Stress-induced buried waveguides in the $0.8\text{CaSiO}_3\text{--}0.2\text{Ca}_3(\text{PO}_4)_2$ eutectic glass doped with Nd^{3+} ions

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ABSTRACT

In this work the fabrication of buried optical waveguides by femtosecond laser inscription in the $0.8\text{CaSiO}_3\text{--}0.2\text{Ca}_3(\text{PO}_4)_2$ eutectic glass doped with Nd^{3+} ions is reported. The glass samples were prepared by melting the eutectic powder mixture in a Pt–10 wt.% Rh crucible at 1600°C and pouring it in a preheated brass mould. Afterwards, the glass was annealed to release the inner stresses. Buried waveguides were fabricated by focusing beneath the surface a pulsed Ti:sapphire laser with a pulsewidth of 120 fs working at 1 kHz. Two adjacent parallel tracks were written to define a region where an increase in the refractive index occurs. The effects produced by the variation of the laser pulse energy as well as the lateral separation between tracks, scanning speed and focusing distance were studied. After the laser processing, the near-field intensity distribution at 633 nm of the waveguide's modes was studied demonstrating the confinement of both, the TE as the TM polarizations. In order to diminish the losses induced by colour centres absorption, heat treatments were carried out in the samples. The waveguide's modes were compared with respect to the samples without heat treatments. The spectroscopic properties of the neodymium ions have been characterized to evaluate in what extent their optical properties could be modified by the waveguide fabrication process and to elucidate the potential application of such waveguides as integrated laser sources.

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1. Introduction

The recent development of lasers with short output pulses in the femtosecond range has opened up a wide variety of new applications of great interest in the field of optics, microelectronic, telecommunication and aerospace. The high local spatial and temporal electronic and vibrational excitation densities produced by the absorption of ultrashort pulses, together with the laser pulse duration, short compared to the relevant relaxation processes, and the laser-induced nonlinear processes, such as multiphoton absorption, have provided a new materials processing regime [1].

Modern communication technology is based on integrated optical devices to control the properties of light in all-optical networks. Key elements within these networks are active and passive waveguides, splitters and filters. The optical function of these elements is

based on spatial refractive index modification within the substrate. This modification can be carried out by a novel technique developed in recent years based on the use of ultra-short laser pulses for direct writing [2,3]. Although permanent structural modifications can be attained by crystallization processes in the nanosecond range [4], when intense ultra-short laser pulses are tightly focussed inside transparent materials, nonlinear absorption in the focal volume takes place, leading to weak local refractive index variations or to different kinds of damage [1–3,5–7]. Stress-induced waveguides produced by the processing of buried single and pair of tracks have been studied along the last decade in crystalline and glassy matrices doped with rare earths (RE) since their interest for the production of active photonic devices [8–16].

Eutectic ceramics are composite materials formed in situ from a melt. Eutectic ceramic oxides have been studied along the last decades due to their outstanding mechanical properties, microstructural stability and corrosion resistance up to temperatures very close to their melting point, which make them suitable for functional and structural purposes [17]. Furthermore, they can also be used for optical applications, since eutectic materials are

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usually made from large optical band gap materials [17]. In particular, the $\text{CaSiO}_3\text{--Ca}_3(\text{PO}_4)_2$ eutectic composite presents two interesting properties: in the first place, it is a bioactive material since tricalcium phosphate (TCP), $\text{Ca}_3(\text{PO}_4)_2$, is osteoconductive and bioactive (reabsorbable) [18] and wollastonite (W), CaSiO_3 , is bioactive with osteostimulative properties [19]. The features, microstructure, bioactivity, biocompatibility, in vitro and in vivo behaviours of this binary system have been widely studied, both in crystalline and glassy form [19–23]. In the second place, this eutectic glass has excellent optical properties. In particular, it was found that the lifetimes and emission cross-sections of the $1.06\text{ }\mu\text{m}$ (Nd^{3+}) and $1.5\text{ }\mu\text{m}$ (Er^{3+}) emissions in this glass are equivalent to those of the best commercially used alkaline-silicate glasses [24]. More recently, it has been demonstrated laser emission under pulsed pumping which showed a behaviour close to a Q-switch operation. Wavelength-resolved pump excitation of Nd^{3+} ions in this glass allowed for a broad band tunability (10 nm) of the laser emission which is related with the variety of quasi-isolated crystal field site distributions of Nd^{3+} ions in this glass matrix [25,26].

