

Concentration quenching in an Er-doped phosphate glass for compact optical lasers and amplifiers

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Abstract

In this paper, highly (up to 5.25 mol% Er₂O₃) Er-doped phosphate bulk glasses were synthesized by conventional melt-quenching method and their physical, thermal and spectroscopic properties are reported. The influence of Er³⁺ doping concentration on emission spectra and lifetimes was investigated in order to study the concentration quenching effect on luminescence performance and therefore to evaluate the most suitable rare earth content for developing compact fiber laser and optical amplifier operating at 1.5 μm. A radiative lifetime and a quenching concentration equal to $\tau_0 = 7.05$ ms and $N_0 = 9.92 \times 10^{20}$ ions/cm³ were respectively calculated by fitting the fluorescence lifetime experimental data with Auzel's limited diffusion model.

Keywords: Phosphate glass; Erbium; Spectroscopic analysis; Concentration quenching; Photonic device.

1. Introduction

Due to the isotropy of its physical properties and the low cost of synthesis and processing [1], glass has been regarded as the most suitable material for latest applications of modern optoelectronics, such as the development of all-optical networks to transfer data with a higher bit rate [2] and the fabrication of optical fibers for optical amplifiers and lasers [3].

The search for glasses possessing required optical and thermal properties is fundamental in view of obtaining optical fibers, including fibers doped with high rare-earth (RE) ion concentrations [4,5], suitable for the fabrication of compact optical devices. Furthermore, the isotropic properties of glasses ensure a significant degree of the disordered state around the doped RE ions, which results in the broadening of the luminescence band [6] and in turn makes it possible to build broadband amplifiers or pulsed lasers.

The reason for the interest towards erbium as RE doping ion in a host glass medium is that its radiative transition (${}^4I_{13/2} \rightarrow {}^4I_{15/2}$) at 1.5 μm coincides with the third optical communication window, corresponding to minimum attenuation (0.2 dB/km) in silica glass [7], and is located in the eye-safe spectral region [8].

Current amplifier and laser technologies rely almost entirely on erbium-doped fiber amplifiers (EDFAs) and lasers (EDFLs) made from silicate-based glass fibers [9,10]. Silica glass, however, is well known from several decades to suffer for a very low solubility of RE ions [11]. This still constitutes an important technological issue for the improvement of fiber lasers because it prevents the fabrication of more compact (only few centimetres long) optical gain devices [12,13,14], indispensable for optical networks or high power lasers [4].

Phosphate glasses, characterized by having a large number of promising properties such as easy processing, good chemical durability, excellent optical properties, ion exchangeability, no clustering effect and above all very high solubility of rare earth ions, represent an interesting alternative to the more traditional and employed silica-based glasses for this kind of application [15,16,17,18]. This is particularly interesting when pulsed sources with limited stimulated Brillouin scattering (SBS) are sought, since the high doping level of the phosphate glass hosts can be combined with a large core area single mode configuration [19]. In recent years, these features have made phosphate glass an attractive rare-earth host matrix also in other research fields, like optical communications [15] and microsurgery [20].

It is worth highlighting, however, that even for phosphate glasses a too large amount of RE ions results in concentration quenching caused by ion clustering [21,22]. This non-radiative decay process is detrimental because it leads to a loss of excitation with consequent reduction of fluorescence emission [23]. Within this framework, a careful analysis aimed to estimate the optimal RE doping concentration proves to be essential, considering that erbium concentration quenching in phosphate glass was reported in few papers [24,25,26], since most of the research activity on this subject was dedicated to silica-based glass.

This paper reports the design and fabrication of a thermally stable phosphate glass and the study of its spectroscopic properties with increasing the Er^{3+} ion content. The major task of the work is to thoroughly investigate the effect of Er^{3+} doping concentration on glass optical properties, in view of determining the maximum doping level allowed without the occurrence of concentration quenching phenomena. This work is intended to be a preliminary study towards the development of a compact short pulsed eye-safe fiber laser as a promising infrared light source for LIDAR systems.

