

## CO<sub>2</sub> laser annealing on erbium-activated glass–ceramic waveguides for photonics

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### ABSTRACT

Silica-based sol–gel waveguides activated by Er<sup>3+</sup> ions are one of the most important materials for integrated optics devices. In this paper, we present an alternative method combining sol–gel route and CO<sub>2</sub> laser annealing for planar optical waveguides processing. The effects of pulsed and continuous CO<sub>2</sub> laser irradiation on the optical and spectroscopic properties of SiO<sub>2</sub>–ZrO<sub>2</sub> and SiO<sub>2</sub>–HfO<sub>2</sub> planar waveguides are evaluated and the thermal conventional annealing effects for these systems are reported for comparison. All the planar waveguides, doped with 0.5 and 5 mol% Er<sup>3+</sup>, were prepared by sol–gel route using dip-coating deposition on v-SiO<sub>2</sub> substrates. An increase of the refractive index of approximately 0.04 at 1.5 μm has been observed on 70SiO<sub>2</sub>–30HfO<sub>2</sub> planar waveguide after continuous CO<sub>2</sub> laser annealing. A similar refractive-index variation was detected in all SiO<sub>2</sub>–ZrO<sub>2</sub> planar waveguides after CO<sub>2</sub> laser irradiation. We have observed, moreover, that continuous CO<sub>2</sub> laser annealing can lead to waveguides with a lower attenuation coefficient with respect to the attenuation coefficient measured for thermal annealed waveguides. Upon excitation at 514.5 nm continuous-wave laser light, on the irradiated sample, the shape is found to be almost independent on the time and irradiation power with CW laser annealing but a decrease of the FWHM of approximately 46–12 nm has been observed on planar waveguides after pulsed laser annealing. Before and after conventional thermal annealing, the <sup>4</sup>I<sub>13/2</sub> level decay curves present a single-exponential profile with a lifetime of 4.0 and 5.7 ms, respectively, but the lifetime increases up to 7.0 ms, after pulsed laser annealing treatment. X-ray diffraction and optical spectroscopy showed that after an adapted pulsed CO<sub>2</sub> laser annealing, the resulting materials showed a crystalline environment.

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### 1. Introduction

Over the last few years, considerable efforts have been made in order to obtain rare earth doped glass–ceramic materials with active ions embedded in the crystalline phase [1]. The glass–ceramic materials are of great importance in photonics, may be a valid alternative method to control chemical parameters of the rare earth, and thus may avoid undesirable effect like clustering. Erbium containing nanocrystallites in a glassy matrix exhibit higher optical cross-section of the erbium transitions and also low phonon energies strongly reduce non-radiative multiphonon relaxation [2].

In order to produce active rare earth nanocrystals in a glass matrix, heat treatment using a furnace has been commonly used, but a potential candidate for reaching future technology nodes is the laser annealing (LA) process. For laser annealing several types of lasers have been used, differing primarily in wavelength (e.g. XeCl 308 nm, frequency doubled Nd-YAG 532 nm, Nd-YAG 1064 nm, CO<sub>2</sub> 10.6 μm) [3,4]. It was reported that CO<sub>2</sub> laser annealing can reduce scattering losses in Corning 7059 glasses [5–6] and ZnO [7] thin-film waveguides fabricated on thermally oxidized silicon substrates; losses as low as 0.05 dB/cm for Corning 7059 glass waveguide [5] and 0.01 dB/cm for ZnO waveguides [7] have been achieved by this technique. This study was extended by the same author to reduce optical scattering losses in the fabrication of other waveguides: Si<sub>3</sub>N<sub>4</sub> films fabricated by low pressure chemical vapor deposition, Nb<sub>2</sub>O<sub>5</sub> films by RF Sputtering, and Ta<sub>2</sub>O<sub>5</sub> films by both

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reactive sputtering and thermal oxidation of sputtered tantalum films [4].

