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Waveguides and nonlinear index of refraction of borate glass doped with transition metals

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ABSTRACT

The ability to write 3D waveguides by femtosecond laser micromachining and the nonlinear refractive index (n_2) spectrum of a new borate glass matrix, containing zinc and lead oxides – (BZP) have been investigated. The transparent matrix was doped with transition metals ($CdCl_2$, Fe_2O_3, MnO_2 and CoO) in order to introduce electronic transitions in visible spectrum, aiming to evaluate their influence on the waveguides and n_2 spectrum. We observed that n_2 is approximately constant from 600 to 1500 nm, exhibiting an average value of 4.5×10^{-20} m^2/W, which is about twice larger than the one for fused silica. The waveguide profile is influenced by the self-focusing effect of the matrix owing to its positive nonlinear index of refraction in the wavelength used for micromachining. A decrease in the waveguide loss of approximately four times was observed for the sample doped with Fe in comparison to the other ones, which may be associated with the change in the optical gap energy.

1. Introduction

Fabrication of three-dimensional waveguides in glasses by femtosecond laser micromachining was first demonstrated in 1996 [1]. Since then, many researches have been focusing on understanding details about the effect of ultra-short laser pulses on glasses, aiming at developing several applications in photonics. It has been reported that laser pulses cause structure densification and therefore an increase on the refractive index, enabling the light guiding [2–4]. In addition, the influences of the laser parameters and irradiation conditions have been fairly investigated [5–7]. For instance, the pulse energy and scan speed have an effect on the waveguide size, while the numerical aperture of the objective lens and the sample displacement direction change its shape [6,8]. Moreover, the oxidation states of ions within the waveguide are influenced by the laser repetition rate [5]. Recently, we reported the nucleation and growth of silver nanoparticles in waveguides micromachined using a MHz femtosecond laser system, whereas color center formation was observed for experiments carried with repetition rate of kHz [9].

Despite the knowledge on the requirements for femtosecond laser micromachining of glasses, the optical properties of a specific glassy matrix may strongly influence the processing, with implication, for instance, on features of the waveguides produced. It is known that new electronic states can be introduced in glasses by doping them with transition metals. Such doping significantly affects the optical properties in the visible region without changing the glass structure. In this work, a new glass composition based on B_2O_3, ZnO and PbO was doped with $CdCl_2$, Fe_2O_3, MnO_2, CoO to introduce electronic transitions that could lead to the resonant enhancement of optical nonlinearities. The influence of the doping was evaluated on fs-laser micromachined waveguides. Given the novelty of the developed glass matrix, the nonlinear index of refraction spectra of the sample, from 550 to 1500 nm, were also studied through the Z-scan technique.

2. Materials and methods

The glass matrix was formulated to present high refractive index, without compromising its transparency at the visible spectrum, and allowing the incorporation of transition metals; therefore, a good stability against the devitrification is also required. Such features were achieved through the matrix composition that contains $50B_2O_3$–15ZnO–10PbO–8MgO–$6K_2O$–$2Al_2O_3$–$2Nb_2O_5$–$5Si_2O$–$2Na_2O$ (wt%), here named BZP. The high atomic number elements, as zinc, lead and niobium have been added to favor the optical nonlinearities, while the other modifier oxides were used to decrease the viscosity and improve the homogeneity of the liquid phase. A batch of 120 g was synthesized by melt-quenching technique, using a platinum crucible and melting temperature/time of 1170 °C/3 h. Transition metal doped samples –

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$CdCl_2$, Fe_2O_3, MnO_2, CoO (0.1 mol%) were prepared from BZP matrix, using the same melting temperature for 1 h. Doped liquids were quenched in a stainless-steel mold at 450 °C and annealed at this temperature during 24 h. The thermal behavior of the samples was investigated by differential thermal analysis (DTA), in a DSC 2910 Thermal Analyzer with heating rate of 10 °C/min and synthetic air as atmosphere. Archimedes method was carried out with a digital balance (Mettler Toledo AG 285 model) and distilled water at room temperature. Vickers hardness was obtained with microhardness tester (VHMT MOT), operating with a pyramidal indenter and load of 25 gf during 5 s. X-ray diffraction (Rigaku, Rotaflex RU200B) confirmed the amorphous feature of all samples.

