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Production of defects in ZBLAN, ZBLAN:Tm^{3+} and ZBLAN:Cr^{3+} glasses by ultra-short pulses laser interaction

Lilia C. Courrol[a,*], Younes Messaddeq[b], Sandra H. Messaddeq[c], Sidney J.L. Ribeiro[b], Ricardo E. Samad[d], Anderson Z. de Freitas[d], Nilson D. Vieira Jr.[d]

[a] *Departamento de Ciências Exatas e da Terra/UNIFESP, R. Prof. Artur Riedel, 275740, Diadema, 09972-270 SP, Brazil*
[b] *Instituto de Química, UNESP-Araraquara, Brazil*
[c] *Instituto de Física de São Carlos, São Carlos, Brazil*
[d] *Centro de Lasers e Aplicações, IPEN/CNEN-SP, Brazil*

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Abstract

In this work we have studied pure and thulium- and chromium-doped ZBLAN glasses irradiated by ultra-short laser pulses. A Ti:sapphire CPA system was used, producing a 500 Hz train of pulses, centered at 830 nm, with 375 μJ of energy and 50 fs of duration (FWHM). The beam was focused by a 20 mm lens, producing a converging beam with a waist of 12 μm. The absorption spectra before and after laser irradiation were obtained showing production of color centers in pure, thulium-doped and chromium-doped ZBLAN glasses. A damage threshold of 9.56 T W/cm^2 was determined for ZBLAN.

PACS: 42.55−f; 45.79−e; 42.70−a

Keywords: A. Glasses; D. Colour centres; D. Optical properties; D. Radiation damage

1. Introduction

The interaction of femtosecond (fs) laser pulses with matter results in many non-linear processes such as multiphoton absorption, plasma formation, color center (CC) generation and so on. In recent years, the use of infrared fs lasers to induce changes in refractive index in transparent materials has been widely investigated [1,2]. These changes can be used to generate three-dimensional integrated photonic structures in a variety of glasses, and this technique has been applied to fabricate photonic structures, such as passive optical waveguides, gratings and couplers [3].

It is known that the fluoride glasses like ZBLAN (ZrF_4–BaF_2–LaF_3–AlF_3–NaF) exhibit several interesting properties that can be exploited for the fabrication of photonic devices [4] in particular their excellent infrared transparency (from near UV to far IR) and a very low theoretical attenuation around 2.7 μm are suitable for creating photonic devices.

The present investigation is intended to have a comprehensive understanding of the influence of chromium (Cr^{3+}) and thulium (Tm^{3+}) ions on the optical properties and structure of ZBLAN glasses, and also the effects produced in these properties after ultra-short laser irradiation. Chromium ions with $3d^2$ configurations are of interest for solid state laser materials due to their ability to generate laser emission in the near infrared spectral region between 1.2 and 1.7 μm [5]. Among various transition metal ions, chromium ion is a paramagnetic ion that, when dissolved in glass matrices in very small amounts, strongly affects the optical transmission and the insulating strength of the glasses. Over the past several years, Tm^{3+}-doped glasses have been widely investigated since Tm^{3+}-doped

*Corresponding author. Tel.: +55 11 40436425; fax: +55 11 38169315.
E-mail addresses: lcourrol@gmail.com, lcourrol@unifesp.br (L.C. Courrol).

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glass-based fiber amplifiers (TDFAs) expanded the communication window to the S-band and enable more information to be transmitted [6]. In general, the attractive hosts for TDFAs are glasses with low phonon energy, such as fluorides [7,8].

Most studies using direct fs laser writing have investigated waveguide fabrication in oxide glasses [9–12] and recently a permanent structure of a single-mode waveguide in optical multimode fluoride fibers was fabricated using self-channeled plasma filaments excited by a fs laser [13]. The experimental time-resolved dynamics of self-channeled plasma filament and refractive index bulk modification in the ZBLAN glass was also observed in situ [14,15]. Nevertheless, fs writing in doped ZBLAN glasses was not investigated, to our knowledge.