This paper is devoted to the sol–gel preparation and the investigation of the properties of  $\text{Er}^{3+}$  doped  $\text{SiO}_2\text{--ZrO}_2$  and  $\text{Er}^{3+}$  doped  $\text{SiO}_2\text{--HfO}_2$  planar waveguides, where an annealing alternative method based on  $\text{CO}_2$  laser irradiation ( $\lambda = 10.6 \mu\text{m}$ ) is used. The optical and spectroscopic properties, tailored with the pulsed and continuous  $\text{CO}_2$  laser irradiation process, in  $\text{SiO}_2\text{--ZrO}_2$  and  $\text{SiO}_2\text{--HfO}_2$  planar waveguides are measured and discussed having in mind a contribution to the new EDWA production processes employing light irradiation.

## 2. Experimental

We prepared several samples of Er-doped silica–zirconia and silica–hafnia materials by a sol–gel technique. The starting solution, for both systems, was obtained by mixing tetraethylorthosilicate (TEOS), ethanol, de-ionized water, and hydrochloric acid as a catalyst, and prehydrolysed for 1 h at  $65^\circ\text{C}$ . The molar ratio of  $\text{TEOS}:\text{HCl}:\text{EtOH}:\text{H}_2\text{O}$  was 1:0.01:37.9:2. For  $\text{SiO}_2\text{--HfO}_2$  an ethanolic colloidal suspension was prepared using as a precursor  $\text{HfOCl}_2$  and was then added to the solution containing TEOS, with a Si/Hf molar ratio of 70/30. For the  $\text{SiO}_2\text{--ZrO}_2$  waveguide, the precursor was  $\text{ZrOCl}_2$  and was then added to the solution containing TEOS with a Si/Zr molar ratio of 70/30 and 80/20. Erbium was added as  $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  with an  $\text{Er}/(\text{Si} + \text{Hf} \text{ or } \text{Zr})$  molar concentration of 0.5 and 5 mol%. The final mixture was left at room temperature under stirring for 16 h. The obtained sol was filtered with a  $0.2 \mu\text{m}$  Millipore filter. The films were deposited on cleaned pure v- $\text{SiO}_2$  substrates by dip coating with a dipping rate of 40 mm/min. Before further coating, each layer was annealed in air for 50 s at  $900^\circ\text{C}$ . After 10 and 20 dipping cycles, the films were heated for 2 min at  $900^\circ\text{C}$ . Some samples were stabilized by a last treatment for 5 and 30 min in air at  $900^\circ\text{C}$ , as presented in Table 1. Other samples were stabilized with  $\text{CO}_2$  laser annealing treatment, as shown in Table 2.

A continuous  $\text{CO}_2$  laser of  $10.6 \mu\text{m}$  wavelength with a beam diameter of 6 mm was used for annealing both  $\text{SiO}_2\text{--HfO}_2$  and  $\text{SiO}_2\text{--ZrO}_2$  planar waveguides. The power density of the  $\text{CO}_2$  laser beam, with a Gaussian distribution, was around  $5.7 \text{ W}/\text{cm}^2$ , and the irradiated zone of the waveguide was adjusted to 2 cm diameter; the Gaussian distribution is along the beam cross-section. The

waveguides were positioned at around 50 cm from the laser. The samples were irradiated in air with power and irradiation time ranging from 10 to 13 W and from 10 to 30 min, respectively. For the pulsed  $\text{CO}_2$  laser irradiation,  $80\text{SiO}_2\text{--}20\text{ZrO}_2$  planar waveguides has been used. The laser power density, with a Gaussian distribution, was  $78 \text{ W}/\text{cm}^2$  for pulsed  $\text{CO}_2$  laser irradiation and a pulse period of 400 and  $32 \mu\text{s}$  pulse width. The sample was about 1.5 m from the laser head and Argon C45 was used as a shroud gas for the annealing processes at a flow rate of 2.0 l/min. The gas was fed through a copper tube of 6 mm diameter; the tube exit was 20 mm from the laser spot, and parallel to the sample surface. The samples were annealed with an irradiation time ranging from 2.5 to 15 min.

