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SABRINA NICOLETI CARVALHO DOS SANTOS

**Third-order optical nonlinearities and fs-laser microfabrication of
3D waveguides in borate glasses doped with rare-earth ions**

São Carlos
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SABRINA NICOLETI CARVALHO DOS SANTOS

Third-order optical nonlinearities and fs-laser microfabrication of 3D waveguides in borate glasses doped with rare-earth ions

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Advisor: Prof. Dr. Cleber Renato Mendonça

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“The saddest aspect of life right now is that science gathers knowledge faster than society gathers wisdom.”

Asimov, Isaac

ABSTRACT

SANTOS, S. N. C. **Third-order optical nonlinearities and fs-laser microfabrication of 3D waveguides in borate glasses doped with rare-earth ions**. 2019. 117p. Thesis (Doctor of Science.) – São Carlos School of Engineering, University of São Paulo, São Carlos, 2019.

Technological breakthroughs have allowed the development of lasers capable of generating ultrashort pulses of high intensity. In this direction, femtosecond laser pulses have proven to be an excellent tool for both processing and nonlinearity studies in materials. Vitreous materials, in general, have stood out for presenting interesting nonlinear optical processes, and are promising candidates for the development of photonic devices. Borate glasses, specifically, have been only sparsely investigated concerning nonlinear optics. The addition of rare-earth ions in these glasses has attracted considerable attention due to its multifunctionality for the development of optoelectronic and photonic devices. Considering the importance of this glass as a nonlinear optical material, this work aimed to use femtosecond laser pulses in two main directions: (i) the study of borate glass optical nonlinearities, as well as the analysis of the effect of rare-earth ions on these properties and (ii) the production of three-dimensional waveguides using laser processing. These results were obtained using Z-scan techniques and femtosecond laser microfabrication, which allowed nonlinear optical characterization and waveguide production, respectively. Initially, the third-order nonlinear optical properties of $\text{B}_2\text{O}_3\text{-BaO}$ e $\text{B}_2\text{O}_3\text{-BaO-SiO}_2\text{-DyEu}$ glasses were investigated. By modeling the experimental results it was possible to show that oxygen in the vitreous matrix plays a fundamental role in nonlinearities. It was also demonstrated the fabrication of waveguides in the $\text{B}_2\text{O}_3\text{-BaO-SiO}_2$ sample doped with the Dy^{3+} e Eu^{3+} ions, which were able to propagate the fluorescence of the glass by coupling the ultraviolet light. The same procedures were performed on the calcium

lithium tetraborate (CaLiBO) system doped with two rare-earth ions, Tb³⁺ and Yb³⁺. The results from the nonlinear optical characterization were modeled, revealing that the nonlinearity has a significant contribution associated with the oxygen present in the matrix. However, the electronic molar polarizability evidenced that there is a strong influence of rare- earth ions polarizability in these properties. Thus, it can be inferred that the combination of oxygen and the polarizability of rare-earth ions are responsible for the nonlinearity present in the vitreous system. The fabrication of three-dimensional waveguides in CaLiBO samples showed homogeneity, with single-mode operation at 632.8 nm, 612 nm, 594 nm, 543 nm, and 405 nm wavelengths. Summing up, the results presented here are of great importance and expand the knowledge regarding the nonlinear optical characterization and the manufacture of waveguides in rare-earth ion doped borate glasses that are important for the research in the field of photonics.

Keywords: Femtosecond laser. Nonlinear refraction index. Z-scan technique. Femtosecond laser micromachining. Glass waveguides. Borate glasses. Rare-earths

RESUMO

SANTOS, S. N. C. **Não-linearidades ópticas de terceira ordem e microfabricação de guias de onda 3D com pulsos de femtossegundos em vidros boratos dopados com terras-raras**. 2019. 117p. Tese (Doutorado) – Escola de Engenharia de São Carlos, Universidade de São Paulo, São Carlos, 2019.