In this work we report the fabrication of buried optical waveguides by femtosecond laser inscription in the $0.8\text{CaSiO}_3\text{--}0.2\text{Ca}_3(\text{PO}_4)_2$ eutectic glass doped with Nd^{3+} ions. The waveguides were fabricated under the double line configuration. It consists on the production of two parallel damage tracks inside the sample by scanning the focus of the laser beam along the sample length, leading to a refractive index increase in the central volume due to the stress induced during the irradiation. The effects caused by the variation of the processing conditions as well as the waveguiding characteristics in the confined region between tracks have been studied. The spectroscopic properties of the neodymium ions have also been characterized in the confined region to evaluate if their optical properties have been modified during the laser processing.

2. Experimental

2.1. Glass fabrication

The glass samples were obtained from the powder mixture of wollastonite (high-purity reagent-grade CaSiO_3 , 99 wt.%, –200 mesh, Aldrich Chemistry, St. Louis MO, USA) and synthesized tricalcium phosphate (purity >99.9% and 1.50 Ca/P molar ratio, which characteristics were reported previously [23]) in the eutectic composition: 80% CaSiO_3 , 20% $\text{Ca}_3(\text{PO}_4)_2$ expressed in mol%. Furthermore, a 1 wt.% of Nd_2O_3 was added to the eutectic composite to obtain the doped samples. The resulting powders mixture was melted using a Pt–10 wt.% Rh crucible at 1600°C in an electric furnace for 1 h to ensure a homogeneous liquid. The melt was poured onto a preheated brass mould obtaining a homogeneous, bubble-free and transparent bulk glass. Afterwards, the glass was annealed at 795°C for 30 min and then slowly cooled down to room temperature in order to eliminate the stress formed during the fast cooling process after pouring the glass. For the measurement of thermal properties, cubic-shaped specimens were cut from the bulk samples using a slow speed saw (Buehler, Lake Bluff, IL). Glass transition temperature, T_g , dilatometric softening temperature, T_d , and coefficient of thermal expansion, α , were measured in air (Netzsch dilatometer, Netzsch-Gerätebau GmbH, Selb, Germany) at a heating rate of 5°C min^{-1} .

2.2. Waveguide fabrication

Cubic samples of $5 \times 5 \times 5\text{ mm}^3$ were prepared from the glass by cutting with a diamond blade. The surface to be processed was subsequently polished by means of sandpapers, increasing

Fig. 1. Sketch of the waveguide laser inscription. Two parallel damage tracks are generated inside the sample focusing the laser beam with a $20\times$ microscope objective ($\text{NA}=0.4$) and scanning the focus along the sample length using a XYZ motorized stage.

the grade from 800 up to 2500, and diamond polishing abrasives up to $0.25\text{ }\mu\text{m}$. The waveguides were fabricated under the double line configuration by using a pulsed Ti:sapphire laser system that delivered transform limited 120 fs pulses with central wavelength of 796 nm at a repetition rate of 1 kHz. The laser beam was focused by a $20\times$ microscope objective ($\text{NA}=0.4$) and the sample was placed in a XYZ motorized stage with spatial resolution of $0.2\text{ }\mu\text{m}$. Fig. 1 shows a sketch of the waveguide laser inscription. The processing conditions were modified to determine the damage threshold of this glass and to study the spatial distributions of the tracks and, in this way, how this feature may affect to the guiding behaviour. Hence, the geometrical focus was located 150 and $250\text{ }\mu\text{m}$ beneath the surface of the sample and the pulse energy was varied between 5.04 and $0.021\text{ }\mu\text{J}$ with the help of a calibrated neutral density filter, a linear polarizer and a half-wave plate. Under these conditions two parallel damage tracks were written with a lateral separation of 15 and $20\text{ }\mu\text{m}$ by scanning the piece at speeds of 25 and $50\text{ }\mu\text{m/s}$. The polarization of the laser was kept in all the cases perpendicular to the scanning direction.