The thickness of the waveguide and the refractive index at 543.5, 632.8, 1319 and 1542 nm were measured by an m-line apparatus (Metrcion model 2010) based on the prism coupling technique [8]. The losses at 632.8 nm for the  $\text{TE}_0$  mode were evaluated by photometric detection of the light intensity scattered out of the waveguide plane [9,10]. The  $\text{TE}_0$  mode waveguiding excitation was used for photoluminescence (PL) measurements, using the 514.5 nm emission of  $\text{Ar}^+$  ion laser, detecting the light coming-out from the waveguide surface. The signal in the visible region was selected by a double monochromatic and analyzed by a photon-counting system. The PL spectroscopy in the region of  $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$  transition of  $\text{Er}^{3+}$  ions, was performed using the 514.5 nm emission of  $\text{Ar}^+$  ion laser. The luminescence was dispersed by a 320 mm single-grating monochromator with a resolution of 2 nm. The light was detected using an InGaAs photodiode and a standard lock-in technique. Decay curves were obtained by chopping the CW exciting beam with a mechanical chopper and recording the signal with a digital oscilloscope. All the measurements were performed at room temperature.

The samples have been characterized by X-ray diffraction measurements (XRD) using a X-Pert pro equipment with the  $\text{Cu K}\alpha$  radiation at  $1.5426 \text{ \AA}$ . The diffracted intensity was measured in the  $2\theta$  range between  $10^\circ$  and  $100^\circ$ , with a step of  $0.05^\circ$ . The crystal phases were determined with the help of software which identifies the crystal phase by fitting the diffraction peaks.

## 3. Results and discussion

The optical and spectroscopic parameters for the continuous  $\text{CO}_2$  laser irradiated samples are reported in Table 3. The thermal annealed samples are also reported for comparison. The waveguides present a thickness ranging from 0.63 to  $0.99 \mu\text{m}$ . All waveguides support one TE and TM mode at 1319 and 1542 nm. For the  $70\text{SiO}_2\text{--}30\text{HfO}_2$  and  $70\text{SiO}_2\text{--}30\text{ZrO}_2$  planar waveguides doped with 5 mol%  $\text{Er}^{3+}$  after thermal annealing (SH1\_B and SZ1\_B, see Table 3), the refractive indices measured in TE polarization are quite similar to those obtained in TM polarization ( $\text{SiO}_2\text{--HfO}_2$ :  $\Delta n_{\text{TE-TM}} = 0.005 \pm 0.001$ ;  $\text{SiO}_2\text{--ZrO}_2$ :  $\Delta n_{\text{TE-TM}} = 0.007 \pm 0.002$ ), indicating that the birefringence is negligible in the systems and similar differences are obtained for the refractive indices for the samples treated

**Table 1**  
Thermal annealing characteristics for  $\text{Er}^{3+}$ -activated  $\text{SiO}_2\text{--ZrO}_2$  and  $\text{SiO}_2\text{--HfO}_2$  planar waveguides.

Waveguide label	Concentration (molar ratio)	Er concentration (mol%)	Time (min)
SZ1	B_70SiO <sub>2</sub> –30ZrO <sub>2</sub>	5	5
SH1	B_70SiO <sub>2</sub> –30HfO <sub>2</sub>	5	5
SZ6	B_80SiO <sub>2</sub> –20ZrO <sub>2</sub>	0.5	5
	C_80SiO <sub>2</sub> –20ZrO <sub>2</sub>	0.5	30

**Table 2**  
 $\text{CO}_2$  laser annealing characteristics for  $\text{Er}^{3+}$ -activated  $\text{SiO}_2\text{--ZrO}_2$  and  $\text{SiO}_2\text{--HfO}_2$  planar waveguides.