Here, we report the production of CC originated structures inside Tm^{3+}- and Cr^{3+}- doped ZBLAN glasses by fs pulses from a Ti:sapphire laser. We propose that these structures can be used to the fabrication of optical devices.

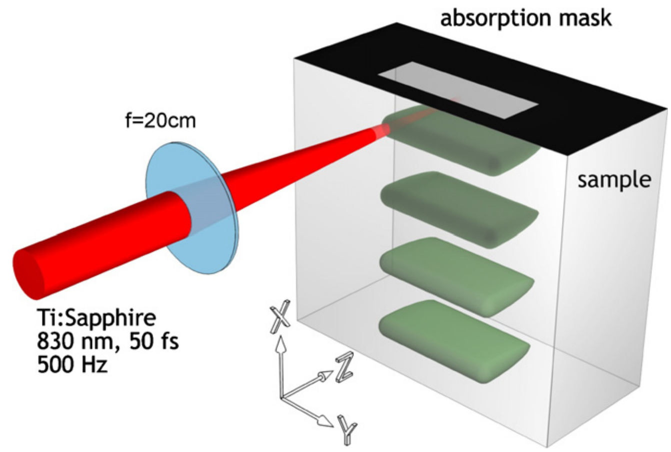

Fig. 1. Ultra-short laser pulses irradiation setup for the creation of color center planes. This was done to increase the centers optical density for absorption measurements.

2. Experimental setup

A series of ZBLAN glasses with composition $52ZrF_4$–$19BaF_2$–$4AlF_3$–20NaF–$(5-x)LaF_3$ was prepared. The rare earth ions and chromium ions were introduced in fluoride forms with x mol% compositions, and the values used were 1 mol% Tm and 1 mol% Cr. Only highly pure, dried fluorides were used for the preparation of the glasses, which were melted in platinum crucibles under dry nitrogen. After casting the samples were annealed at T_g (glass transition temperature) and subsequently polished with commercial media and water-free lubricant.

To irradiate the samples, a Ti:sapphire CPA (Chirped Pulse Amplifier) laser system operating at 830 nm was used, producing a train of 400 μJ, 50 fs linearly polarized pulses, at 500 Hz repetition rate, in a beam with a $M^2 = 1.6$ and a peak power of 8 GW. The beam was focused by a 20 cm lens to a radius of 12 μm, in the low-power limit (no self-focusing), and each sample was placed in such way that the beam waist was inside it without ablation occurring at the sample surface. The studied samples had dimensions of $10 \times 7 \times 3\,mm^3$ each. Four CC tracks vertically (x direction in Fig. 1) spaced by 1 mm were produced in each sample by moving it 3 mm across the laser beam by a motorized table during 20 s (this was done to increase the CCs optical density to improve absorption measurements). The irradiation setup is schematized in Fig. 1, where it can be seen that the CCs were produced in the yz plane. The irradiations were done at room temperature (RT), and after each irradiation the samples were stored at liquid nitrogen temperature.

The 50 fs ablation threshold was determined for the pure ZBLAN glass sample, using the diagonal translation method introduced by Samad and Vieira [16], at four different laser energies: 135, 265, 330 and 396 μJ.

The absorption spectra in the range 200–900 nm were obtained using a dual-beam spectrophotometer (Varian Cary 17D). The samples absorption spectra were measured transversally (x direction in Fig. 1) to the laser irradiation direction, using a $3 \times 1\,mm^2$ absorption mask made with black adhesive tape, to ensure that all the samples had the same illuminated area, as schematized in Fig. 1.

3. Results

All samples were irradiated under the same experimental conditions for comparisons. Immediately after irradiation at RT, the samples were kept in nitrogen liquid just before absorption measurements. It was possible to notice a yellow-green color around and behind each trace showing production of CCs inside ZBLAN and thulium-doped ZBLAN glasses. Absorption spectra measurements were performed in each sample before and after the laser irradiation, making a mask in the irradiation area. The results obtained for ZBLAN and ZBLAN:1%Tm are shown in Fig. 2a and b. The absorption peaks around 270, 340, 460 and 660 nm, observed in Fig. 2b, are thulium absorption bands. The presence of CCs can be demonstrated by the observation of a large absorption band in the visible range (line symbol curves in Fig. 2a and b). These centers are very unstable and disappear after some hours at RT.