2. Materials and methods

2.1 Glass fabrication

Glass samples used in this work were synthesized by conventional melt-quenching method using chemicals (P_2O_5 - Li_2O - Al_2O_3 - BaO - MgO - Gd_2O_3) with high purity level (99+%). The host glass was *ad hoc* developed for this research in view of fabricating a stable and robust glass, able to incorporate high amount of RE ions and suitable for fiber drawing.

Five different glasses, named for short Er1 ÷ Er5, were obtained by doping the host material with an increasing level of Er₂O₃ (ranging from 0.01 to 5.25 mol %) added in substitution of Gd₂O₃. The chemicals were weighted and mixed within a dry box in order to minimize the hydroxyl ions (OH⁻) content in the glass.

The batched chemicals were melted at a temperature of 1400 °C for 1 h in a vertical furnace under controlled atmosphere to minimize the content of OH⁻ groups in the glass.

The melt was cast into a preheated brass mould, then annealed at a temperature around the transition temperature, T_g , for 3 h to relieve glass internal stresses, and finally cooled down slowly to room temperature. The obtained glasses were cut and optically polished to 1 mm-thick samples for optical and spectroscopic characterization.

2.2 Glass characterization

The density of the glasses was measured at room temperature by the Archimedes method by using distilled water as immersion fluid. The Er³⁺ ion concentrations were calculated from measured sample densities and their initial compositions.

Thermal analysis was performed on fabricated glasses using a Netzsch DTA 404 PC Eos differential thermal analyzer up to 1200 °C with a heat rate of 5 °C/min in sealed Pt/Rh pans. Thermal analysis was carried out in order to measure the characteristic temperatures T_g (glass transition temperature) and T_x (onset crystallization temperature). An error of ± 3 °C was observed in measuring the characteristic temperatures.

The coefficient of thermal expansion (CTE) was measured with a horizontal alumina dilatometer (Netzsch, DIL 402 PC) on 5 mm long specimens operating at 5 °C/min up to 1200 °C. The measure was automatically interrupted when shrinkage higher than 0.13% was reached (softening point). CTE values were calculated in the 200-400 °C temperature range.

The refractive index of the glasses was measured at 1.3 μm , where Er³⁺ ions do not display ground state absorption, by prism coupling technique (Metricon, model 2010). Ten scans were performed for each measurement. Estimated error of the measurement was ± 0.001 .

The absorption spectra were measured at room temperature for wavelengths ranging from 350 to 3000 nm using a double beam scanning spectrophotometer (Varian Cary 500).

Fourier transform infrared (FTIR) spectrometer (Alpha, Bruker Optics, Ettlingen, Germany) working in transmission mode and equipped with a DTGS detector was employed. Spectra of the five samples with different Er₂O₃ content were taken between 1800 and 7500 cm⁻¹, with a resolution of 4 cm⁻¹ and acquiring an average of 16 scans. OPUS software (v. 6.5, Bruker Optics, Ettlingen, Germany) was used for instrumental control and for spectral acquisition. The transmittance FTIR spectra are reported in terms of attenuation loss.

CW photoluminescence spectra were acquired by a Jobin Yvon iHR320 spectrometer equipped with a Hamamatsu P4631-02 detector, using standard lock-in technique. Emission spectra were obtained by exciting the sample with a monochromatic light at the wavelengths of 976 nm, emitted by a single mode fiber pigtailed laser diode (CM962UF76P-10R).

The fluorescence lifetime of $\text{Er}^{3+}:^4\text{I}_{13/2}$ level was obtained by exciting the samples with light pulses of the 976 nm laser diode, recording the signal by a digital oscilloscope (Tektronix TDS350) and fitting the decay traces by single exponential. Estimated error of the measurement was ± 0.20 ms. The detector used for this measurement was a Thorlabs PDA10CS.

All measurements were performed at room temperature.