Waveguide label	Concentration (molar ratio)	Er concentration (mol%)	$\text{CO}_2$ laser type	Average power (W)	Irradiation time (min)
SH1	C_70SiO <sub>2</sub> –30HfO <sub>2</sub>	5	Continuous	13	15
SZ1	C_70SiO <sub>2</sub> –30ZrO <sub>2</sub>	5	Continuous	13	15
SZ5	B_80SiO <sub>2</sub> –20ZrO <sub>2</sub>	0.5	Continuous	10	10
	C_80SiO <sub>2</sub> –20ZrO <sub>2</sub>	0.5	Continuous	10	20
	D_80SiO <sub>2</sub> –20ZrO <sub>2</sub>	0.5	Continuous	10	30
	B_80SiO <sub>2</sub> –20ZrO <sub>2</sub>	0.5	Pulsed	30	2.5
SZ8	C_80SiO <sub>2</sub> –20ZrO <sub>2</sub>	0.5	Pulsed	30	10
	D_80SiO <sub>2</sub> –20ZrO <sub>2</sub>	0.5	Pulsed	30	15
	B_80SiO <sub>2</sub> –20ZrO <sub>2</sub>	0.5	Pulsed	30	15

**Table 3**  
Optical and spectroscopic parameters of the Er<sup>3+</sup>-activated SiO<sub>2</sub>-ZrO<sub>2</sub> and SiO<sub>2</sub>-HfO<sub>2</sub> planar waveguides.

Waveguide label	Annealing treatment	Refractive index at 1.3 μm ± 0.005		Refractive index at 1.5 μm ± 0.005		Bandwidth (±2 nm) @ λ <sub>ex</sub> = 514.5 nm	Lifetime (±0.5 ms) @ λ <sub>ex</sub> = 514.5 nm	Attenuation coefficient (±0.3 dB/cm) @ λ <sub>ex</sub> = 632.8 nm
		TE	TM	TE	TM			
SH1_	A_before TA	1.586	1.578	1.583	1.575	50	≤0.5	≥2
	B_after TA T = 900 °C; t = 5 min	1.593	1.587	1.589	1.585	47	0.8	≥2
	C_after CW LA IT = 15 min	1.624	1.616	1.621	1.616	49	0.7	0.8
SZ1_	A_before TA	1.621	1.614	1.617	1.613	48	≤0.5	≥2
	B_after TA T = 900 °C; t = 5 min	1.623	1.616	1.621	1.616	46	0.8	≥2
	C_after CW LA IT = 15 min	1.631	1.625	1.629	1.623	48	0.6	1.2
SZ5_	A_before LA	1.551	1.543	1.548	1.542	46	4.6	≥2
	B_after CW LA IT = 10 min	1.564	1.557	1.561	1.555	48	4.5	1.5
	C_after CW LA IT = 20 min	1.566	1.558	1.563	1.558	48	5.4	1.4
	D_after CW LA IT = 30 min	1.570	1.563	1.566	1.560	48	5.9	1.1

TA, thermal annealing; LA, laser annealing; IT, irradiation time.

with CO<sub>2</sub> laser annealing, SH1\_C and SZ1\_C (SiO<sub>2</sub>-HfO<sub>2</sub>: Δn<sub>TE-TM</sub> = 0.007 ± 0.003; SiO<sub>2</sub>-ZrO<sub>2</sub>: Δn<sub>TE-TM</sub> = 0.007 ± 0.001) indicating that the laser annealing do not induce birefringence in these systems.

Comparing the refractive indices in the SiO<sub>2</sub>-HfO<sub>2</sub> samples before and after the CO<sub>2</sub> laser irradiation (see Table 3) we observe a variation Δn of about 0.04. For example for the sample (SH1\_A) at 1542 nm the refractive index in TE polarization is 1.583 before any final treatment, 1.589 after thermal conventional annealing and 1.621 after CO<sub>2</sub> laser annealing. The increasing of the refractive index observed with laser annealing can suggest that with this laser treatment a better densification of the system is achieved with respect to thermal annealing. As a matter of fact, as appears in the Table 3, the SiO<sub>2</sub>-ZrO<sub>2</sub> sample, shows similar values of refractive index before and after the thermal annealing, but with CO<sub>2</sub> laser annealing we observe a variation Δn of about 0.01.