To explain the production of CCs by the ultra-short pulses, we propose a mechanism based in the electron avalanche that develops due to a strong initial non-linear multiphoton absorption [17,18]. This avalanche promotes many electrons to the conduction band, where they acquire kinetic energy from the laser field and create vacancies by impact with the fluorine ions. When this anion vacancy traps an electron (neutralizing the vacancy charge), an F center is created. The second step in the production of defects involves the migration of primary defects and the formation of complex defects. These secondary processes are temperature and intensity rate dependent.

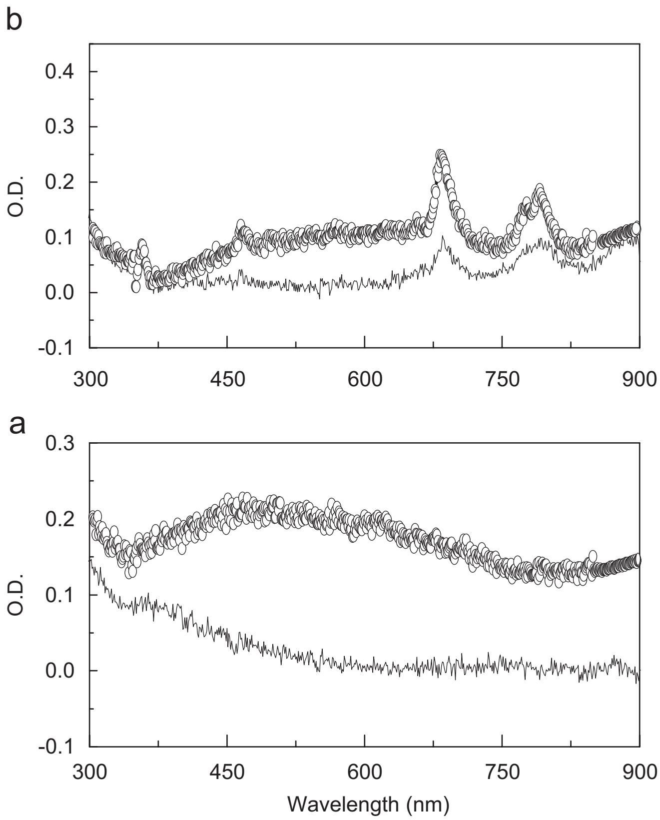

Fig. 2. Absorption spectra of the tracks created in pure ZBLAN (a) and 1 mol% Tm-doped ZBLAN (b). Continuous line is before and line + symbol is after laser irradiation.

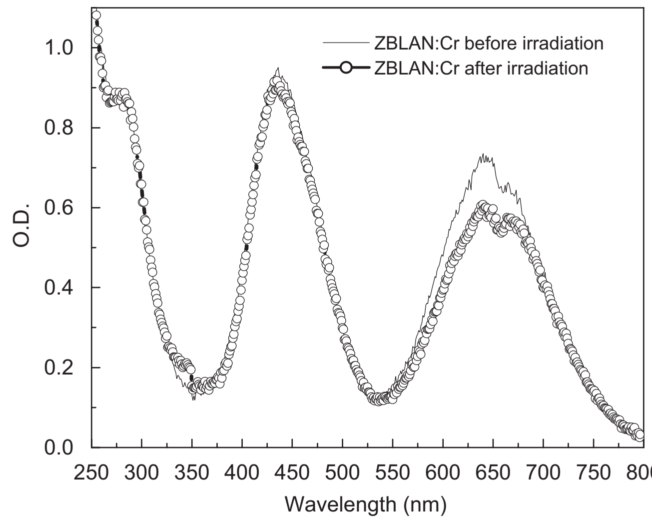

Fig. 3. Absorption spectra of pure and 1 mol% Cr-doped ZBLAN before (line) and after (line + circles) laser irradiation.