In order to diminish the absorption by colour centres, thermal treatments were carried out on the sample between 300 and 550°C for 30 min with heating/cooling rates of 900°C/h .

2.3. Characterization techniques

The glass matrix composition was determined by means of scanning electron microscopy (SEM) using a field emission JEOL JSM-7000F with EDX analysis. The amorphous character of the glass sample was characterized by XRD analysis by using a X'Pert Pro MPD diffractometer.

Frontal and cross-section photographs of the waveguides were taken with a Zeiss Axiomager Z1 optical microscope.

Near-field intensity distribution of the waveguide's modes was characterized by using a He-Ne laser with 30 mW of output power, working in continuous mode emitting at 633 nm and using entrance and outside objectives DIN 10/0.25 and DIN 40/0.65 respectively, 1% neutral filter, two polarizers and a CCD camera.

Luminescence was determined by means of a home-made confocal microscope pumping the sample at 808 nm by a single mode fibre coupled diode. Lifetime measurements were performed by exciting the samples with a pulsed Ti:sapphire laser and processing the data with an oscilloscope.

Fig. 2. XRD diffraction pattern of the glass sample.

3. Results and discussion

The TCP–W–Nd₂O₃ ternary composition was completely melted at 1600 °C after 1 h and the melt was easily cast, resulting in a homogeneous and transparent glass without devitrifications or crystallizations. Neither cracks nor other defects were detected in the glass samples. The obtained glass was stable under H₂O and could be cut and polished using water media. The annealed stress-free glass was amorphous with no crystalline phases present, as confirmed by X-ray diffraction (Fig. 2). The amorphous XRD pattern registered only one broad peak (centre: ca. 30°, 2θ), which is a characteristic feature of alkaline-earth silicophosphate glasses [27]. Neither evidence of phase separation nor devitrification or crystallization were observed by optical inspection and SEM analyses. Microstructural and compositional analysis of the glass sample were carried out to verify that the composition of the processed sample was close to the eutectic point, 50.7 CaO + 31.0 SiO₂ + 18.3 P₂O₅ in wt.% [20] and to check the amount of RE the sample was doped with. Table 1 shows how the composition of the glass as well as the percentage of the doping material were close to the nominal value. The linear thermal expansion curves of pure and Nd₂O₃ doped TCP–W annealed glasses showed that the glass transition temperature (*T_g*) of both glasses did not change significantly with the Nd₂O₃ addition (790 ± 3 °C and 796 ± 3 °C respectively). The neodymium addition slightly changed the dilatometric softening temperature (*T_d*) from 811 ± 3 °C to 817 ± 3 °C. The measured coefficient of thermal expansion for the glass obtained in the present work, α_(50–400 °C), was 10.5 (±0.1) × 10^{−6} K^{−1}. The substitution of Ca²⁺ for Nd³⁺ (ionic radius 0.99 Å and 1.08 Å respectively) produced a doped glass bulk density slight increase (2.91 ± 0.02 g cc^{−1} versus 2.97 ± 0.02 g cc^{−1}).

The variations in the morphology of the tracks inscribed in the glass sample with the femtosecond laser were studied by varying the laser pulse energy, the focusing distance, the scanning speed and the lateral separation between tracks. Fig. 3 shows the cross-section (a), where the irradiation direction is from top to bottom, and the top view (b) of pairs of tracks produced by focusing the laser beam 150 μm beneath the surface and processing with a scanning

Fig. 3. Cross-section (a) and top view (b) of pairs of tracks produced by focusing the laser beam 150 μm beneath the surface and processing with a scanning speed of 50 μm/s, with 15 μm between tracks for pulse energies of 0.42, 0.84, 1.26 and 1.68 μJ. The energy increase is pointed out by the arrow.