We have observed that laser annealing can lead to waveguides with a lower attenuation coefficient, than the attenuation coefficient obtained after the thermal annealing. In fact, we observe an attenuation coefficient at 632 nm of 0.80 and 1.2 dB/cm for silica-hafnia and silica-zirconia waveguides, respectively for the irradiated systems while we obtain attenuation coefficient higher than 2 dB/cm for the systems processed with thermal annealing. The decrease in the attenuation coefficient on the CO<sub>2</sub> laser irradi-

ated systems, has been attributed by Dutta et al. [6] to the elimination of surface irregularities. An increase of the lifetime, related to the decay of the <sup>4</sup>I<sub>13/2</sub> level of Er<sup>3+</sup> ions in the 80SiO<sub>2</sub>-20ZrO<sub>2</sub>, with the increase in irradiation time of CO<sub>2</sub> laser annealing, was observed (see Table 3).

The effect of the CO<sub>2</sub> laser irradiation time on the attenuation coefficient at 1319 and 1542 nm is shown in Table 4. The losses were observed for the samples SZ5\_B, SZ5\_C, and SZ5\_D. The optical and spectroscopic parameters for the both, annealed for several time duration in oven and CO<sub>2</sub> pulsed laser annealed samples 80SiO<sub>2</sub>-20ZrO<sub>2</sub> doped with 0.5 mol% of Er<sup>3+</sup>, are reported in Table 5. The 80SiO<sub>2</sub>-20ZrO<sub>2</sub> optical waveguides doped with 0.5 mol% Er<sup>3+</sup>, after laser annealing, shows enough low propagation losses at all wavelengths studied, including at 1542 nm which thus makes suitable candidate to develop amplifier in the C band of telecommunication.

Evidence of embedding erbium ions in zirconia nanocrystals, after an adapted CO<sub>2</sub> laser annealing comes from the visible luminescence spectra as shown in Fig. 1. The differences as a function of the annealing treatment, in the shape of the spectra relative to the emission of the erbium ions due to the transitions <sup>2</sup>H<sub>11/2</sub> → <sup>4</sup>I<sub>15/2</sub> and <sup>4</sup>S<sub>3/2</sub> → <sup>4</sup>I<sub>15/2</sub> (Fig. 1I) and relative to the <sup>4</sup>I<sub>13/2</sub> → <sup>4</sup>I<sub>15/2</sub> transition (Fig. 1II) indicate the different crystal field structures, and suggest that erbium can be in a crystalline environment after 30 min at 900 °C in oven (SZ6\_C waveguide), but these differences are strongly evident after 10 min at 30 W-pulsed CO<sub>2</sub> laser irradiation (SZ8\_C waveguide). The modifications of the spectra confirm the significant change of erbium ions' environment in a more ordered system induced by the pulsed laser annealing treatment.

An increase of the lifetime from 4.6 ms before to 7.0 ms after pulsed CO<sub>2</sub> laser annealing was measured for 80SiO<sub>2</sub>-20ZrO<sub>2</sub> with 0.5 mol% Er<sup>3+</sup>-activated waveguide (SZ8\_C) as appears in Fig. 2. This behavior can be related to a better structural order of the