O avanço tecnológico permitiu o desenvolvimento de lasers capazes de gerar pulsos ultracurtos de altas intensidades. Nesta direção, pulsos laser de femtossegundos têm se mostrado uma excelente ferramenta tanto para o processamento quanto para o estudo das não linearidades em materiais. Materiais vítreos, de maneira geral, tem se destacado por apresentarem interessantes processos ópticos não lineares, sendo promissores candidatos para o desenvolvimento de dispositivos fotônicos. Vidro boratos, especificamente, tem sido pouco investigado no que diz respeito à óptica não linear. A adição de íons terras-raras nesses vidros tem atraído uma considerável atenção devido a sua multifuncionalidade para o desenvolvimento de dispositivos optoeletrônicos e fotônicos. Com base na importância desse vidro como um material óptico não linear, esse trabalho teve como objetivo utilizar pulsos laser de femtossegundos em duas principais direções: (i) no estudo das não linearidades ópticas de vidros borato, bem como na análise do efeito de íons terras raras nessas propriedades e (ii) na produção de guias de onda tridimensionais usando processamento à laser. Esses resultados foram obtidos utilizando as técnicas de varredura-Z e a microfabricação com laser de femtossegundos, que permitiram a caracterização óptica não linear e a produção de guias de onda, respectivamente. Inicialmente foram investigadas as propriedades ópticas não lineares de terceira ordem dos vidros B_2O_3 -BaO e B_2O_3 -BaO-SiO₂-DyEu. A partir de um modelamento dos resultados experimentais foi possível mostrar que os oxigênios presentes na matriz vítrea desempenham papel fundamental nas não linearidades. Também foi

demonstrada a fabricação de guias de ondas na amostra B_2O_3 -BaO-SiO₂ dopadas com os íons Dy³⁺ e Eu³⁺, que foram capazes de propagar a fluorescência do vidro ao acoplar luz ultra-violeta. Os mesmos procedimentos foram realizados no sistema tetraborato de cálcio-lítio (CaLiBO) dopado com dois íons terras-raras, Tb³⁺ e Yb³⁺. Os resultados provenientes da caracterização óptica não linear foram modelados, revelando que a não linearidade tem parcela significativa associada aos oxigênios presente na matriz. Contudo, a polarizabilidade molar eletrônica evidenciou que há uma forte influência da polarizabilidade dos íons terras-raras nessas propriedades. Assim, pode-se inferir que a combinação dos oxigênios e a polarizabilidade dos íons terras-raras são responsáveis pelas não linearidades presente no sistema vítreo. A fabricação de guias de ondas tridimensionais nas amostras CaLiBO mostraram homogeneidade, com operação monomodo para os comprimentos de onda em 632.8 nm, 612 nm, 594 nm, 543 nm e 405 nm. Sumarizando, os resultados aqui apresentados são de grande importância e ampliam o conhecimento em relação à caracterização óptica não linear e a fabricação de guias de onda em vidros boratos dopados com íons terras-raras, que são relevantes para a pesquisa na área de fotônica.

Palavras-chave: Laser de femtossegundos. Índice de refração não-linear. Técnica de varredura-Z. Microestruturação a laser de femtossegundos. Guias de ondas vítreos. Vidros boratos. Terras-raras.

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LIST OF ABBREVIATIONS AND ACRONYMS

SHG	second-harmonic generation
RE	rare-earth
BBO	abbreviation of B_2O_3 - BaO
BBS-DyEu	abbreviation of B_2O_3 - BaO - SiO_2 : Dy_2O_3 - Eu_2O_3
CaLiBO	lithium-calcium tetraborate
GTH	third-harmonic generation
2PA	two-photon absorption
NT	normalized transmittance
ΔT_{PV}	peak-valley transmittance variation
Δz_{PV}	peak-valley variation of z
$\Delta\phi_0$	phase change
NA	numerical aperture
TIR	total internal reflection
CCD	charge coupled device
BGO	Boling-Glass-Owyoung
OLED	organic light-emitting diode
LED	light-emitting diode
CPA	chirped pulsed amplification
HeNe	helium-neon laser
HeCd	helium cadmium laser
A, B, C, D, E	Sellmeier coefficients
R-squared	coefficient of determination
SI	system of units
NIR	near-infrared

