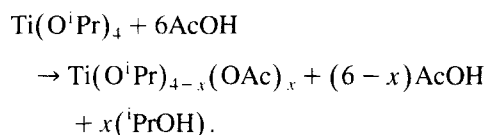
2.1. Waveguide preparation

2.1.1. Sol preparation

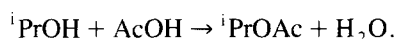
The TiO_2 sol was prepared using titanium isopropoxide ($\text{Ti}(\text{O}^i\text{Pr})_4$ -Aldrich), isopropanol ($(^i\text{PrOH})$ -Merck) and acetic acid ((AcOH) -Prolabo)

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with a molar ratio $\text{AcOH}/\text{Ti} = 6$. At first, the titanium isopropoxide was mixed with acetic acid which acts as a modifier following an exothermic reaction:



The modified titanium alkoxide $(\text{Ti}(\text{O}^i\text{Pr})_{4-x}(\text{OAc})_x)$ has a lower hydrolysis/condensation rate which enhances the possibility of obtaining stable and clear sol for a dip-coating process. Reaction was allowed to continue for 1 h under vigorous stirring. In the second step, we add the isopropanol ($^i\text{PrOH}$) which reacts with acetic acid to generate water in situ by an homogeneous esterification reaction:



In this case, each molecule of the modified alkoxide is coordinated with an uniform distribution of reactant water molecules, thus enabling uniform hydrolysis and polymerisation to take place. The mixture was stirred for 1 h before use. The solution obtained is clear and its viscosity is adjusted by adding methyl alcohol. Er^{3+} ions were introduced by adding $\text{Er}(\text{NO}_3)_3$ in a molar ratio $\text{Er}(\text{NO}_3)_3/\text{Ti} = x$ (x ranges from 0.2 to 15 mol%). The solution obtained was filtered on a $0.2 \mu\text{m}$ Millipore filter and remains stable for four days which is long

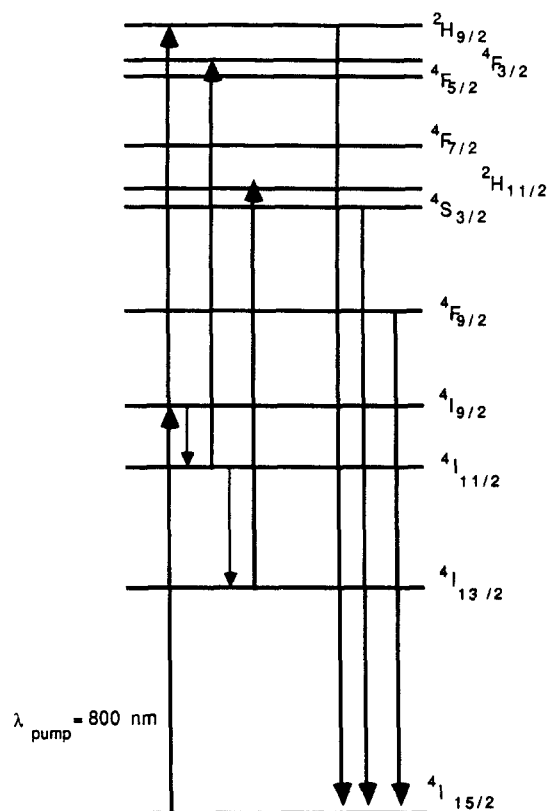


Fig. 2. Energy-level diagram and mechanisms of two-step excitation for the Er^{3+} ion under 800 nm excitation.

enough for a multiple dip-coating process. All these operations were performed at room temperature.

2.1.2. Film formation

The $\text{Er}^{3+}:\text{TiO}_2$ waveguides sol-gel are synthesized in thin films on pyrex substrates ($75 \times 25 \text{ mm}^2$) deposited by the standard dip-coating technique [6]. Indeed, pyrex substrates were carefully cleaned, then immersed into the mixture and withdrawn from the bath at a rate of 40 mm/min . The $\text{Er}^{3+}:\text{TiO}_2$ films obtained are first dried at 100°C for 15 min and then heated in the oven at 600°C under a constant flow of pure and dry oxygen for 1 h. The resulting films are $d \approx 80 \text{ nm}$ thick and their refractive index ranges from 1.8 to 2.1 depending on the annealing temperature. Such a single film is a monomode waveguide for wavelengths in the visible region and has losses less than 1 dB/cm at 632.8