2.3 Setup of optimal conditions for glass fabrication

In order to target a good quality optical material for emission in the eye-safe wavelength region, the control of water content in the glass is crucial. To this aim a preliminary work was devoted to the definition of a glass fabrication protocol able to minimize OH^- content in the prepared glasses. For this work a set of glass samples with the same content of Er^{3+} ions ($2.6 \times 10^{20} \text{ cm}^{-3}$) were prepared varying the batch chemical mixing procedure and the glass melting and processing conditions. As control parameters, in particular, the lifetime value of $\text{Er}^{3+}:^4\text{I}_{13/2}$ level and the absorption of the glass samples at 3000 cm^{-1} were selected. The resulting fabrication procedure was employed for the fabrication of the Er1 ÷ Er5 glasses studied in this paper.

3. Results and discussion

3.1. Definition of the procedure for glass fabrication

The preliminary work aiming at defining the glass fabrication protocol allowed assessing a precise correlation between the $\text{Er}^{3+}:^4\text{I}_{13/2}$ level lifetime and the glass water content. Twelve glass samples were fabricated for this study and Fig. 1 shows the results of the measurement campaign, which demonstrate that a careful control of the overall fabrication process is crucial in achieving high quality glasses. The main improvements regarded the selection of high purity chemicals, the use of a dry box to weigh the chemicals and the flow of dry air inside the furnace during glass melting.

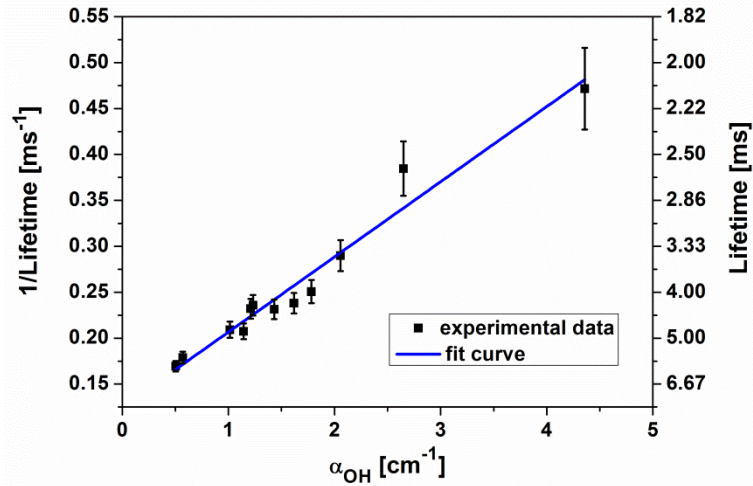


Fig. 1. Decay rate, defined as the inverse of the $\text{Er}^{3+}:^4\text{I}_{13/2}$ level lifetime, as a function of the absorption coefficient α_{OH} of OH^- vibration band at 3000 cm^{-1} of all glass samples prepared for the definition of the optimized fabrication process. The experimental data were fitted through the formula (2) reported in Ref. [27]. For the benefit of the reader, measured lifetime values are reported on the right y-axis.

3.2. Glass physical and thermal properties

All fabricated glasses were crystallization free and homogeneous.

Table 1 reports their thermal properties, density, refractive index and the calculated Er^{3+} ion concentration.

It is worth noting that the physical properties did not change significantly by varying the doping level of the glasses, due to the fact that the doping oxide Er_2O_3 was added in substitution of Gd_2O_3 in the host matrix, both quite close in terms of molecular weight.

An average value of $\Delta T = 496 \pm 3 \text{ }^\circ\text{C}$ was measured, which suggests that these glasses are very stable against de-vitrification and suitable for crystal-free fiber drawing. Furthermore, a typical linear thermal expansion coefficient value of $9 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ was assessed, which is similar to other phosphate glasses [28], but an order of magnitude higher than silica glasses.

Table 1

Er^{3+} ion content in mol%, Er^{3+} ion concentration, glass transition temperature (T_g), crystallization temperature (T_x), density, and refractive index of the manufactured phosphate glasses.