LIST OF SYMBOLS

f_s	femtosecond
P	polarization
E	electric field
ϵ_0	permittivity of the vacuum
X	electric susceptibility
n	nonlinear refraction
α	nonlinear absorption
ω	frequency
v	velocity propagation of light in the medium
c	speed of light in vacuum
n_0	linear refractive index
I	intensity
Z_0	Rayleigh parameter
w_0	beam waist
k	wave vector
L_{eff}	effective length of the sample
f_{rep}	laser repetition frequency
t_0	temporal width pulse
β	two-photon absorption coefficient
E_g	energy gap
h	Planck constant
n	photon number
σ	multiphoton absorption coefficient
γ	Keldysh parameter
E_c	critical energy
nJ	nanojoules
mJ	milijoules
μs	microseconds
m^*	effective mass of the electron
e	charge of the electron
Δn	refractive index change

n_a	linear refractive index of medium a
n_b	linear refractive index of medium b
θ_L	limit angle
α_{total}	total losses
α_{coupl}	coupling losses
α_{prop}	propagation losses
dB	decibel
P_{input}	input power
P_{output}	output power
g	anharmonicity parameter
s	effective oscillator strength
N	density of nonlinear oscillators
$\hbar$	reduced Planck's constant
λ	wavelength
ω_0	resonance frequency
N_{ox}	density of oxygen ion
$\text{\AA}$	angstrom
α_m	electronic molar polarizability
N_A	Avogadro's number
R_M	molar refraction
M	molecular weight
ρ	density
E_{th}	threshold energy
L	line width

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Chapter 1. Introduction

The development of the laser in the early 1960s give rise to nonlinear optics with the pioneering second-harmonic generation experiment, performed by Franken and collaborators¹. Subsequently, with the advancement of lasers technology the field of photonics has emerged, basically consisting of the application of photons to generate, detect and transmit optical signals. Its rapid insertion in the areas of science and technology has triggered a great advance in both, the fabrication of devices and the processing of materials by laser, which has led to the development of new materials for optical and photonic applications.

Since then, the nonlinear optical properties of various materials such as glasses², polymers³, semiconductors⁴, composites⁵, graphene-based materials⁶, crystals⁷ among others, have been investigated for the development of materials with optical characteristics suitable for the production of optical devices with specific applications. Among the materials mentioned, glasses have great prominence scientifically as well as technologically. Various combinations of glasses can be prepared according to the chemical elements that act as network formers, being typically classified as oxides, halides, chalcogenides, organic, and metallic. The unique properties that each class presents can be intentionally altered by the incorporation of modifiers compounds (alkali and earth alkaline metals), allowing the manufacture of a wide variety of glasses with improved properties. Other aspects that favor interest in these materials are ease of production, obtainment by different methods (melt tempering, chemical vapor deposition, among others), possibility of molding of various sizes and shapes such as bulk, fibers, and thin films. In general, glasses present high transparency, chemical durability, excellent thermal, electrical and optical properties; the last property being very important for many applications.

Glassy materials exhibit high transmission at visible and near-infrared and, therefore, have been widely used as passive elements with numerous optical applications such as optical temperature sensors^{8,9}, and optical transmission fibers that are essential in telecommunications systems^{10,11}. The use of these materials as active components is achieved when doped with rare-earth elements and can act as gain media for lasers and light amplifiers^{12–15}. All these applications, with the exception of the laser action, are under the regime of linear optics. The gradual development of nonlinear optics has aroused interest in different types of material, with special attention to vitreous materials. Aiming at the nonlinear optical properties, boron oxide is a versatile compound, since most borates can be obtained both in the crystalline and glass phase. Borate crystals have been gradually recognized as one of the important nonlinear optical materials that possess properties such as a broad range of transparency (190-3500 nm), large birefringence, large nonlinear coefficients, and high laser damage threshold¹⁶. Among the borate crystals currently known, the BBO (β -BaB₂O₄) crystal is the most outstanding one. It displays second-order nonlinear process, for second-harmonic generation (SHG), photorefractive and electro-optical devices¹⁷.