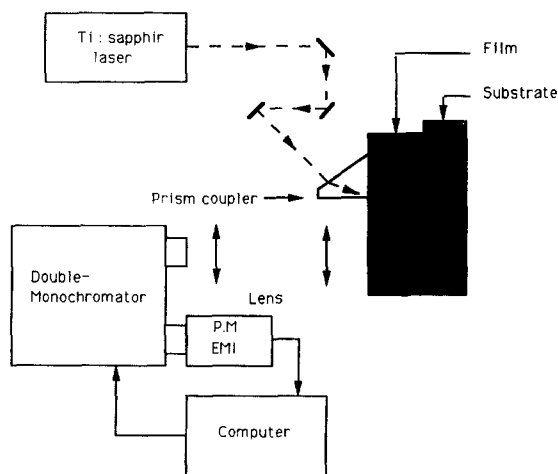
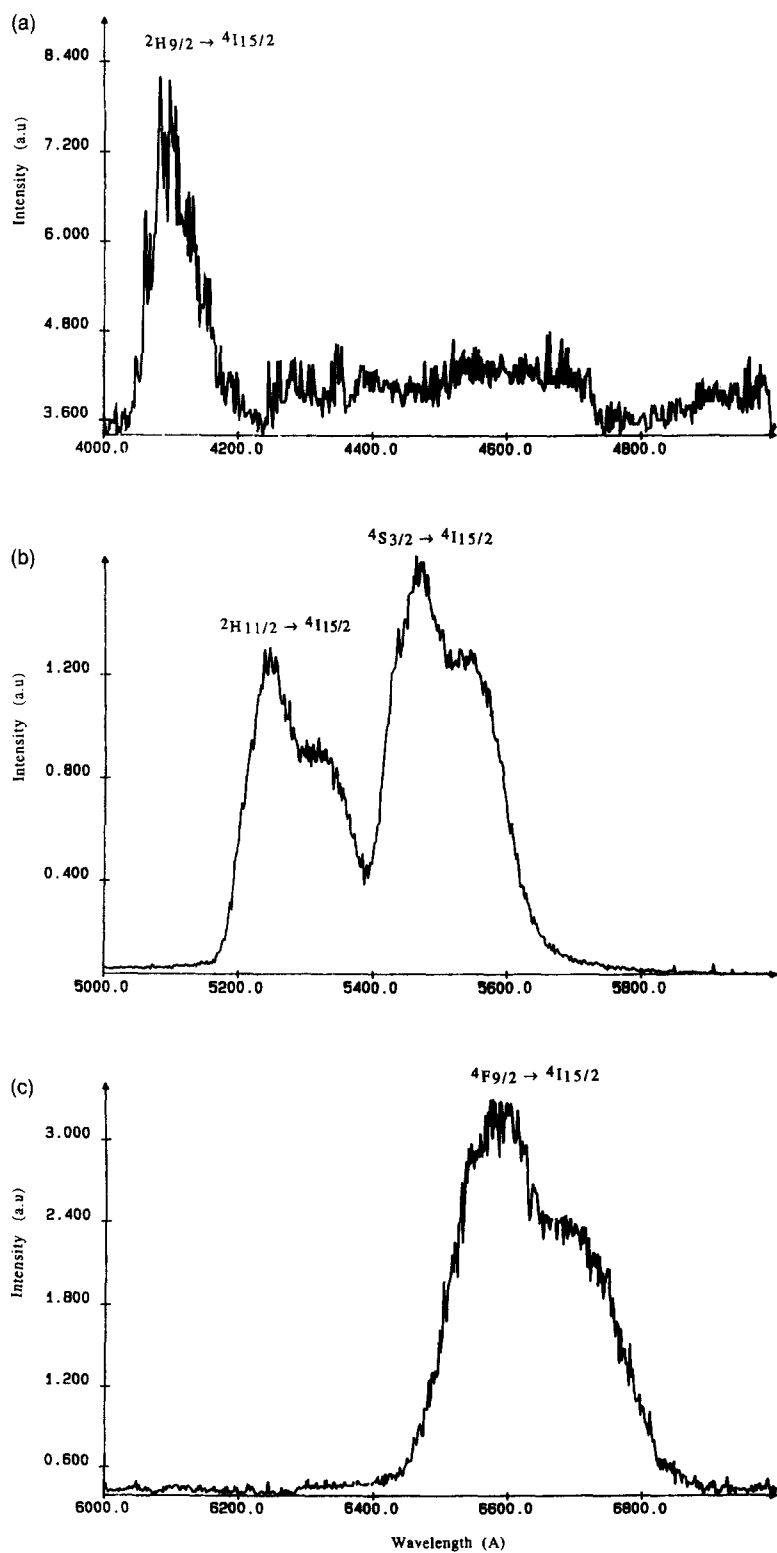


