

## Enhanced spectroscopic properties in Er<sup>3+</sup>/Yb<sup>3+</sup>-activated fluoride glass–ceramics planar waveguides

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### ABSTRACT

Bulk and planar waveguides fluoride glass–ceramics activated by erbium and ytterbium ions were prepared in the ZrF<sub>4</sub>–LaF<sub>3</sub>–ErF<sub>3</sub> system. Waveguides were obtained by use of physical vapor deposition process. All samples were characterized by luminescence spectroscopy. The results are discussed with the aim of assessing the role of ytterbium on the optical and spectroscopic properties of erbium doped glass–ceramics bulk and waveguides.

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## 1. Introduction

Erbium doped waveguide amplifiers (EDWA) are attractive for integrated optical devices operating in metropolitan area networks [1]. Integrated amplifiers should be as short as possible (a few centimeters long) so that high concentrations and/or high absorption and emission cross-sections are required. Although, silica is one of the best low-cost materials, fluoride glasses remain competitive, in terms of rare-earth solubility ( $>5 \times 10^{21}$  ions cm<sup>-3</sup>) and low phonon energy. Moreover, Mortier et al. demonstrated that transparent glass–ceramics could be obtained by spinodal decomposition in ZrF<sub>4</sub>–(La,Er)F<sub>3</sub>-based glass with high erbium content (8 mol%) with absorption cross-section increased by 20% [2]. Fluoride glass waveguides with composition close to bulk glass can be obtained by physical vapor deposition (PVD) [3]. Therefore, it is possible to consider the use of fluoride glass–ceramics materials for photonic application. When only erbium ions are present in short waveguides, the pumping at 980 nm is not very efficient,

the Er<sup>3+</sup> absorption cross-section at this wavelength being quite low. This problem can be overcome by the addition of Yb<sup>3+</sup> as a sensitizing ion. The strong near-infrared absorption of the Yb<sup>3+</sup> at 980 nm in combination with efficient Yb → Er energy transfer increases the <sup>4</sup>I<sub>13/2</sub> population density in Er<sup>3+</sup>/Yb<sup>3+</sup> activated glasses [4,5]. Since vapor pressure of rare-earth fluoride are quite similar, copoding can be easily reproduced in evaporated ZrF<sub>4</sub>–(La,Er)F<sub>3</sub>-based glass, provided that the type of evaporation of rare-earth mixture (mainly non-congruent) is known [6].

In this work, we present results on the fabrication and spectroscopic features of Er<sup>3+</sup>/Yb<sup>3+</sup>-codoped bulk and planar waveguide glass–ceramics prepared by PVD.

## 2. Experimental

The bulk glasses, called ZELAG xEr/yYb, with x and y the mol% of ErF<sub>3</sub> and YbF<sub>3</sub> were prepared by classical fluoride glass preparation techniques (melting at 850 °C for 15 min – casting of the melted glass rapidly heated at 925 °C) from the following constituents in mol%: 63.3ZrF<sub>4</sub> 24.1LaF<sub>3</sub> xErF<sub>3</sub> yYbF<sub>3</sub> (6–x–y)YF<sub>3</sub> 0.6 AlF<sub>3</sub> 6 GaF<sub>3</sub>. Through thermal treatment at 470 °C for 40 min in inert

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atmosphere, transparent glass–ceramics were obtained. ZrF<sub>4</sub>–LaF<sub>3</sub>–ErF<sub>3</sub>–YbF<sub>3</sub> (ZLE and ZLEYb) waveguides stabilized by a few % of AlF<sub>3</sub> were prepared by PVD, in dual configuration. Details of the procedure are described in Ref. [3]. The ceramization of as-deposited films (470 °C – 20 min) was carried out under primary vacuum. Because heating at 470 °C could not be achieved in the evaporation vessel, the film was on contact with air before the heat-treatment.

Optical absorption experiments in the ultraviolet, visible and near-infrared (UV–vis–NIR) regions were performed at room temperature with a double beam spectrophotometer (UV–vis–NIR Cary 5000 Varian) with a resolution of 1 nm. The 514.5 nm line of an Ar<sup>+</sup>-ion laser and the 980 nm line of a Ti:Sapphire laser were used as excitation sources for photoluminescence (PL) spectroscopy measurements. The spectra of the waveguides were obtained by exciting the propagation modes by prism coupling technique. Details of the experimental set-up are given in [5]. The lifetime  $\tau$  was defined as the 1/e decay time of the fluorescence intensity because the decay of luminescence was not always single exponential especially for samples with low content of erbium (<1 mol%).