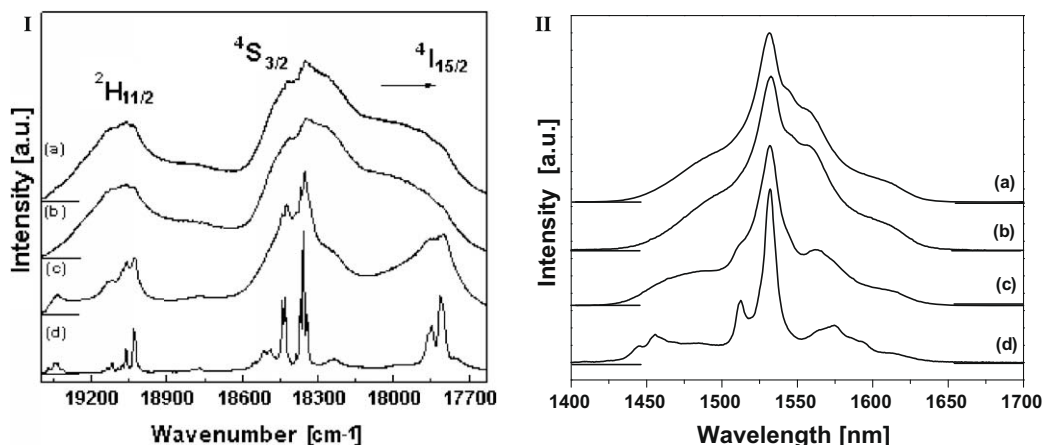
**Table 4**  
Attenuation coefficient of the Er<sup>3+</sup>-activated SiO<sub>2</sub>-ZrO<sub>2</sub> planar waveguides at different time of CW CO<sub>2</sub> laser irradiation.

Waveguide label	SZ5-B	SZ5-C	SZ5-D
Time of laser annealing (min)	10	20	30
Attenuation coefficient @ 1319 nm (±0.3 dB/cm)	0.6	0.6	0.3
Attenuation coefficient @ 1542 nm (±0.3 dB/cm)	0.8	0.6	0.6

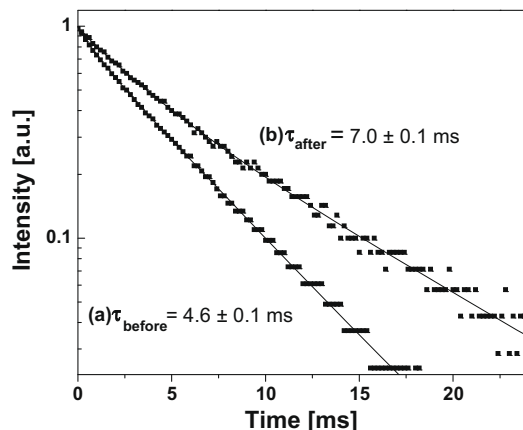
**Table 5**  
Optical and Spectroscopic parameters of 80SiO<sub>2</sub>-20ZrO<sub>2</sub> optical waveguides doped with 0.5 mol% Er<sup>3+</sup>.

Waveguide label	Annealing treatment	Refractive index at 1.3 μm ± 0.005		Refractive index at 1.5 μm ± 0.005		Bandwidth (±2 nm) @ λ <sub>ex</sub> = 514.5 nm	Lifetime (±0.5 ms) @ λ <sub>ex</sub> = 514.5 nm
		TE	TM	TE	TM		
SZ6_	A_before TA	1.5509	1.5431	1.5480	1.5420	46	4.1
	B_after TA T = 900 °C; t = 5 min	1.5591	1.5534	1.5561	1.5522	42	4.9
	C_after TA T = 900 °C; t = 30 min	1.5615	1.5539	1.5580	1.5521	22	5.7
SZ8_	A_before LA	1.5494	1.5395	1.5469	1.5390	46	4.1
	B_after pulsed LA IT = 2.5 min	1.5593	1.5502	1.5558	1.5471	12	8.2
	C_after pulsed LA IT = 10 min	1.5590	1.5512	1.5558	1.5497	12	7.0
	D_after pulsed LA IT = 15 min	1.5538	1.5464	1.5505	1.5431	12	7.2

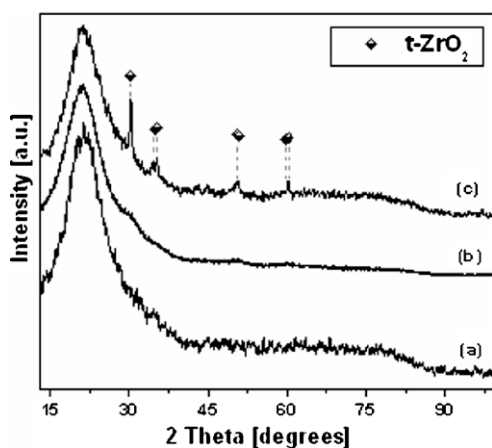
TA, thermal annealing; LA, laser annealing; IT, irradiation time.