Glass label	Er^{3+} [mol%]	Er^{3+} [$\times 10^{20}$ ions/cm ³]	T_g [$^\circ\text{C}$] $\pm 3 \text{ }^\circ\text{C}$	T_x [$^\circ\text{C}$] $\pm 3 \text{ }^\circ\text{C}$	$\Delta T = T_g - T_x$ [$^\circ\text{C}$] $\pm 6 \text{ }^\circ\text{C}$	ρ [g/cm ³] $\pm 0.05 \text{ g/cm}^3$	n ± 0.001
Er1	0.02	0.02	485	1017	532	3.42	1.570
Er2	1	1.30	489	986	497	3.45	1.573
Er3	2	2.59	482	1009	527	3.41	1.569
Er4	6	7.76	480	889	409	3.42	1.568
Er5	10	13.73	495	1008	513	3.47	1.570

3.3. Absorption and transmission spectra

UV-Vis and FTIR analyses were carried out on all prepared samples and absorption and transmission spectra were respectively recorded.

Absorption cross-section σ_a [cm^{-3}] was calculated from experimental data using the following formula:

$$\sigma_a(\lambda) = \frac{2.303 \log\left(\frac{I_0}{I}\right)}{NL}$$

where $\log(I_0/I)$ is the absorbance, L the glass sample thickness in cm and N is the concentration of the Er^{3+} ions per cm^3 .

Fig. 2 shows the absorption cross-section values obtained for glass sample Er5. The inhomogeneously broadened bands are assigned to the transitions from the ground state $^4I_{15/2}$ to the excited states of Er^{3+} ions (see inset of Fig. 2).

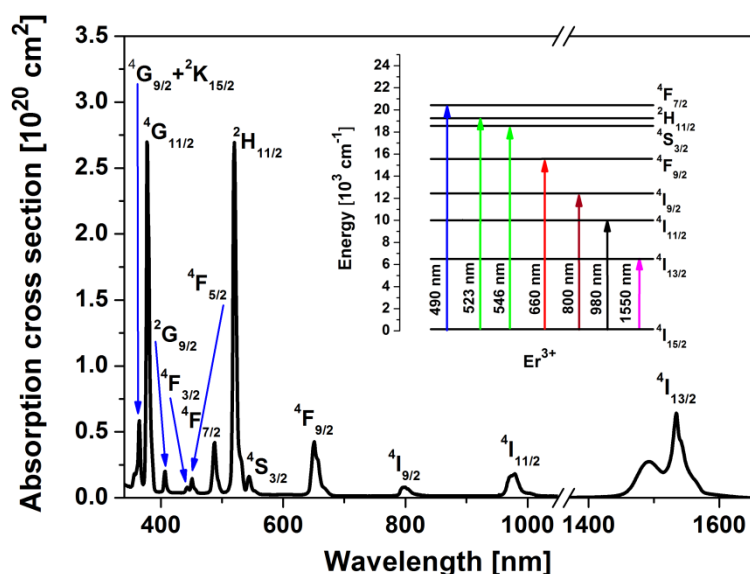


Fig. 2. Absorption cross-section spectrum of sample Er5. The main Er^{3+} levels are labeled, considering absorption from the ground state $^4I_{15/2}$. The inset shows the Er^{3+} ion energy levels.

Fig. 3 shows the IR spectrum of glass sample Er5 between 1800 and 7500 cm^{-1} , as an example. In the medium IR region, between 1800 and 4000 cm^{-1} , the spectrum clearly reveals a group of prominent absorption bands due to the hydroxyl groups and very weak peaks at around 2850 cm^{-1} due to some organic contamination on the surface of the samples. In the NIR region a broad and intense band associated with the transition from the ground state $^4I_{15/2}$ to the excited level $^4I_{13/2}$ of the Er^{3+} ion is detected at around 6500 cm^{-1} .