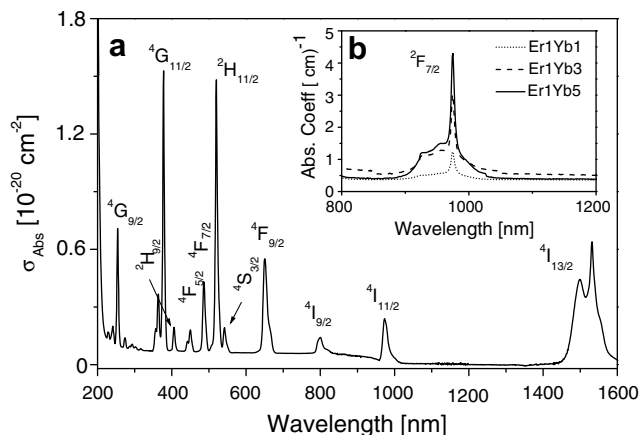
### 3. Results and discussion

#### 3.1. Bulk glasses and glass–ceramics

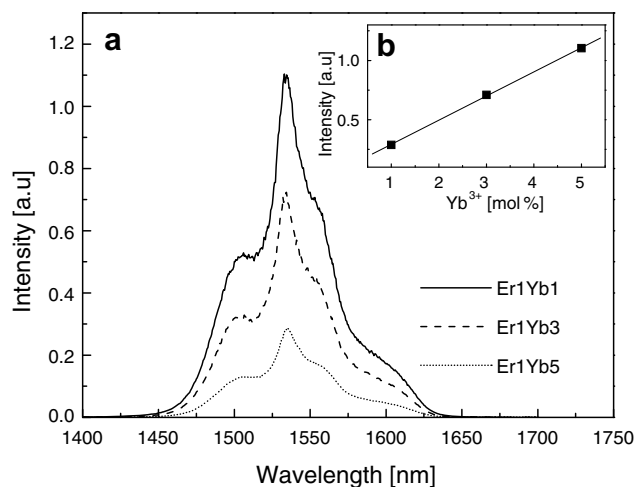
The UV–vis–NIR absorption spectrum obtained for the 6 mol% Er<sup>3+</sup> doped glass is plotted in Fig. 1a. The spectrum is characteristic of Er<sup>3+</sup>-doped fluoride glasses with absorption bands identified with the transitions from the <sup>4</sup>I<sub>15/2</sub> ground state to the excited states of the Er<sup>3+</sup> ions. The absorption spectra of the samples codoped with 1 mol% erbium and 1–5 mol% ytterbium are presented in Fig. 1b.

The spectra show, in addition to the bands related to erbium absorption, a strong absorption peak centred at 980 nm, typical of <sup>2</sup>F<sub>7/2</sub> → <sup>2</sup>F<sub>5/2</sub> Yb<sup>3+</sup> absorption [7] which indicates clearly the increase of the absorption coefficient at this wavelength for the codoped samples. The absorption due to Yb<sup>3+</sup> can be estimated to be about four times higher than the erbium one.

Photoluminescence spectra of the bulk glasses activated with 1 mol% of erbium and *x* mol% of ytterbium (*x* = 1, 3, 5) which have been measured in the region of the <sup>4</sup>I<sub>13/2</sub> → <sup>4</sup>I<sub>15/2</sub> transition upon excitation at 980 nm are reported in Fig. 2a.



**Fig. 1.** UV–vis–NIR absorption spectrum of the fluoride glasses (a) doped with 6 mol% Er<sup>3+</sup> and (b) codoped with 1 mol% Er<sup>3+</sup>–*x* mol%Yb<sup>3+</sup> with *x* = 1, 3, 5. Some of the final states of the <sup>4</sup>I<sub>15/2</sub> → <sup>2</sup>S<sup>+1</sup>L<sub>J</sub> transitions of erbium and transition related to Yb<sup>3+</sup> absorption are labeled.



**Fig. 2.** (a) Photoluminescence spectra of the <sup>4</sup>I<sub>13/2</sub> → <sup>4</sup>I<sub>15/2</sub> transition of Er<sup>3+</sup> in bulk glasses doped with 1 mol% erbium and 1, 3, 5 mol% ytterbium obtained upon excitation at 980 nm and (b) related evolution of the intensity of photoluminescence emission at 1532 nm as a function of ytterbium concentration.