**Fig. 1.** (I): Room temperature luminescence spectra in the visible region to the  $^2H_{11/2}$ ,  $^4S_{3/2} \rightarrow ^4H_{15/2}$  transitions of the  $Er^{3+}$  ions for (a) as deposited, SZ5\_A, (b) after CW LA IT = 10 min, SZ5\_B, (c) after TA  $T = 900^\circ C$ ;  $t = 30$  min, SZ6\_C and (d) after pulsed LA IT = 10 min, SZ8\_C planar waveguides upon excitation at 514.5 nm. (II): Room temperature luminescence spectra of the  $^4I_{13/2} \rightarrow ^4I_{15/2}$  transition of  $Er^{3+}$  ions for (a) as deposited, SZ5\_A, (b) after CW LA IT = 10 min, SZ5\_B, (c) after TA  $T = 900^\circ C$ ;  $t = 30$  min, SZ6\_C and (d) after pulsed LA IT = 10 min, SZ8\_C planar waveguides upon excitation at 514.5 nm.



**Fig. 2.** Decay curves of the luminescence from the  $^4I_{13/2}$  metastable state of  $Er^{3+}$  ions for (a) as deposited, SZ5\_A and (b) pulsed LA IT = 10 min, SZ8\_C planar waveguides, upon 514.5 nm excitation.



**Fig. 3.** X-ray diffraction pattern for the waveguides: (a) SZ5-A, (b) SZ6-C and (c) SZ8-B. The phase  $ZrO_2$  (■) are also reported.

erbium environment. In fact, it is well known that a crystalline environment around the rare earth induces a shortening in the phonon energies [11]. Indeed, the phonon energy of the surrounding envi-

ronment of the rare earth ions is proportional to the non-radiative contribution of the  $^4I_{13/2} \rightarrow ^4I_{15/2}$  transition. So the main effect of the crystallization is decrease in the non-radiative process thus inducing a lengthening of the lifetime of the metastable level  $^4I_{13/2}$ .

The Fig. 3 represents the X-ray diffraction pattern for the waveguides laser annealing and heat treated. It clearly shows crystallization embedded in the glass matrix for a pulsed laser annealed sample. The fitting procedure of the spectra indicates that the dominant structure is the tetragonal phase  $ZrO_2$ ; the main peaks are also reported in the Fig. 3. As shown in Fig. 3, the SZ6\_C and SZ5\_B samples does not show any peaks originating from crystalline  $ZrO_2$  phase, indicating the amorphous nature of these film.

#### 4. Conclusions

In conclusion,  $(100-x)SiO_2-xZrO_2$  ( $x = 20, 30$  mol) planar waveguides, doped with 5 and 0.5 mol%  $Er^{3+}$  and  $70SiO_2-30HfO_2$  doped with 5 mol%  $Er^{3+}$  planar waveguides were prepared by the sol-gel method and dip coating processing. In this study, we note that using an adapted setup, the continuous and pulsed  $CO_2$  laser irradiation induced optical and structural changes in all treated samples. The refractive index changes in the  $Er^{3+}$ -activated  $70SiO_2-30HfO_2$  planar waveguides on  $CO_2$  laser irradiation were 0.04. For all samples of  $SiO_2-ZrO_2$  and  $SiO_2-HfO_2$ , it was experimentally demonstrated that the refractive-index change is induced by the effect of the irradiation, and the change is higher than that obtained with the same system with the conventional annealing in oven. On the other hand, the technique of laser annealing has been shown to significantly reduce propagation loss on  $SiO_2-HfO_2$  and  $SiO_2-ZrO_2$  planar waveguides.  $80SiO_2-20ZrO_2$  optical waveguide doped with 0.5 mol%  $Er^{3+}$  was fabricated and treated with CW  $CO_2$  laser irradiation. Low attenuation coefficients of 0.3 and 0.6 dB/cm at 1319 and 1542 nm, respectively, were measured. The X-ray results and the modifications of the luminescence in the visible region and photoluminescence spectra for the pulsed  $CO_2$  laser annealed samples, confirm the significant modification of erbium ions' environment in glass-ceramic systems because of the irradiation treatment.