From the technological point of view, glasses are more favorable when compared to the crystals, because the growth process of boron-based monocrystals is difficult, expensive, and long-term¹⁸. The borate glasses are interesting basically because of four reasons; (i) low melting temperatures, (ii) compatibility with rare-earth elements and transition metals, (iii) extensive range of glass formation and (iv) second- and third-order optical nonlinearities. Its applications are diverse, from optical devices to optoelectronics and photonics. Besides, its production is generally intended for specific applications and research¹⁹

These glasses are notable due to their glass network structure. The boron oxide (B_2O_3) has the capacity to become a pure glass, whose basic structural presents triangular (BO_3) and the structural group known as boroxol ring (B_3O_6)^{3-20,21}. However, its pure form is not useful for applications because of its low chemical stability and hygroscopicity²². The addition of oxide modifiers (alkaline and earth alkaline metals) in B_2O_3 glasses modifies the arrangement of the glass network, causing the triangles (BO_3) to be converted into tetrahedra (BO_4)^{23,24}. In addition, superstructural units are formed from the bonding of BO_3 and (BO_4)⁻. The incorporation of these oxides helps reducing hygroscopicity, increases the resistance to moisture and density, decreases melting temperature, and improves thermal stability and generally physical properties²⁵⁻³⁰.

The presence of modifying oxides has been investigated in borate glasses, aiming at different applications. Barium borate glasses have shown potential for the development of gamma-ray shielding applications³¹. Studies of alkaline bismuth borate glass revealed that the absorption of two photons increases with the substitution of alkaline earth elements, due to the variation in the hyperpolarizability of Sr^{2+} and Ca^{2+} ions³². Also, glasses obtained with Ba^{2+} showed to be favorable as optical limiters³².

An important property that borate glass presents is its capacity to host various types of dopants, as rare-earth, transition metal ions and metal nanoparticles³³⁻³⁸. This feature expanded the study of these materials in the area of photonics. In the last decades, rare-earth (RE) doped glasses have attracted much interest due to its multifunctionality in several applications, among them lasers, optical detectors, Q-switching devices, fiber optics amplifiers, waveguides, solar energy collectors, optical communication and optoelectronics devices³⁹⁻⁴⁵. It was demonstrated that the nonlinear optical response was improved in vitreous materials with the gradual

incorporation of Sm^{3+} ions into barium-zinc-borate glasses. An increasing trend was observed in the coefficient of absorption of two-photons, nonlinear refractive index, and nonlinear optical susceptibility⁴⁶. In recent years, studies have been reported using two-way co-doping of boron glasses as $\text{Tb}^{3+}/\text{Sm}^{3+}$ for solid-state lighting⁴⁷, $\text{Pr}^{3+}/\text{Dy}^{3+}$ and $\text{Dy}^{3+}/\text{Eu}^{3+}$ for white light generation^{48,49} and $\text{Tb}^{3+}/\text{Yb}^{3+}$ for applications in solar cell^{50,51}.