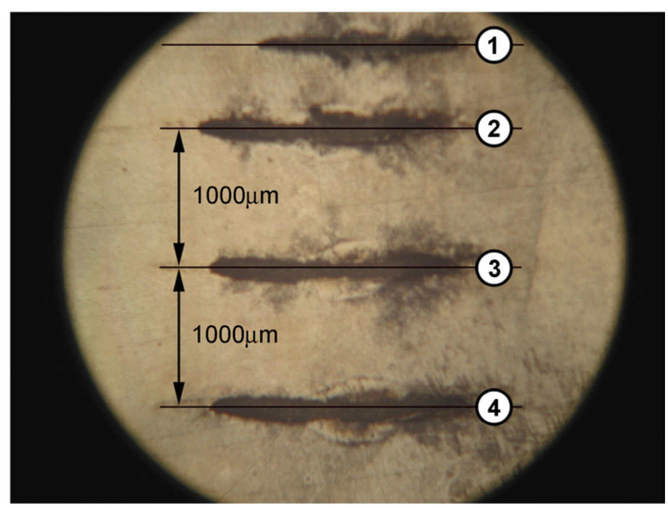

Fig. 4. Optical microscope photography of ablation tracks made by ultra-short laser pulses in pure ZBLAN glass with energies 135, 265, 330 and 396 μJ.

The difference of using a focused laser beam is that the density of primary defects formed is so much higher than irradiation by electron beam, for example, and therefore the probability of aggregation is very much increased. We propose that there is equilibrium between the creation and destruction processes that occur simultaneously, during the ultra-short pulses irradiation, since the fundamental and the harmonics [19] of pumping laser can be absorbed by the defects as well as the white light generation. These centers are generally unstable with the combination of temperature and intense light [20]. When CCs are bleached, the surplus refractive index change is determined by the structural changes induced by an fs laser [3]. Mechanisms leading to the refractive index increase have been identified as structural densification accompanied by the formation of CC defects [21].

A different behavior occurs in the chromium-doped ZBLAN sample, in which the presence of CCs was not observed. The absorption spectra of ZBLAN:Cr before laser irradiation, shown in Fig. 3, is characterized by two broad spin-allowed bands, which can be identified as the vibronically broadened transitions ${}^4T_2 \leftarrow {}^4A_2$, ${}^4T_1 \leftarrow {}^4A_2$, in the order of increasing energy. The low-energy band shows a fine structure due to the spin-forbidden ${}^2E \leftarrow {}^4A_2$ and ${}^2T_1 \leftarrow {}^4A_2$ transitions [22]. The absorption measurements after irradiation, also shown in Fig. 3, demonstrate a reduction of the absorption band at 650 nm. That occurs due to valence modification of chromium ions. Regarding the creation of CCs, a different effect can be observed in ZBLAN:Cr^{3+} (Fig. 6, one of the tracks observed approximately 24 h after irradiation). We propose that the presence of chromium in the samples reduces multiphoton absorption process considering that Cr^{3+} absorbs fundamental laser energy. The reduction of the 650 nm absorption band corroborates this affirmation [23]. By focusing the laser beam into a ZBLAN:Cr^{3+} glass sample and moving the focal point parallel to the surface, it was possible to induce a line of permanent change in refractive index into the material, which might act as a single-mode optical guide. In fact, due to the absorption decrease shown in Fig. 3, one might expect an index of refraction decrease according to the Kramers–Kronig relations [24]. Assuming that waveguides can be fabricated in chromium-doped glasses, characterization of these will be necessary in order to elucidate their potential applications (for example, modal waveguide characterization by reflectivity spectra), and will be presented in the future.