speed of 50 μm/s, with 15 μm between tracks for pulse energies of 0.42, 0.84, 1.26 and 1.68 μJ. The energy increase is pointed out by the arrow. It can be observed how the length of the damaged region induced by the laser irradiation increased with the pulse energy from 16 up to 40 μm (Fig. 3(a)). For higher energies the damage tracks obtained were no longer than 40 μm. It could also be observed an affected zone produced in the surroundings of each track and in the region between tracks, i.e., in the confined region, which size also increased with the pulse energy and that was caused by the generation of colour centres. It is known that the interaction of high intensity ultra-short laser pulses with matter modifies the material properties at atomic scale by the photophysical and photochemical interactions that take place after the laser absorption. These interactions, especially in insulators, involve the creation of colour centres [1]. The top view (Fig. 3(b)) shows that the whole track could be made without the production of cracks for any of

Table 1
Compositional analysis of the W-TCP eutectic glass in wt.%.

	SiO ₂	P ₂ O ₅	CaO	Nd ₂ O ₃
Theoretical	31.00	18.30	50.70	1.00
Measured	29.08	19.95	50.97	0.92

Fig. 4. Cross-section view of tracks made by focusing the laser beam 150 μm beneath the surface, processing with scanning speeds of 50 and 25 $\mu\text{m/s}$, (a) and (b) respectively, with 15 (left) and 20 μm (right) between tracks for a pulse energy of 3.36 μJ .

the investigated laser pulse energies, which would lead to losses in the guiding behaviour.

In order to determine the damage threshold, the incoming pulse energy was diminished until there was no effect observed in the sample by inspection with the optical microscope. It was obtained that pulse energies lower than 0.021 μJ did not produced enough energy density to modify the inner structure of the glass sample, thus determining such value as the damage threshold for our experimental conditions.

In Fig. 4 the cross-section view of tracks made by focusing the laser beam 150 μm beneath the surface, processing with scanning speeds of 50 and 25 $\mu\text{m/s}$, Fig. 4(a) and (b) respectively, with separation of 15 (left) and 20 μm (right) between tracks for a pulse energy of 3.36 μJ is presented. The figure shows that the decrease in the distance between tracks or in the scanning speed led to an increase in the generation of colour centres. With regards to the focussing distance, there were not found significant variations in the morphology of the tracks when it was varied from 150 to 250 μm .

Next, the waveguide properties of the generated damaged regions between tracks were examined at 633 nm. The near-field intensity distribution at 633 nm of the waveguide's modes was studied for the different processing conditions. It was found that the light guiding was only possible for pair of tracks produced with pulse energies higher than 0.42 μJ . For lower pulse energies the stress-induced between tracks was not high enough to confine and guide the light, thus determining the guiding threshold in 0.42 μJ . Furthermore, it was observed that for the waveguides processed with higher pulse energies both, the TE and the TM polarizations

Fig. 5. Near-field intensity pattern of the TE and the TM modes, (a) and (b) respectively, of a waveguide produced by focusing the laser beam 150 μm beneath the surface and processing with pulse energy of 1.68 μJ , a scanning speed of 50 $\mu\text{m/s}$, with 15 μm between tracks.

were guided. As an example, Fig. 5 shows the near-field intensity pattern of the TE and the TM modes, (a) and (b) respectively, of a waveguide produced by focusing the laser beam 150 μm beneath the surface and processing with pulse energy of 1.68 μJ , a scanning speed of 50 $\mu\text{m/s}$, with 15 μm between tracks, where it can be observed how the guiding was produced for both polarizations. In order to determine the modal sizes as well as the light confinement a modal study was carried out in function of the processing conditions. The modal sizes along the x and y directions were estimated by fitting the intensity profiles to Gaussian curves and taking the full width at half maximum *FWHM*, *Dx* and *Dy* respectively. Likewise, the modal areas were estimated by means of the areas corresponding to the ellipses of semi-axes *Dx*/2 and *Dy*/2. With regards to the laser pulse energy, Fig. 6 shows that the width of the mode was slightly shorter for the TM than for the TE mode along the x-axis, and in both cases, this dimension was shorter than the orthogonal one, *Dy*. Furthermore, the modal width along the x direction decreased with the pulse energy for both polarizations. This effect was related with the fact that as the pulse energy increased a higher stress between tracks and a higher damage in the surroundings of each track were produced. Regarding the modal dimension in the y-direction, the width tended to increase with the pulse energy for