At the same time, technological development over the years has allowed lasers capable of generating ultrashort pulses and high intensities. The use of femtosecond laser pulses has been demonstrated for about two decades, since then, it has stood out as a versatile tool that can be used for the study of optical nonlinearities in the regime of ultrashort pulses and the processing of materials in micro and nanoscale. The use of lasers with ultrashort pulses was extended to the area of spectroscopy; this allowed to obtain information about the properties of materials, which include nonlinear refractive index, multiphoton absorption, generation of second and third harmonics, among others⁵², as well as understanding some of the related phenomena as self-focusing, self-phase modulation, optical phase conjugation. The knowledge and mastery of the nonlinear effects in materials allowed the development of devices such as amplifiers, modulators, memories, optical limiters, among others^{52–56}. Particularly, the nonlinear refractive index is an interesting property, since the propagation of a Gaussian beam by a material induces a lens-like refractive index profile⁵⁷, which can be used for specific applications. In this direction it has been demonstrated that some glasses presented third-order optical nonlinearities up to three orders of magnitude higher than silica^{58–60}.

On the other hand, femtosecond laser microfabrication is a material processing technique governed by nonlinear absorption. This technique consists of focusing the

laser beam on the surface or inside the volume of a material, which results in ablation or modification of the material around the focal volume. Thanks to the nonlinear nature of the light-matter interaction, this method allows three-dimensional (3D) processing of materials, which can be used for the production of various photonic devices or optical components. Femtosecond laser irradiation has been applied to rare-earth doped boron-based vitreous systems. In a sample of $\text{Dy}_2\text{O}_3\text{-MoO}_3\text{-B}_2\text{O}_3$, it was shown that the formation of DMO crystals strongly depends on the temperature induced by femtosecond laser irradiation⁶¹. The production of borate glass waveguides has been reported to investigate ion migration in and around the region affected by the laser⁶² and maximum high-index contrast values that can be obtained by varying the concentration of the index carrier modifier⁶³. Active waveguides were produced in an erbium-doped phospho-tellurite glass that due to the broadband emission that the matrix presents, resulted in an internal gain including the band of optical communications (1530-1610 nm)⁴³. Channel waveguides in sodium-magnesium-aluminium-phosphate glasses doped with Dy^{3+} showed the generation of fluorescence that is well confined in these waveguides with high potential for the production of waveguides for thrombolysis⁶⁴. The production of waveguides, particularly waveguides in rare-earth doped materials, are promising for the fabrication of gain waveguides, amplifiers, and waveguides for spectral down conversion^{65–67}.

1.1. Objectives

The aim of this dissertation is focused on the interest of nonlinear optics glassy materials, particularly borate glasses doped with rare-earth. The interest was to investigate third-order nonlinearities and the production of optical waveguides in this type of glass that has been barely explored as a nonlinear optical material. Besides,

the influence of rare-earth ions on the third-order nonlinear optical response and also on the results obtained from the coupling with different wavelengths were analyzed. The two vitreous systems studied herein are boron-based and doped with rare-earth ions. The first system consists of two samples with compositions (in mol %) of 60%B₂O₃ - 40%BaO (designated here as BBO) and 42.5B₂O₃-42.5BaO-15SiO₂:0.1% Dy₂O₃-0.05% Eu₂O₃ (designated here as BBS-DyEu). The second system is the CaLiBO set, which has the following composition: (99% - x) CaLiBO +1%Yb₂O₃ + x%Tb₄O₇ with x = 0.1; 1.0 and 2.0 (mol %). In this dissertation, femtosecond laser pulses were used in two main directions: (i) the study of optical nonlinearities of borate glasses and to analyze the effect of rare-earths on such properties; and (ii) in the production of waveguides using single-stage laser processing.

1.2. Dissertation outline

The next chapters are structured as follows: in Chapter 2 a brief review of fundamental concepts in nonlinear optics, as well as about the processing of material for the development of optical waveguides is presented. In Chapter 3, we describe in detail the experimental configurations used to investigate the nonlinear refractive index of materials, the fs-laser microfabrication for the production and characterization of waveguides. Chapter 4 presents the studies of the nonlinear optical properties of the BBO and BBS-DyEu samples and the BBS-DyEu sample waveguides. In Chapter 5, the results obtained by the nonlinear optical characterization and the waveguides written in the CaLiBO system. Finally, Chapter 6 presents conclusions and perspectives. The organization of Chapters 4 and 5 are composed of papers that have been previously published in international journals, so the structure of each chapter is a combination of two papers that follows the format of an article, containing an

introduction, experimental procedure, results with the discussion followed by the conclusion.