Fig. 1. Experimental setup.



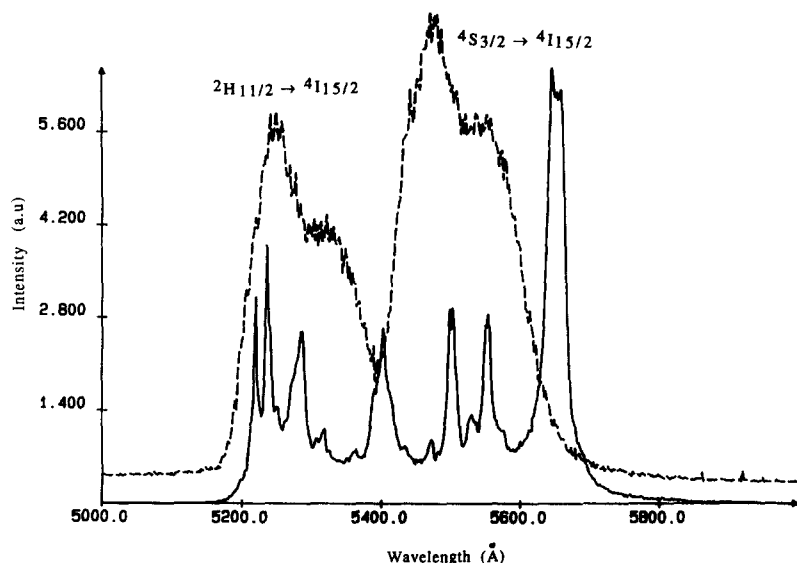


Fig. 4. Up-conversion fluorescence spectra of $\text{Er}^{3+}:\text{TiO}_2$ waveguides obtained by excitation in the $^4\text{I}_{9/2}$ state ($\lambda_{\text{exc}} = 800 \text{ nm}$) for: (a) 15 mol% $\text{Er}^{3+}:\text{TiO}_2$ (dashed-line); and (b) 0.5 mol% $\text{Er}^{3+}:\text{TiO}_2$ (solid-line).

nm. The film composition was established using the Rutherford backscattering (RBS) technique.

2.2. Experimental setup

The up-conversion fluorescence spectra were monitored by using experimental apparatus shown in Fig. 1. A Ti:sapphire laser tuned to 800 nm was used as the excitation source. The pump beam is coupled into the film using a glass prism (refractive index = 2). The light emitted at $\pi/2$ rad from the waveguide was analyzed with a double-monochromator (Jobin-Yvon U-1000) and detected with a photomultiplier (EMI 9863B) cooled at -30°C . The spectral resolution ranged from 1 to 2 Å.

Raman spectra were recorded with the same experimental configuration as shown in Fig. 1 except for the Ti:sapphire laser which was replaced by a krypton laser ($\lambda = 676 \text{ nm}$).

The lifetime measurements were performed using a pulsed excimer-pumped dye laser (Lumonics, model Hyperdye 300), which delivers pulses of 10 ns duration and 0.1 cm^{-1} spectral width. The fluores-

cences up to 800 nm were analyzed with a 1 m monochromator, detected by a fast response AsGa photomultiplier (RCA 31084) and the signal fed a multichannel analyzer (Canberra) for the lifetime data. All the experiments were made at room temperature.