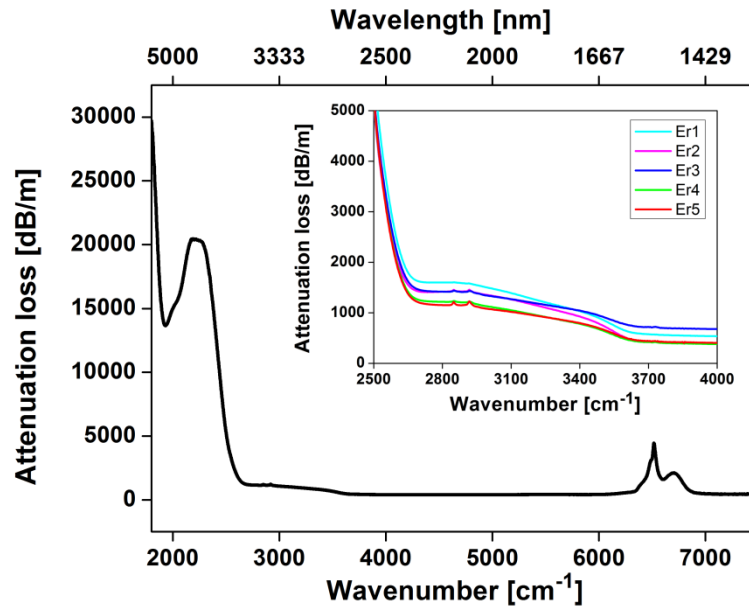


Fig. 3. IR spectrum of glass sample Er5; the inset shows the zoom-up of the OH⁻ broad band at 3000 cm⁻¹ of all the manufactured samples Er1 ÷ Er5.

Phosphate glass hosts are well known from the literature to be particularly vulnerable to OH⁻ contamination because they tend to absorb water molecules readily during melting process, and although sophisticated methods may be used, some residual hydroxyl groups remain in the glass typically at concentrations greater than 100 ppm, even in commercial phosphate laser glasses [29].

As it can be clearly noticed in Fig. 3, the main contribution due to the presence of water in the glass host is given by the intense peak observed at about 2200 cm⁻¹ [30]. Nevertheless, a greater interest is commonly devoted to the broad band at about 3000 cm⁻¹, since it provides useful information on the concentration of OH⁻ groups inside the glass. The content of hydroxyl groups has been evaluated through the application of the formulas proposed by Speghini *et al.* [31] and Ehrmann *et al.* [29], and medium values of 21 and 170 ppm have been respectively obtained.

The inset of Fig. 3 reports the zoom-up of the spectra of the five samples with different erbium content (Er1 ÷ Er5) in the region between 2500 and 4000 cm⁻¹. It is worthwhile noting that in this medium IR region the spectra show a similar profile for all glasses, thus demonstrating that the manufacturing process has been correctly optimized and standardized.

3.4. Fluorescence emission spectra

Normalized fluorescence spectra of the Er³⁺-doped glass samples, measured in the wavelength range 1400 ÷ 1700 nm under excitation at 976 nm are illustrated in Fig. 4. A broad and intense emission is evident, which is assigned to the Er³⁺:⁴I_{13/2} → ⁴I_{15/2} transition.

The FWHM is a critical parameter commonly used to evaluate the gain bandwidth properties of the optical amplifiers. In the manufactured samples, it slightly increases with increasing the Er³⁺ concentration.

Values range from 30 to 39 ± 2 nm, similar to other phosphate glasses (37 nm) and to silicate glasses (40 nm) [32].