Table 2Modal sizes in function of the scanning speed V , lateral separation between tracks Δ and focus position Z for a laser pulse energy of 5.04 μJ .

E (μJ)	V ($\mu\text{m/s}$)	Δ (μm)	Z (μm)	TE		TM		Area (μm^2)	
				D_x (μm)	D_y (μm)	D_x (μm)	D_y (μm)	TE	TM
5.04	50	15	150	4.9	12.6	5.0	15.8	48.6	62.6
5.04	50	20	150	4.7	13.3	5.6	15.7	49.2	69.0
5.04	25	20	150	5.8	19.3	5.6	16.1	87.5	71.2
5.04	50	15	250	5.5	24.0	5.5	16.4	103.3	71.4

Fig. 6. Modal sizes of the waveguides produced by focusing the laser beam 150 μm beneath the surface and processing with a scanning speed of 50 $\mu\text{m/s}$, with 15 μm between tracks for pulse energies between 0.84 and 5.04 μJ .

the TE mode whereas no clear trend was observed for the TM mode. In both cases, the modal area decreased with the pulse energy thus increasing the light confinement and being slightly higher for the TM mode. Next, the modal sizes were measured in function of the scanning speed V , lateral separation between tracks Δ and focus position Z . Table 2 shows that the better confinement conditions were produced for the shortest Δ and Z and the highest V , obtaining in this case modal areas of 48.6 and 62.6 μm^2 for the TE and the TM modes respectively. For any other processing conditions, the variations in the modal sizes D_x and D_y led to an increase in the modal area of up to 103.3 μm^2 for the TE mode and 71.4 μm^2 for the TM mode.

Colour centres absorption generated during the laser writing can be significantly reduced or even erased by photobleaching processes at wavelengths ranging from 400–650 nm or by means of heat treatments [28–30]. In this case, in order to decrease the absorption by colour centres and thus to reduce the waveguide

Fig. 7. Output power measured in each guide after heat treatments between 300 and 550 $^{\circ}\text{C}$.

losses, heat treatments were carried out between 300 $^{\circ}\text{C}$ and 550 $^{\circ}\text{C}$. Fig. 7 shows the output power measured after the heat treatment in waveguides produced by focusing the laser beam 150 μm beneath the surface and processing with a scanning speed of 50 $\mu\text{m/s}$, with 15 μm between tracks for pulse energies of 5.04, 4.20, 3.36, 2.52 and 1.68 μJ (1–5 respectively). It was found that in the 300–350 $^{\circ}\text{C}$ range an improvement of up to a 29% in the transmitted power could be attained (guide 4). Higher annealing temperatures produced a reduction in the stress-induced in the confined region between tracks, leading to a diminution in the refractive index and thus in the light confinement. In this way, regarding the annealing temperature, a commitment must be taken in order to reduce the losses by colour centres absorption without significant reduction of the stress-induced, 300–350 $^{\circ}\text{C}$ in this case.