Waveguides were fabricated into the glass bulk by fs-laser micromachining, which basically requires an objective lens and an *xyz* translational stage, besides the femtosecond laser. Particularly, we used 40× objective lens ($NA = 0.65$) to focus the beam delivered by a Ti:sapphire laser (operating at 5 MHz with pulses of 50 fs at 800 nm) inside the sample, which was moved at 100 μm/s in the perpendicular plane to the laser propagation. The experimental setup for coupling the light into those waveguides is based on a 0.65 NA objective lens, used to couple the light from a He–Ne laser (632.8 nm), and a 0.25 NA objective lens and a CCD camera employed to observe the propagation mode. Total losses were determined by measuring the input and output power in the waveguide, sizing 3.8 mm of length. Details about our experimental setup for laser writing and waveguide characterization are available in Ref. [9].

Linear optical characterization of pure and transition metal doped glass was evaluated through the linear absorption spectrum obtained with a Shimadzu UV-1800 spectrometer. For the nonlinear optical measurements, we used the Z-scan technique [10] with femtosecond laser pulses, which allow us to obtain the nonlinear refractive index (n_2) associated with the electronic response. Briefly, in this method, a single laser beam induces a self-phase modulation as it propagates along the sample, which causes a distortion in the beam wave front. By measuring the beam transmittance through an aperture, placed in the far field, as a function of the sample position with respect to the focal plane of a Gaussian laser beam, we are able to determine the sign and magnitude of n_2 [10]. For a refractive nonlinearity, the light field induces an intensity dependent refraction, $n = n_0 + n_2 I$, where I is the laser beam irradiance, n_0 and n_2 are the linear and nonlinear refractive indexes respectively. As the sample approaches the focus, the induced self-phase modulation diverge the beam into the far field, assuming $n_2 > 0$, leading to a decrease in the transmission through the iris. After the focus, the effect is to converge the beam, which in turn increases the light transmitted through the iris. Therefore, by monitoring the transmittance change as the samples is scanned along the focal plane, a refractive Z-scan signature is obtained. By fitting such Z-scan signature, according to Ref. [10], one is able to obtain the nonlinear refractive index n_2. For the Z-scan experiments, we used an optical parametric amplifier (OPA), which provides 120-fs pulses from 460 up to 2000 nm. Such OPA was pumped by a chirped-pulse amplified Ti:sapphire laser system (150 fs, 775 nm and 1 kHz). To ensure a Gaussian profile for the laser beam, spatial filtering was performed before the Z-scan setup. We employed laser pulse energies ranging from 10 to 200 nJ, and beam waist sizes at the focus varying from 12 to 28 μm, depending on the excitation wavelength. Details of the Z-scan experimental setup and data analysis can be found in Refs. [11–13].

3. Results and discussion

Table 1 summarizes the characteristic temperatures, density and Vickers hardness of the BZP glass matrix. Such properties were not altered by the doping with transition metals, within the experimental error. As it can be seen, BZP matrix has a great stability against the devitrification, once ΔT values higher than 70 °C are considered enough to avoid undesirable crystallization. Neither phase separation (on liquid or solid phase), nor chemical reactivity at room atmosphere/temperature have been observed, encompassing the basic features for samples used in optics.

Table 1
Glass transition temperature (T_g), onset of the crystallization peak (T_x), glass stability against the devitrification ($\Delta T = T_x - T_g$), density and Vickers hardness (H_v) of the BZP glass matrix.