We have determined the pure ZBLAN ablation threshold intensity, I_t, using the diagonal translation method [16], and knowing the laser pulses incident power, P_0, and the maximum radius of the ablation track, ρ_{max}:

$$I_t = \frac{P_0}{e\pi\rho_{max}^2}. \quad (1)$$

The diagonal translations, whose ablation tracks can be seen in the optical microscope photography shown in Fig. 4, were made at four different pulse energies (135, 265, 330 and 396 μJ) and the pulses peak powers were calculated knowing the pulses duration (50 fs FWHM). The maximum ablation radii were measured from Fig. 4 using as a scale the 1000 μm vertical separation between each of the three lower tracks. Table 1 shows for each track measured maximum ablation radius (ρ_{max}), pulse energy (E_{pulse}) and peak power (P_{pulse}), and intensity (I_{th}) and fluence (F_{th}) calculated ablation thresholds. Fig. 5 shows the intensity ablation threshold values dependence on the pulse energy (Table 1), always following the tracks numbering of Fig. 4. The four tracks average value for the ablation threshold $I_t = (9.56 \pm 0.72) \times 10^{12}$ W/cm², corresponding to an ablation threshold fluence of 0.48 ± 0.03 J/cm². This value corresponds to an ablation threshold electric field of $E_t = (6.92 \pm 0.26) \times 10^7$ V/cm, almost two orders of magnitude higher than chalcogenides [25], and was obtained from the relation between the intensity and the electrical field:

$$E\left(\frac{V}{m}\right) = \sqrt{\frac{2}{\varepsilon_0 cn} I} = 27.43\sqrt{\frac{I(W/m^2)}{n}}, \quad (2)$$

where ε_0 is the vacuum permittivity, c the speed of light and n the medium refractive index. For pure or thulium-doped ZBLAN glasses the same ablation profile was observed independent of thulium concentrations, probably due to the instability of CCs. Consequently the ablation threshold for pure and thulium-doped ZBLAN does not change significantly.

Table 1

Track	ρ_{max} (μm)	E_{pulse} (mJ)	P_{pulse} (GW)	I_{th} (TW/cm²)	F_{th} (J/cm²)
1	56.9±5.9	135±9	2.7±0.2	9.76±2.15	0.49±0.11
2	81.6±5.9	265±9	5.3±0.3	9.33±1.43	0.48±0.07
3	90.4±5.9	330±11	6.6±0.3	9.46±1.32	0.47±0.06
4	97.42±5.9	396±8	7.9±0.4	9.77±1.26	0.49±0.06

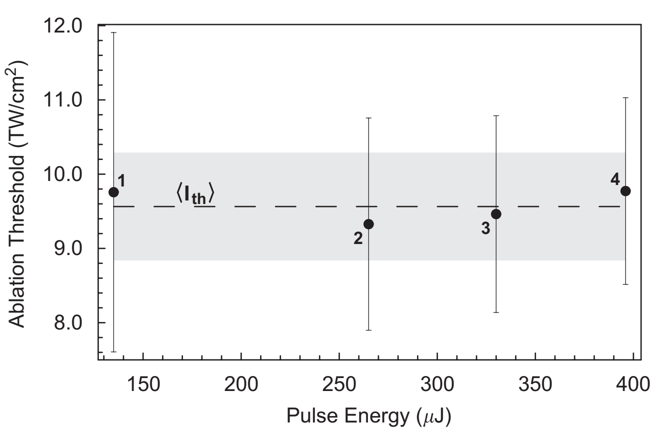

Fig. 5. Ablation threshold intensities for each track, following the numbering on Fig. 4. The dashed line is the threshold mean value, and the shaded region represents the standard deviation.

4. Conclusions

We have demonstrated different interactions of ultrashort pulse laser with ZBLAN glass. The ablation threshold for pure ZBLAN glasses was measured and found to be 9.56×10^{12} W/cm². As can be seen in expression 1, it is possible to control the maximum defect radius by controlling the incident power P_0. It is then possible to write a track with desired dimension. This controlled ablation capability can be ultimately used to machine structures such as diffraction gratings in ZBLAN glasses.

The interaction of the laser with the ZBLAN glass is modified with the presence of chromium ions, reducing mechanical stresses.

The application of fs laser pulses in transparent materials to induce a change in the refractive index provides an excellent technique for production of integrated optical circuits.

Fig. 6. Optical microscope photography of a track produced inside ZBLAN:1% Cr with femtosecond laser interaction longitudinally along the beam propagation axis.

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