This behaviour was corroborated by microluminescence (μL) measurements carried out by a confocal microscope pumping the sample at 808 nm. Fig. 8 shows the μL map of the waveguide's cross-section where the spatial variation of the Nd^{3+} fluorescence

Fig. 8. Spatial variation of the Nd^{3+} fluorescence intensity for the sample at room temperature (a) and after a heat treatment at 550 $^{\circ}\text{C}$ (b) for a waveguide produced by focusing the laser beam 150 μm beneath the surface and processing with pulse energy of 4.2 μJ , a scanning speed of 50 $\mu\text{m/s}$ and with 15 μm between tracks.

intensity is presented for the sample at room temperature (a) and after a heat treatment at 550 °C (b) for a waveguide produced by focusing the laser beam 150 μm beneath the surface and processing with pulse energy of 4.2 μJ , a scanning speed of 50 $\mu\text{m/s}$ and with 15 μm between tracks. Fig. 8(a) shows that the Nd^{3+} fluorescence intensity was well preserved at the waveguide's volume, decreasing in the damage zones induced by the laser irradiation. Furthermore, as shown in Fig. 8(b), a heat treatment at a temperature too high recombined the damage produced along the tracks, being concentrated at the edges, obtaining as a consequence a worse light confinement. The fluorescence lifetimes in the bulk and in the waveguide's volume were also measured obtaining 250 and 242 μs respectively. The invariance of the lifetimes inside and outside the waveguide indicated that the spectroscopic properties of the Nd^{3+} ions in this glass had not been deteriorated during the waveguide fabrication process.

Finally, according to the damage tracks dimensions obtained by the laser processing and the waveguide's modes characterization the refractive index modification was estimated in $\Delta n \approx 5 \times 10^{-3}$. This value, which explains the appearance of a waveguide in the confined region between tracks, was in the range of those previously reported for other waveguides inscribed by femtosecond laser writing, such as $\text{Nd}:\text{YAG}$ ceramics ($\Delta n \approx 5 \times 10^{-3}$) [31], $\text{Nd}:\text{YVO}_4$ ($\Delta n \approx 1.5 \times 10^{-3}$) [12] and fused-silica ($\Delta n \approx 1.3 \times 10^{-3}$) [3]. Furthermore, the heat treatment at high temperature released the stress-induced between tracks so that this increment decreased up to values lower than 1×10^{-4} , which was the limit value to confine and guide the He-Ne wavelength.

Laser experiments in these waveguides structures are in progress to ascertain if the samples behave like an integrated waveguide laser system.

4. Conclusions

In this work the fabrication of buried optical waveguides by femtosecond laser inscription in the $0.8\text{CaSiO}_3\text{--}0.2\text{Ca}_3(\text{PO}_4)_2$ eutectic glass doped with Nd^{3+} ions is presented.

Buried waveguides were fabricated under the double line configuration by inscribing beneath the surface two adjacent damage tracks. The region between the tracks showed a refractive index increment giving rise to waveguiding. Regarding the morphology of the tracks, the damaged areas produced by the laser beam increased with the laser pulse energy up to 40 μm . By decreasing the pulse energy the damage threshold was determined in 0.021 μJ . The formation of colour centres was observed in the surrounding areas of the tracks and in the confined region. An increase in the pulse energy or a diminution in the distance between tracks or in the scanning speed led to an increase in the generation of colour centres.

The characterization of the near-field intensity distribution of the waveguide's modes at 633 nm determined that for pairs of tracks produced with laser pulse energies lower than 0.42 μJ the stress-induced between tracks was not high enough to confine and guide the light. For higher laser pulse energies both, the TE and the TM polarizations were guided. It was observed that the modal width in the x direction decreased with the pulse energy for both modes and that the light confinement was slightly higher for the TM mode. Moreover, the best confinement conditions were obtained for the shortest lateral separation between tracks and focus position and the highest scanning speed. It was found that a heat treatment in the 300–350 °C range led to an increase of up to a 29% in the transmitted power thus reducing losses coming from absorption by colour centres. Microluminescence characterization revealed that the Nd^{3+} fluorescence intensity was well preserved at the

waveguide's volume, decreasing in the damage zones induced by the laser irradiation. Fluorescence lifetime measurements indicated that the spectroscopic properties of the Nd^{3+} ions in this glass had not been deteriorated during the waveguide fabrication process. Finally, the refractive index modification was estimated in $\Delta n \approx 5 \times 10^{-3}$. The reported properties of the fabricated waveguides suggest a great potential for the application of such waveguides as integrated laser sources or in the fabrication of other active photonic devices.

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