Chapter 2. Fundamental aspects

2.1. Nonlinear optical concepts

Previously to the development of lasers, it was considered that all optical media were linear, that is, the optical properties of materials are independent of the incident light intensity. This is because the electric field of a common light source is much smaller than the interatomic electric field that binds electrons to atoms. Thus, these properties are originated from an induced polarization ($\vec{P}$) that responds linearly to an electromagnetic field ($\vec{E}$) by means of

$$\vec{P} = \varepsilon_0 \chi^{(1)} \vec{E} \quad (2.1)$$

being ε_0 the permittivity of the vacuum and $\chi^{(1)}$ is the first order susceptibility of the medium. The linear refractive coefficient and linear absorption are some effects that are associated with the linear susceptibility of the material.

When intense lasers are used, the dominant regime is nonlinear optics, in which the electric field of the electromagnetic wave is comparable with the interatomic electric field. In this way, when such type of light passes by a given medium, the induced polarization becomes exhibits a nonlinear dependence with the applied external electromagnetic field. The polarization response can be described by a series expansion of powers in the electric field of radiation as

$$\vec{P} = \varepsilon_0 (\chi^{(1)} \vec{E} + \chi^{(2)} \vec{E}^2 + \chi^{(3)} \vec{E}^3 + \dots) \equiv \vec{P}^{(1)} + \vec{P}^{(2)} + \vec{P}^{(3)} + \dots \quad (2.2)$$

in which $\chi^{(1)}$ is the first order susceptibility described by Eq. 2.1. $\chi^{(2)}$ and $\chi^{(3)}$ are the second and third-order nonlinear optical susceptibilities, respectively. Each polarization term is assigned to different types of nonlinear processes and is associated with the symmetry conditions of the material. The second-order term in Eq. 2.2) is observed in non-centrosymmetric means, being responsible for second-order nonlinear effects^{64,65}. On the other hand, the third-order term in Eq. 2.2 does not depend on the medium symmetry, such that liquids, gases and glasses, and related to third-order nonlinear optical effects^{64,65}. In addition, $\chi^{(3)}$ is a complex quantity in which the nonlinear refraction (n) is related with its real part, while the nonlinear absorption (α) is related with the imaginary part.

2.2. Nonlinear refractive index

The third-order nonlinearity is responsible for some effects, one of them known as the optical Kerr effect which is the dependence of the refractive index with the incident light intensity and it is quantified by the nonlinear refractive index, n_2 . Some effects, such as self-focusing are observed from the optical Kerr effect.

To demonstrate how this effect is manifested, let us consider that the electric field from the laser is monochromatic at the frequency ω , and can be described as

$$E(t) = E_0 \cos(\omega t) \quad (2.3)$$

If we substitute Eq. 2.3 in Eq. 2.2, the polarization can be expressed as follows:

$$P = \varepsilon_0 \chi^{(1)} E_0 \cos(\omega t) + \varepsilon_0 \chi^{(2)} E_0^2 \cos^2(\omega t) + \varepsilon_0 \chi^{(3)} E_0^3 \cos^3(\omega t) \quad (2.4)$$

Some trigonometric relations were used as $\cos^2(\omega t) = \frac{1+\cos(2\omega t)}{2}$, $\cos^3(\omega t) = \frac{3\cos(\omega t)+\cos(3\omega t)}{4}$ and Eq. 2.4 can be rewritten as:

$$P = \varepsilon_0 \chi^{(1)} E_0 \cos(\omega t) + \frac{1}{2} \varepsilon_0 \chi^{(2)} E_0^2 [1 + \cos(2\omega t)] + \frac{1}{4} \varepsilon_0 \chi^{(3)} E_0^3 [3 \cos(\omega t) + \cos(3\omega t)] \quad (2.5)$$