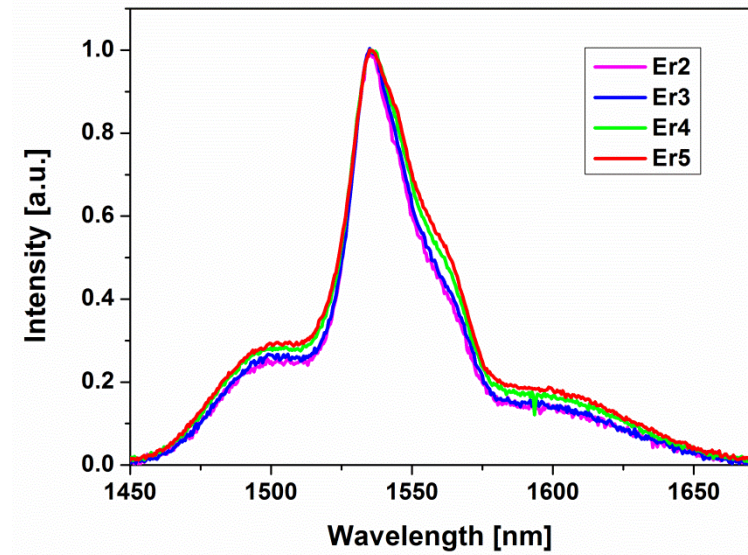


Fig. 4. NIR emission spectra of the manufactured phosphate glass samples obtained under excitation at 976 nm with a CW laser diode. Er1 spectrum is not reported since it displays a poor signal to noise ratio.

3.5. Fluorescence lifetime

For optical amplifiers or lasers operating at 1.55 μm , an important parameter is the $\text{Er}^{3+} : ^4\text{I}_{13/2}$ level lifetime: the longer the lifetime, the higher the population inversion between this level and the ground state.

Examples of the luminescence decay curves of the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ emission upon 976 nm excitation are reported in Fig. 5, while the corresponding lifetime values, calculated for all glass samples, are listed in Table 2 and reported as a function of the Er^{3+} ion concentration.

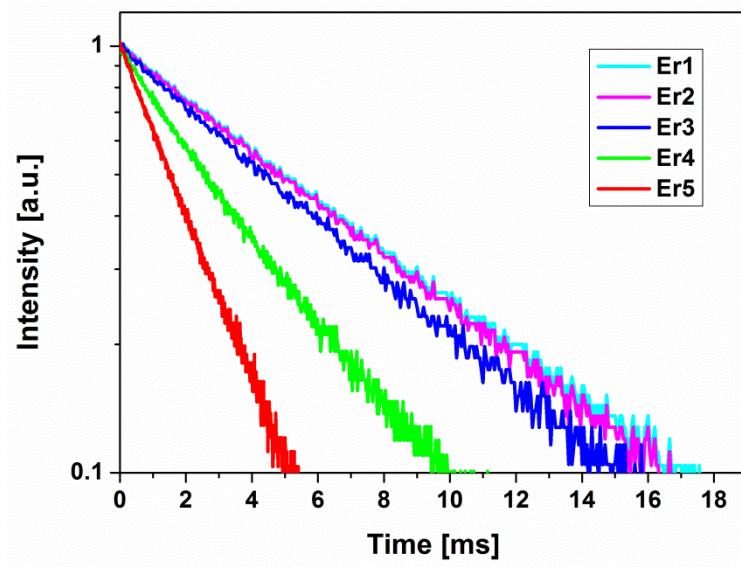


Fig. 5. Room temperature decay curves of the ${}^4I_{13/2}$ level of Er^{3+} ions in the manufactured samples obtained under excitation at 976 nm. The intensity data are reported on a Log scale.

Table 2

Excited state ${}^4I_{13/2}$ lifetime values for Er^{3+} doped samples under laser excitation at 976 nm.

Glass label	Er^{3+} [mol%]	$Er^{3+}:{}^4I_{13/2}$ lifetime [ms] \pm 0.20 ms
Er1	0.02	7.04
Er2	1	7.01
Er3	2	6.33
Er4	6	3.60
Er5	10	2.11

The ${}^4I_{13/2}$ lifetime trend is similar to that observed in other phosphate glasses [25,28,33]: lifetime decreases with rising Er^{3+} concentration due to the increase of energy transfer between neighbourhood Er^{3+} ions and energy transfer from Er^{3+} ions to quenching centers like OH^- groups [23,34]. Specially, the free OH^- groups in the glass are regarded as effective quenchers of the IR radiation in Er^{3+} -doped phosphate glasses [35].

The fluorescence lifetime experimental data were fitted by the empirical formula proposed by Auzel *et al.* [36,37] for the case of limited diffusion, in which the energy transfer from Er^{3+} to nearby defects or trapping centres, also known as quenching traps, is assumed to be the main mechanism responsible for the increase in the quenching process:

$$\tau(N) = \frac{\tau_0}{1 + \frac{9}{2\pi} \left(\frac{N}{N_0}\right)^2}$$

where τ is the measured lifetime at a given Er^{3+} ion concentration (N), τ_0 is the lifetime in the limit of “zero” concentration, i.e. the radiative lifetime and N_0 is the quenching concentration.