3. Results

When a single cw excitation laser is tuned to a strong absorption, $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{9/2}$, of Er^{3+} ions ($\lambda \approx 800 \text{ nm}$), blue, green and red fluorescences from the $^2\text{H}_{9/2}$, ($^2\text{H}_{11/2} + ^4\text{S}_{3/2}$), and $^4\text{F}_{9/2}$ levels, respectively, are observed. The mechanisms for populating these states are shown schematically in Fig. 2. In the first step, the Er^{3+} ion is pumped to the $^4\text{I}_{9/2}$ excited state, from this level the excitation decays through non-radiative processes into the $^4\text{I}_{11/2}$ metastable level and subsequently to the $^4\text{I}_{13/2}$ metastable state. In the second step, the excited absorption transitions near 800 nm from $^4\text{I}_{9/2}$ and both metastable levels, $^4\text{I}_{11/2}$ and $^4\text{I}_{13/2}$, populate

Fig. 3. Up-conversion fluorescence spectra of $\text{Er}^{3+}:\text{TiO}_2$ waveguides obtained by excitation in the $^4\text{I}_{9/2}$ state ($\lambda_{\text{exc}} = 800 \text{ nm}$) for 15 mol% Er^{3+} ion concentration.

the upper levels, $^2H_{9/2}$, ($^2H_{11/2} + ^4S_{3/2}$), and $^4F_{9/2}$. The radiative decay from these levels to the ground state gives rise to up-conversion fluorescences. The green emission (548 nm) is seen by eye over the entire length of the guide (≈ 4 cm) where the infrared light is coupled into the waveguide.

Fig. 3 shows fluorescence spectra for 15 mol% $Er^{3+}:TiO_2$ waveguide. In this case, four broad bands are observed around 410, 525, 548, and 660 nm. They are characteristics of Er^{3+} ion emissions embedded in an amorphous structure. These bands are due to the transitions identified in Fig. 3. The observation of the $^4H_{9/2} \rightarrow ^4I_{15/2}$ transition (410 nm) indicates that the second step excitation starts also from the $^4I_{9/2}$ excited state. Otherwise, the weakness of this transition ($\approx 1/100$ of $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition) shows that the $^4I_{9/2}$ level decays to the $^4I_{11/2}$ level by a rapid multiphonon relaxation and the excitation processes start efficiently from $^4I_{11/2}$ and $^4I_{13/2}$ states [7].

We have recorded fluorescence spectra for various Er^{3+} ion concentrations from 15% to 0.5%. The main effect we observed is that the emission bands become narrower with the decrease of Er^{3+} ion concentration and split into several lines, for smaller concentrations, which correspond to the transitions between the Stark sublevels of the upper states ($^2H_{9/2}$, $^2H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$) and the ground state $^4I_{15/2}$. This change is clearly observed in Fig. 4, on which the spectra of 0.5 and 15 mol% $Er^{3+}:TiO_2$ are shown for the wavelength region corresponding to the $(^2H_{11/2} + ^4S_{3/2}) \rightarrow ^4I_{15/2}$ transition. Further experiments at low temperature are necessary for the identification of the Stark transitions.

4. Discussion

The change of the fluorescence spectra with the Er^{3+} ion concentration is due to the modification of the TiO_2 gel network resulting from the Er ion incorporation. Fig. 5(a) shows that the Raman spectrum of 15 mol% $Er^{3+}:TiO_2$ is characteristic of an amorphous structure. Indeed, the bands due to amorphous structure are expected to be broad and since the film is thin (80 nm) their intensities would be weak and so they were not observed and consequently a flat spectrum was recorded. Otherwise, for