Let us focus on the effects obtained from $\chi^{(3)}$, then the field-induced polarization of the third-order becomes,

$$P^{(3)}(t) = \frac{1}{4} \varepsilon_0 \chi^{(3)} E_0^3 \cos(3\omega t) + \frac{3}{4} \varepsilon_0 \chi^{(3)} E_0^3 \cos(\omega t) \quad (2.6)$$

The first term in Eq. 2.6 refers to the third-harmonic generation (GTH), a nonlinear process that describes the response of the medium at the frequency 3ω , where three photons of frequency ω are converted into a photon of frequency 3ω with the same direction of propagation of the incident photons.

The second term in Eq. 2.6 represents the nonlinear contribution of the polarization at the same frequency as the incident field ω , which causes effects of the two-photon absorption (2PA) and the optical Kerr⁶⁵.

As previously mentioned, the effects related to $\chi^{(3)}$ do not require the medium to exhibit some special type of symmetry. From Eq. 2.5 we can write the field-induced polarization, considering only the polarization term dependent on ω as:

$$P(\omega) = \varepsilon_o \chi^{(1)} E_0 \cos(\omega t) + \frac{3}{4} \varepsilon_o \chi^{(3)} E_0^3 \cos(\omega t) \quad (2.7)$$

which can be simplified to

$$P(\omega) = \varepsilon_o \left[\chi^{(1)} + \frac{3}{4} \chi^{(3)} E_0^2 \right] E(t) \quad (2.8)$$

where $E(t) = E_0 \cos(\omega t)$ as shown in Eq. 2.3. Considering that the beam propagates only in the z-direction, the scalar wave equation is given by:

$$\frac{\partial^2 E}{\partial z^2} - \mu_0 \varepsilon_0 \frac{\partial^2 E}{\partial t^2} = \mu_0 \frac{\partial^2 P}{\partial t^2} \quad (2.9)$$

Substituting Eq. 2.8 into Eq. 2.9, we get

$$\frac{1}{v^2} = \mu_0 \varepsilon_0 \left[1 + \chi^{(1)} + \frac{3}{4} \chi^{(3)} E_0^2 \right] \quad (2.10)$$

where v is the velocity propagation of light in the medium and $c^2 = 1/\mu_0 \varepsilon_0$, thus,

$$\left(\frac{c}{v} \right)^2 = \left[1 + \chi^{(1)} + \frac{3}{4} \chi^{(3)} E_0^2 \right] = n^2 \quad (2.11)$$

It can be rewritten as,

$$n = \sqrt{1 + \chi^{(1)}} \left[1 + \frac{3\chi^{(3)}E_0^2}{4(1 + \chi^{(1)})} \right]^{\frac{1}{2}} \quad (2.12)$$

Expressing the linear refractive index, $\sqrt{1 + \chi^{(1)}}$ by n_0 and considering that the third-order susceptibility is much smaller than the first-order susceptibility we have:

$$n \approx n_0 \left[1 + \frac{3\chi^{(3)}E_0^2}{8(n_0)} \right] \quad (2.13)$$

From the Pointing vector, the magnitude of the electric field is related to the intensity by

$$I = \frac{1}{2} cn_0 \varepsilon_0 E_0^2 \quad (2.14)$$

Substituting Eq. 2.14 into Eq. 2.13 we can obtain the expression for the refractive index as a function of the intensity (I),

$$n = n_0 + \frac{3\chi^{(3)}}{4cn_0^2\varepsilon_0} I \quad (2.15)$$

Eq. 2.15 can be written more commonly,

$$n = n_0 + n_2 I \quad (2.16)$$

where n_2 is the nonlinear refractive index of the material, that in SI units is written as

$$n_2 = \frac{3\chi^{(3)}}{4cn_0^2\epsilon_0} \quad (2.17)$$

Equation 2.16 shows that the change in the refractive index is proportional to the intensity of light passing through the material. Generally the values of n_2 are comprised in the range of 10^{-18} to 10^{-20} m^2/W for glassy materials.