A good agreement ($R = 0.9937$) with the fit curve for the whole range of concentrations was found (see Fig. 6), and in addition the values of $\tau_0 = 7.05$ ms and $N_0 = 9.92 \times 10^{20}$ ions/cm³ obtained from the fitting are considerably higher with respect to those reported in literature for other phosphate glasses ($\tau_0 = 1.09$ ms and $N_0 = 2.5 \times 10^{20}$ ions/cm³ in [32]). The reason is probably due to a reduced incorporation of OH⁻ groups in our glasses, thanks to the use of controlled dry atmosphere during the melting process. This result is of great importance for the future development of efficient fiber laser sources and paves the way towards an optical cavity characterized by high efficiency (high lifetime values) and compactness (high concentration of rare earth ions).

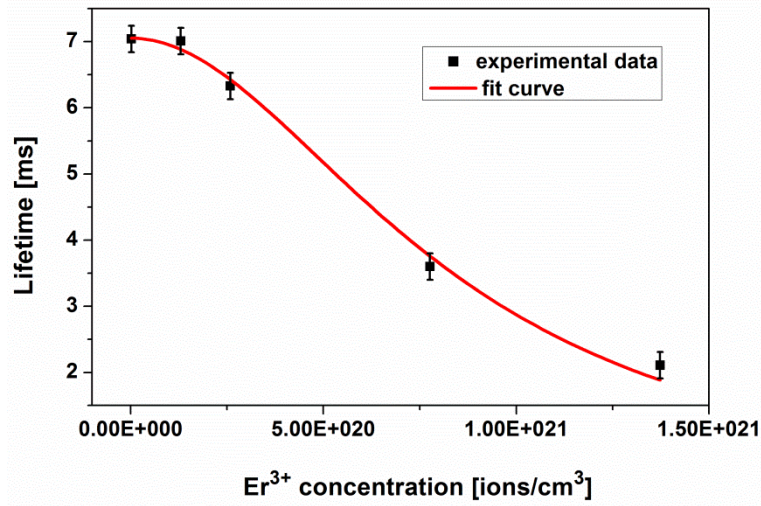


Fig. 6. Experimental and fitted values of $\text{Er}^{3+} : ^4\text{I}_{13/2}$ excited state lifetime in samples Er1 ÷ Er5.

4. Conclusions

This paper reports the fabrication and the thermal and spectroscopic characterization of five phosphate glasses doped with a variable Er^{3+} ions content. All prepared samples were homogeneous and presented a good thermal stability and thus are suitable for fiber drawing.

The influence of Er^{3+} ions doping concentration on optical properties was investigated in order to study the concentration quenching effect on luminescence performance. With increasing the concentration of Er^{3+} ions, the 1.5 μm emission band became broader, while the lifetime of the $^4\text{I}_{13/2}$ state decreased due to unwanted energy transfer between RE ions. FWHM ranged from 30 to 39 ± 2 nm at concentration of Er^{3+} ions corresponding to 0.02 and 13.73×10^{20} ions/cm³, respectively.

The fluorescence lifetime data were fitted to the limited diffusion model proposed by Auzel and a radiative lifetime and a quenching concentration of $\tau_0 = 7.05$ ms and $N_0 = 9.92 \times 10^{20}$ ions/cm³ were respectively obtained.

The next step in this research will be the employment of the studied phosphate glass doped with the optimal erbium concentration for the design and development of a compact broadband EDFA pumped with a commercial laser diode and of a compact eye-safe fiber laser for environmental monitoring and sensing applications. An Er^{3+} ion concentration of around 2.5×10^{20} ions/cm³, thus similar to Er³, represents a good trade-off between the request of a high doping level for compactness and a high lifetime of the $\text{Er}^{3+} : ^4\text{I}_{13/2}$ emitting level for an efficient operation.

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