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## References

- [1] Y. Jestin, C. Armellini, S.N.B. Bhaktha, A. Chiappini, A. Chiasera, S. Diré, M. Ferrari, C. Goyes, M. Montagna, E. Moser, G. Nunzi Conti, S. Pelli, G.C. Righini, C. Tosello, K.C. Vishunubhatla, Sol-gel derived glass-ceramic waveguides for optical amplification, Oral communication V Workshop Italiano Sol-Gel, Milano, Italy, June 2006.
- [2] Y. Jestin, N. Afify, C. Armellini, S. Berneschi, S.N.B. Bhaktha, B. Boulard, A. Chiappini, A. Chiasera, G. Dalba, C. Duverger, M. Ferrari, C. Goyes, M. Mattarelli, M. Montagna, E. Moser, G. Nunzi Conti, S. Pelli, G.C. Righini, F. Rocca, Er<sup>3+</sup> activated silica-hafnia glass-ceramics planar waveguides, Photonics Europe – SPIE Europe, SPIE vol. 6183 – p1W1–1W8, Strasbourg, France, April 2006.
- [3] M. Zevin, R. Reisfeld, Preparation and properties of active waveguides based on zirconia glasses, *Optical Materials* 8 (1997) 37–41.
- [4] S. Dutta, H.E. Jackson, J.T. Boyd, R.L. Davis, F.S. Hickernell, CO<sub>2</sub> laser annealing of Si<sub>3</sub>N<sub>4</sub>, Nb<sub>2</sub>O<sub>5</sub> and Ta<sub>2</sub>O<sub>5</sub> thin-film optical waveguides to achieve scattering loss reduction, *IEEE Journal of Quantum Electronics* QE 18 (4) (1982) 800–806.
- [5] S. Dutta, H.E. Jackson, J.T. Boyd, Reduction of scattering from a glass thin-film optical waveguide by CO<sub>2</sub> laser annealing, *Applied Physics Letters* 37 (6) (1980) 512–514.
- [6] S. Dutta, H.E. Jackson, J.T. Boyd, Extremely low-loss glass thin-film optical waveguides utilizing surface coating and laser annealing, *Journal of Applied Physics* 52 (6) (1981) 3873–3875.
- [7] S. Dutta, H.E. Jackson, J.T. Boyd, F.S. Hickernell, R.L. Davis, Scattering loss reduction in ZnO optical waveguides by laser annealing, *Applied Physics Letters* 39 (3) (1981) 206–208.
- [8] C. Duverger, C. Turrell, M. Bouazaoui, F. Tonelli, M. Montagna, M. Ferrari, Preparation of SiO<sub>2</sub>-GeO<sub>2</sub>:Er<sup>3+</sup> planar waveguides by waveguide Raman and luminescence spectroscopies, *Philosophical Magazine B* 77–2 (1998) 363–372.
- [9] R.M. Almeida, P.J. Morais, H.C. Vasconcelos, Optical loss mechanisms in nanocomposite sol-gel planar waveguides, *Proceedings SPIE* 3136 (296) (1997).
- [10] C. Tosello, S. Ronchin, E. Moser, M. Montagna, P. Mazzoldi, F. Gonnella, M. Ferrari, C. Duverger, R. Belli, G. Battaglin, Optical properties and structural characterization of erbium-activated SiO<sub>2</sub>-TiO<sub>2</sub> planar waveguides prepared by RF sputtering, *Philosophical Magazine B* 79 (11/12) (1999) 2103–2112.
- [11] P.G. Kik, A. Polman, Erbium-doped optical-waveguides amplifiers on silicon, *MRS bulletin* 23 (4) (1998) 48–54.