T_g (°C)	T_x (°C)	$\Delta T = T_x - T_g$ (°C)	Density (g/cm^3)	H_v (kgf/mm^2)
509 ± 2	733 ± 2	224 ± 4	2.76 ± 0.02	500 ± 30

The linear absorption spectra of the samples are shown in Fig. 1. The undoped matrix (BZP) displays a transparence window in the visible-near infrared, with a band gap energy of 3.7 eV (wavelength cutoff of 330 nm). The absorption spectrum of the $CdCl_2$ doped sample is very similar to that of the BZP glass, being also completely transparent in the visible-near infrared region. For the Fe_2O_3 sample, it is observed a red shift of approximately 70 nm in the absorption spectrum, evidencing the influence of Fe^{3+} in the matrix [14,15]. For the sample with MnO_2, an absorption band is observed at approximately 460 nm, which is derives from different oxidation states of manganese, as Mn^{2+}, Mn^{3+} and possibly Mn^{4+} [16,17]. The glass with CoO shows a broad absorption between 430 and 700 nm, due to the presence of Co^{2+} in the matrix [16,18,19]. By doping the BZP with Cd, Mn and Co ions, there is no change in the band gap energy, while Fe ions cause a decrease of about 0.6 eV on the bandgap ($E_{gap} = 3.1$ eV). Although manganese and cobalt do not affect the optical gap energy, they introduce indirect electronic transitions, changing the absorption at the visible spectral region. On the other hand, cadmium causes no alteration in both direct and indirect transitions.

A representative optical microscopy image of the waveguides produced by fs-laser micromachining is displayed in Fig. 2 for BZP (undoped sample), in which top (a) and cross-section (b) views are illustrated. As it can be seen, the waveguide cross-section presents an elliptical shape, which is probably related to a significant self-focusing effect during the fs-laser micromachining. In spite of that, all microstructures produced into undoped and doped glasses presented light confinement. Fig. 2c shows the near-field output profile of the light guided at 632.8 nm. All images shown in

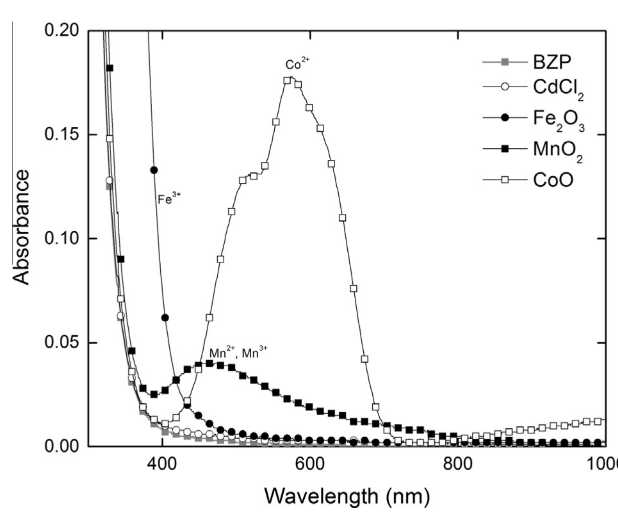

Fig. 1. Linear absorption spectrum of undoped BZP matrix and its doping with transition metals: $CdCl_2$, Fe_2O_3, MnO_2 and CoO.

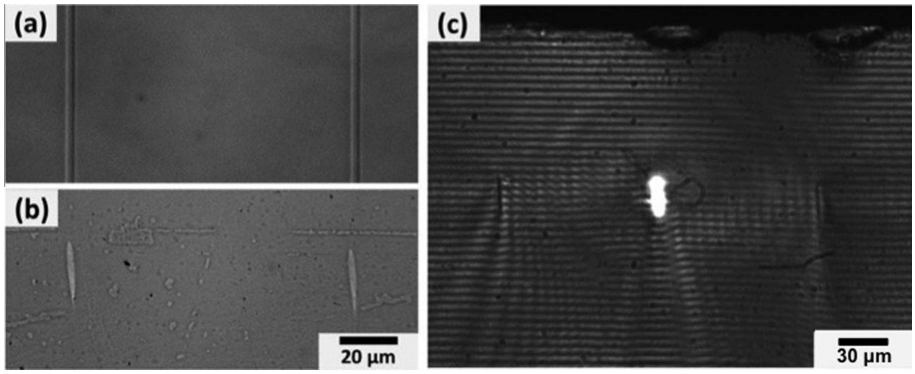

Fig. 2. Images of waveguides produced in the BZP sample: (a) top and (b) cross-section view of two parallel waveguides; (c) near-field output profile of the light guided at 632.8 nm.