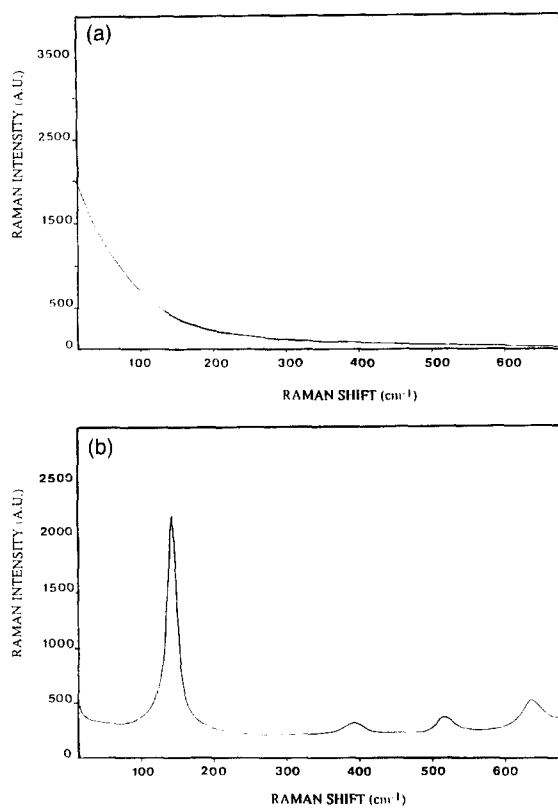


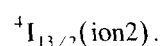
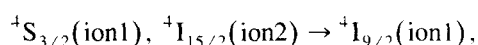
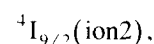
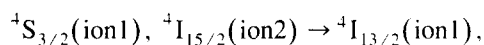
Fig. 5. Raman spectra of $Er^{3+}:TiO_2$ waveguides for: (a) 15 mol% $Er^{3+}:TiO_2$; (b) 0.5 mol% $Er^{3+}:TiO_2$.

the 0.5 mol% $Er^{3+}:TiO_2$ planar waveguide, Fig. 5(b), exhibits an intense and narrow band at 144 cm^{-1} and weaker features at 399, 516 and 639 cm^{-1} attributable to TiO_2 crystals (anatase) [6,8]. We have reported recently a comprehensive study of the TiO_2 sol-gel films versus Er^{3+} ion concentration and annealing temperature [6]. From these results, we deduce that titanium dioxide has a relatively low phonon energy spectrum (Fig. 5(b)), the highest phonon energy is 639 cm^{-1} , compared to other oxide hosts such as silica and phosphates glasses, which is favorable for up-conversion fluorescences from $^4S_{3/2}$ and $^4F_{9/2}$. Indeed, the energy gap between $^4S_{3/2}$ (resp. $^4F_{9/2}$) and the next lowest level $^4F_{9/2}$ (resp. $^4I_{9/2}$) is about 3000 cm^{-1} which means that five phonons are required to make the transition, non-radiatively, from $^4S_{3/2}$ to $^4F_{9/2}$ ($^4F_{9/2}$ to $^4I_{9/2}$, respectively). In such a case, it is well known that the radiative decay rate compete efficiently with the

nonradiative one at room temperature. This effect is more favorable as far as light emission is concerned.

The lifetime measurements of the $^4S_{3/2}$ level were performed using an excimer pumped dye laser. The dye was a DCM (dicyanomethylene) for the red excitation of the $^4F_{9/2}$ level ($\lambda_{\text{exc}} = 650 \text{ nm}$). The upper $^4S_{3/2}$ level was populated by ground state absorption into the $^4F_{9/2}$ state which relaxes to the metastable $^4I_{11/2}$ state followed by the excited state absorption $^4I_{11/2} \rightarrow (^4F_{5/2} + ^4F_{3/2})$ and a nonradiative decay into the $^4S_{3/2}$ level. These measurements were made on $\text{Er}^{3+}:\text{TiO}_2$ powdered samples heated at 600°C for one h (prepared in the same conditions as waveguides). The experiments on waveguides were not possible since when the pulsed excimer dye laser was used, the threshold for prism coupler damage was found to be very low ($\approx 20 \mu\text{J}$ focused) which prevented coupling the pump beam into films.

The fluorescence decays of the $^4S_{3/2}$ level obtained for samples with Er^{3+} ion concentration greater than 1 mol% were found to be nonexponential (Fig. 6(a)). This behavior indicates that the energy transfer due to cross relaxation mechanisms [9,10] cannot be neglected,



Energy transfer occurs in many materials when rare-earth concentrations are as high as 1 mol% [11]. Nevertheless, for the 0.2 mol% $\text{Er}^{3+}:\text{TiO}_2$ powdered sample, the decay was exponential with a lifetime of