As expected, the shape of the transition <sup>4</sup>I<sub>13/2</sub> → <sup>4</sup>I<sub>15/2</sub> of Er<sup>3+</sup> for the glasses activated with erbium and ytterbium ions is the same than that observed for samples without ytterbium [5]. The values of lifetime obtained for the <sup>4</sup>I<sub>13/2</sub> excited state (see Table 1) are close to the radiative one calculated in ZrF<sub>4</sub>-based glasses (10.7 ms in ZBLAN [8]) but slightly higher. This result could be related to a process of radiation trapping [9]. This resonant energy transfer process takes place between two neighbouring ions and gives rise to a measured lifetime artificially lengthen for the considered level.

Spectra and lifetimes obtained upon different excitation are almost identical. Small differences in the values of bandwidths measured can be related to different site selection achieved by the different excitation sources. The spectral width of the emission bands is due to inhomogeneous and homogeneous broadening, plus additional Stark splitting of the excited and ground states.

In order to highlight the influence of the ytterbium on the emission yield of the <sup>4</sup>I<sub>13/2</sub> → <sup>4</sup>I<sub>15/2</sub> transition, the spectra obtained after excitation at 514.5 nm have been normalized to the main component at 1532 nm of the emission band and the respective coefficients obtained from this normalization have been applied to the spectra obtained after excitation at 980 nm for each sample.

Results are presented in Fig. 2b and show a linear increase of the photoluminescence emission intensity at 1532 nm with the content of ytterbium ions (about four times higher for an Yb/Er ratio of 5). From these results, we can suppose that the optimal concen-

**Table 1**

Decay time constants of the <sup>4</sup>I<sub>13/2</sub> excited state in the Er<sup>3+</sup>–Yb<sup>3+</sup>-codoped glasses and glass–ceramics upon excitation at 980 nm (values reported with \* have been obtained upon excitation at 514.5 nm), obtained by a fit at *t* = 1/e and spectral bandwidth (FWHM) of the transition <sup>4</sup>I<sub>13/2</sub> → <sup>4</sup>I<sub>15/2</sub> of erbium.

Sample	Glass		Glass–ceramic	
	$\tau_{1/e} \pm 0.5$ (ms)	FWHM (nm)	$\tau_{1/e} \pm 0.5$ (ms)	FWHM (nm)
Er1Yb0	13.3*	43.5*	13.1*	36.0
Er1Yb1	10.9	41.0	12.1	33.0
Er1Yb3	10.6	41.0	11.0	30.0
Er1Yb5	10.4	43.0	–	–
Er3Yb0	12.0*	43.0*	12.0*	35.5
Er3Yb3	11.2	46.0	13.3	38.0

**Table 2**  
Composition, thermal treatment, decay time constants (in ms) of the  $^4I_{13/2}$  excited state obtained by a fit at  $t = 1/e$  and spectral bandwidth (FWHM) of the transition  $^4I_{13/2} \rightarrow ^4I_{15/2}$  of erbium in  $Er^{3+}$  and  $Er^{3+}-Yb^{3+}$ -codoped glassy and glass–ceramic waveguides upon excitation at 514.5 nm.

Sample	Composition (mol%)					Heat treatment	$\tau_{1/e} \pm 0.5$ (ms)	FWHM (nm)
	ZrF <sub>4</sub>	LaF <sub>3</sub>	ErF <sub>3</sub>	YbF <sub>3</sub>	AlF <sub>3</sub>			
ZLE (a)	69.3	23	7.7	0	<3	as-deposited	1.7	47.5
ZLE (b)						20 min – 470 °C	5.3	44.0
ZLEYb (a)	84.5	12	0.5	3	<3	as-deposited	3.2	47.5
ZLEYb (b)						20 min – 470 °C	7.4	18.0

tration of ytterbium is still not reached. Work is actually in progress to optimize the Er/Yb ratio by partially substituting LaF<sub>3</sub> with YbF<sub>3</sub>.

Measurements of spectroscopic properties of glass–ceramics have been carried out in order to investigate the evolution of spectral characteristics of erbium in these samples with the thermal treatment. Electronic transmission microscopy study on the glass–ceramics has shown that the Er/La ratio is almost constant between glassy and crystalline domains. Moreover, thermal analyses demonstrate that the ratio of crystallites with regards to the glassy phase is quite high.