Fig. 2 are from the same waveguides. We investigated the influence of the pulse energy employed for micromachining the waveguides on their shape. However, no change was observed despite a linear increase on the waveguide size, as shown in Fig. 3. Through the linear fit, we obtained the threshold energy, E_{th} = 20 nJ, which represents the lowest pulse energy required to induce optical damage in BZP glass matrix. We have chosen to produce the waveguides with pulse energy of 70 nJ, in order to obtain structures with a better optical quality. Although the transition metals do not influence the micromachining process, iron ions have an effect on the waveguide loss. Total losses, including coupling and propagation loss at 632.8 nm, are displayed on the inset of Fig. 3. Coupling and propagation losses have not been distinguished on account of expressive systematic errors. Such errors may arise from the short length and the elliptical shape of the waveguide, once scattering due to the surface polishing become relevant and the coupling efficiency is highly dependent on the optical alignment. For the pure matrix, BZP, we obtained a total loss of (2.1 ± 0.1) dB/mm. Such value is not affected by the doping with MnO_2 and CoO, within the experimental error. Nonetheless, the waveguide in Fe_2O_3 doped sample exhibits a total loss of (0.6 ± 0.1) dB/mm, being almost four times better than the loss observed for the other samples. Such behavior might be associated to the decrease in the band gap energy of the sample when iron is added to the BZP matrix. As discussed previously, only Fe ions affect the direct electronic transition of BZP matrix, resulting in a red shift in the absorption spectrum and, therefore, an increase in the refractive index. We believe the coupling efficiency of Fe doped sample is improved on account of its higher refractive index, raising the waveguide efficiency and, consequently, resulting in a better result when compared to the total losses of the other samples.

As most of applications for waveguide aim at photonic devices, in which the nonlinear optical properties are the key ones, we have also carried out a study on the nonlinear refractive index spectrum of the samples. The BZP (matrix) as well as the other samples, doped with transition metals, were evaluated to check if the electronic transitions introduced by such ions induce the resonance enhancement effect on the optical nonlinearity. Fig. 4 displays the spectra of the samples at the visible and near infrared regions. The inset in Fig. 4 is a typical closed aperture Z-scan signature, obtained for the BZP sample, measured at 650 nm, where the solid line represents the fitting according to Ref. [10], from which the n_2 value is determined. The change in the normalized transmittance as a function of z-position presents a valley ahead a peak, indicating a positive nonlinear index of refraction. Z-scan signatures similar to the one presented in the inset of Fig. 4 were obtained for all studied samples in the wavelength range from 550 up to 1500 nm. However, for MnO_2 and CoO doped samples, the closed aperture Z-scan curves were divided by the open aperture ones in order to

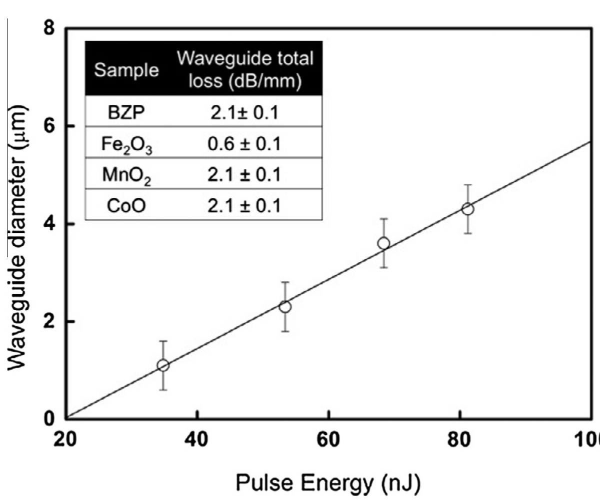

Fig. 3. Changing in the waveguide size as a function of the pulse energy employed to fabricate the waveguide inside the BZP glasses. The inset shows the total losses (coupling + propagation loss) for the pure and transition doped samples at 632.8 nm.