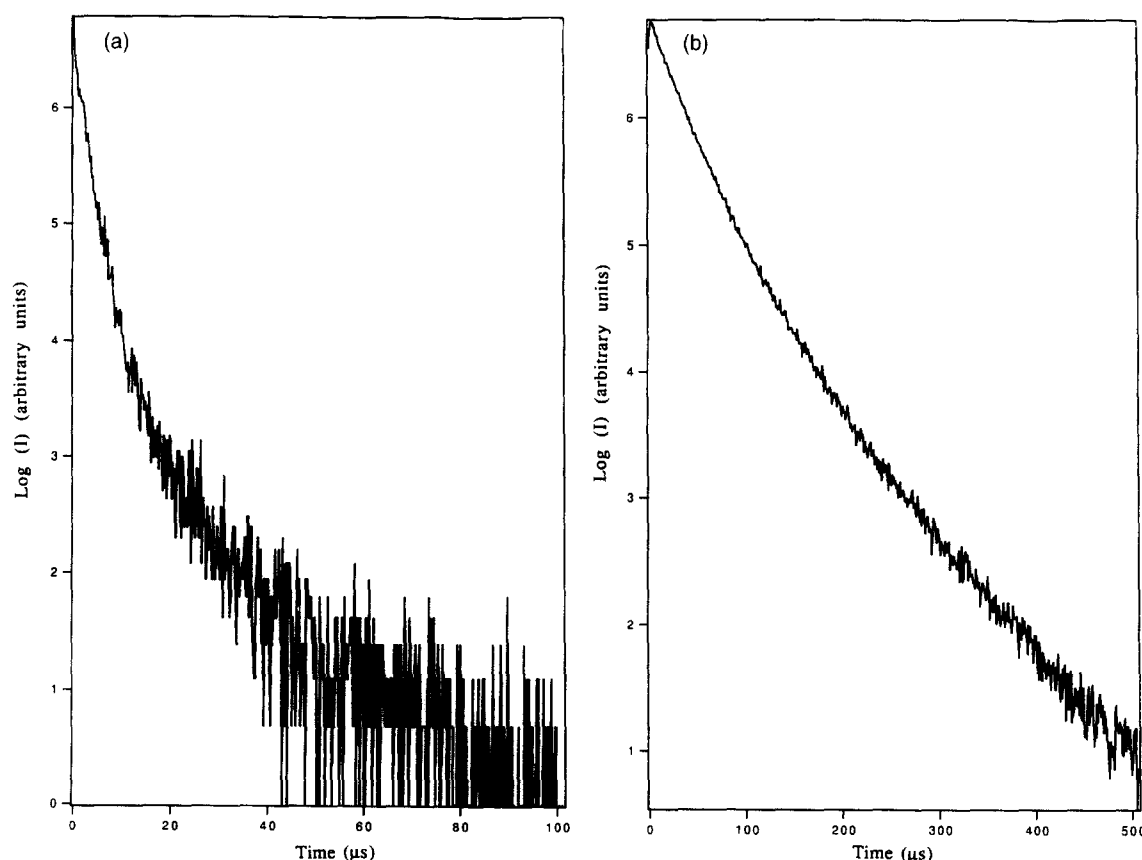


Fig. 6. Emissions decays of: (a) 1 mol% $\text{Er}^{3+}:\text{TiO}_2$; and (b) 0.2 mol% $\text{Er}^{3+}:\text{TiO}_2$.

Table 1

$^4S_{3/2}$ fluorescence decay constants measured in different host materials for Er^{3+} up-conversion at room temperature

	YAG ^a	TiO ₂	CaYAlO ₄ ^b	YAlO ₃ ^c
Wavelength (nm)	561	548	546.5	550
τ ($^4S_{3/2}$) (μ s)	15	45.5	96	100
Er^{3+} ion concentration	0.5%	0.2%	0.5%	1.5%

^a Ref. [3].

^b Ref. [12].

^c Ref. [13].

45.5 μ s (Fig. 6(b)). This value is compared to $^4S_{3/2}$ lifetimes in different host materials for Er^{3+} up-conversion listed in Table 1. It is larger than the $^4S_{3/2}$ lifetime in Er^{3+} :YAG in which laser action on $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition has been reported at room temperature [2,3].

5. Conclusion

In summary, we have observed the Er^{3+} up-conversion fluorescence of Er^{3+} :TiO₂ planar waveguides around 410, 525, 548, and 660 nm. The $^4S_{3/2}$ decay was found to be nonexponential for samples with Er^{3+} concentrations higher than 1 mol% owing to cross relaxation mechanisms. For 0.2 mol% Er^{3+} :TiO₂ sample the decay was exponential with the lifetime of 45.5 μ s. This value is an encouraging

result that allows to consider Er^{3+} :TiO₂ planar waveguide as a candidate for an erbium up-conversion laser.

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