Study of the spectroscopic behaviour of the erbium ions in 1.5  $\mu\text{m}$  region shows that the lifetime of the  $^4I_{13/2}$  state is kept almost constant by the ceramization process (Table 1). Variation of the bandwidth (HWHM) is not significant since only one stark component at 1532 nm increases with thermal treatment

### 3.2. ZLE and ZLEYb glassy and glass–ceramic waveguides

The glassy films, deposited on CaF<sub>2</sub> single crystal plate, were transparent, crack free with very good adhesion to the substrate and exhibited a step-index profile with a refractive index around 1.52.

Table 2 presents the main characteristics of two waveguides: one activated with erbium ions (ZLE) and the other codoped with

erbium and ytterbium ions (ZLEYb) before and after thermal treatment. The related decay time constants of the  $^4I_{13/2}$  state of erbium and the spectral bandwidth of the  $^4I_{15/2} \rightarrow ^4I_{13/2}$  transition are also reported (see also Fig. 3). The shape of the transition does not change a lot with the treatment (only a slight decrease of the value of the bandwidth as observed between bulk glass and glass–ceramics) excepted for the ZLEYb waveguide annealed at 470 °C for 20 min that presents a spectrum totally different related to an environment of the erbium ions different from that in glass but also from what is expected for a ceramized waveguide. This could be related to a deposition temperature too low leading to the presence of residual hydroxyl groups. Other samples that present a spectrum close to that of a bulk glass–ceramic have been obtained for higher deposition temperature.

The evolution of the lifetime of the  $^4I_{13/2}$  state can also be observed for the ZLE waveguides with in the two cases a lifetime twice longer after thermal treatment at 470 °C for 20 min. In this case, the increase of the lifetime is mainly related to a decrease of the residual hydroxyl groups and/or structural defects that have been found in the as-deposited layers [10].

Finally, best result of light propagation with an attenuation coefficient of 1.5 dB/cm has been measured in vitreous waveguide. Unfortunately, the surface of the waveguides after thermal treatment appears damaged, and propagation of the light turns out to be very lossy.

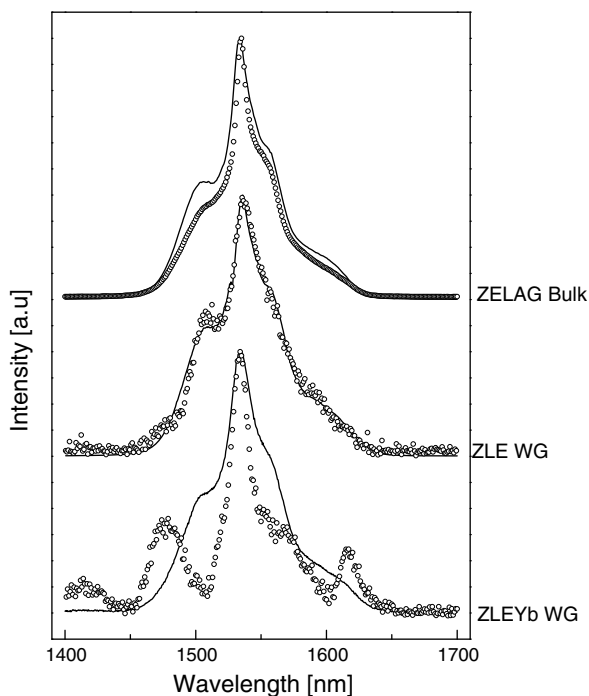
## 4. Conclusion

Bulk fluoride glasses and glass–ceramics activated by erbium and ytterbium ions were prepared in the purpose of quantifying the influence of ytterbium ions on the spectral characteristics of erbium in these systems. Glassy samples codoped with ytterbium ions with an Yb/Er ratio of 5 present an absorption coefficient and an emission intensity four times higher at 1532 nm than samples activated only with erbium ions. In all samples, a process of radiation trapping is observed that leads to a measured lifetime of the  $^4I_{13/2}$  level higher than the radiative one. No significant evolution of the spectroscopic parameters at 1532 nm is observed between amorphous and glass–ceramics samples.

ZLE and ZLEYb waveguides with composition close to bulk parent glass of glass–ceramics and a step-index profile have been prepared by PVD. Photoluminescence properties at 1532 nm for heat-treated waveguides codoped with Yb are not those expected, probably because of the presence of OH groups. Work is actually in progress to optimize the deposition parameters with a substrate temperature higher than glass transition temperature ( $T_g = 400$  °C) to improve chemical durability toward atmospheric moisture.

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**Fig. 3.** Photoluminescence spectra of  $Er^{3+}$  upon excitation at 980 nm in ZELAG bulk, ZLE and ZLEYb planar waveguides (WG) before (---) and after heat-treatment (oooo).

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