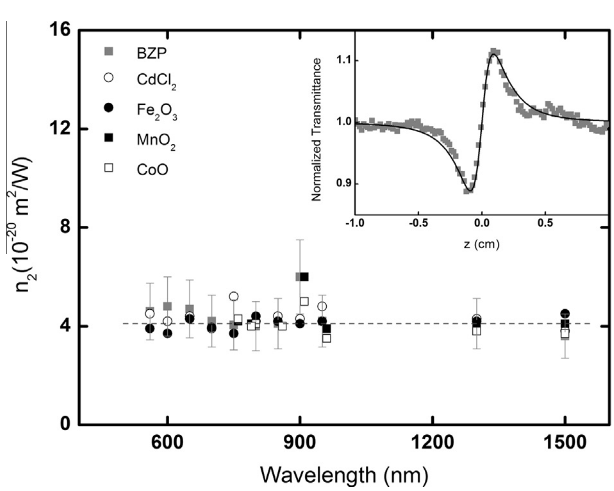

Fig. 4. Spectra of nonlinear refractive index (n_2) of undoped (BZP) and transition metal doped samples ($CdCl_2$, Fe_2O_3, MnO_2 and CoO). The inset shows the closed aperture Z-scan signature at 650 nm, of BZP sample. Symbols are the experimental result and solid line is the theoretical fit, used to obtain n_2 values.

discount the effect of nonlinear absorption caused by electronic transitions at visible. It is important to mention that there is no nonlinear absorption from the investigated wavelength region (550–1500 nm) for the other samples.

As it can be seen in Fig. 4, n_2 values are approximately constant in the studied wavelength range, within the experimental error. The dash line in n_2 spectrum represents its average value at visible and infrared regions, being 4.5×10^{-20} m^2/W, which is about twice larger than the one reported for fused silica [20]. Furthermore, no appreciable difference was observed among the undoped and doped samples.

As it is well known, the nonlinear refraction, that is described by the third-order susceptibility, is expected to present a resonant enhancement when the laser frequency approaches a materiaĺs linear absorption frequency [21]. Although the transition metals change the absorption spectrum of BZP matrix, those transitions do not affect the nonlinear index of refraction, which might be related to the low doping concentration. In addition, the electronic nonlinearity depends on the deformation caused by the laser on the electron clouds associated to the material atoms. Thus, the hyperpolarizable elements in the glass matrix, as Pb, Nb and Zn, contribute to the high nonlinear refractive index of BZP glass (4.5×10^{-20} m^2/W), when compared to fused silica. Such value could be further improved by increasing the concentration of heavy elements, as it has been reported for borate, phosphate and germanate glasses contain high concentration of heavy metals [11,13,22]. However, the good transparence of BZP matrix in the whole visible spectrum could be affected. In this sense, we suggested that the BZP composition reported herein is appropriate for applications that require high optical nonlinearities and transparency at visible.

4. Conclusions

We have developed a new borate glass matrix, which is completely transparent in the visible spectrum and has a nonlinear refractive index twice higher than fused silica. This glass matrix has been doped with transition metals (Cd, Fe, Mn, Co) in order to evaluate the influence of the introduced electronic transitions in the nonlinear optical properties and in the fabrication of waveguides. Cadmium does not affect the absorption spectrum of the glass matrix, while iron causes a red shift, changing its band gap energy; and cobalt and manganese promote new electronic states at the visible region. Although, the nonlinear refractive index is not altered by the dopants, remaining 4.5×10^{-20} m^2/W from visible to NIR region, the total loss of the waveguide micromachined in the Fe doped sample is approximately four fold lower than the other samples. We obtained a total loss of 2.1 ± 0.1 dB/mm for the waveguide in the pure glass matrix and 0.6 ± 0.1 dB/mm for the iron doped sample. This behavior has been associated with the change in the optical band gap, resulting in better coupling efficiency.

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