2.3. Self-focusing and self-defocusing

Self-focusing (Fig. 2.1 (a)) and self-defocusing (Fig. 2.1 (b)) are effects that occur when a laser beam has its wavefront distorted by the laser beam itself along its propagation in a nonlinear material. Considering a Gaussian laser beam that propagates through a material that has a positive nonlinear refractive index, the beam induces a spatial change in the refractive index so that change will be more intense at the center than at the edges of the beam. As a result, the material causes a phase displacement, resulting in a distortion of the wavefront⁷⁰; this effect is known as induced lens. Basically, the beam itself, through the nonlinear interaction, has the ability to make the material behave like a convergent lens⁷¹.

Figure 2.1 - Representation of the effects of self-focusing (a) and self-defocusing (b).
Source: Prepared by the author.

On the other hand, a self-defocusing effect will be dominant if the material has a negative nonlinear refractive index, then the material will behave like a divergent lens.

2.4. Z-scan technique

The Z-scan technique was developed by Sheik-Bahae et al. in 1989⁷², as a sensitive and simple method to perform nonlinear optical measurements of materials. It is a single beam method suitable for estimating both, the signal and the magnitude of third-order optical nonlinearities of materials, specifically the nonlinear absorption coefficient and the nonlinear refractive index.

This method allows measuring the normalized transmittance obtained when a given material is scanned along the propagation axis (z) of a focused Gaussian beam. This

technique allows two types of configuration; the open-aperture configuration, where the beam transmitted through the sample is collected by a detector by means of a lens to evaluate if there is nonlinear absorption, and the closed-aperture configuration, in which the transmitted beam passes through an iris before reaching the detector, which measures the signal variation originated from the self-focusing/defocusing effect produced by the induced nonlinearity in the material, which we will be seen in more detail later. Figure 2.2 shows a schematic representation of the closed- and open-aperture Z-scan setup.

Figure 2.2 - Schematic representation of the (a) closed-aperture and (b) open-aperture Z-scan. Source: Prepared by the author.

For the refractive case (closed-aperture configuration), the Z-scan technique measures the normalized transmittance, $NT(z)$. This quantity is obtained by the ratio of the power transmitted by the material in a given position z divided by the power transmitted when the material is far from the focus (z_{∞}) where no nonlinear effects are present. In this configuration, the measured transmitted powers pass through an

aperture plane in the far field, while the sample is scanned along the propagation axis (z-direction) of a focused Gaussian beam. The normalized transmittance ($NT(z) = P(z)/P(z_\infty)$) is obtained as a function of the sample z-position; such curve is usually known as Z-scan signature.

For a better understanding of the technique, we will assume a medium with a positive nonlinear refractive index ($n_2 > 0$). Initially, we consider that the sample is at a given position far from the focus ($z \ll 0$), such that the beam intensity is low and no nonlinear effect occurs; therefore $NT = 1$ (Fig. 2.3 (a)). As the sample moves towards the focus ($z < 0$), the intensity of the beam increases and begins to induce the lens-like effect. The induced lens in the sample is convergent since we assumed a material with $n_2 > 0$. With the sample positioned before the focal plane ($z < 0$) there is an increase in the divergence of the beam in the far-field and, consequently, the intensity of light that passes through the aperture and is collected by the detector is reduced ($NT < 1$), as can be seen in Figure 2.3(b).

Figure 2.3 - Lens effect on the Z-scan technique for a medium with a positive nonlinear refractive index ($n_2 > 0$).

Source: Prepared by the author.

In the focal region ($z = 0$) the sample has the behavior of a thin lens, such that there is no significant change in the aperture of the beam in the far field and thus $NT = 1$. For the sample positioned after the focus ($z > 0$) (Fig. 2.3(c)) the induced lens effect causes collimation of the beam that results in an increase of the transmittance through the aperture⁷³. Moving the sample away from the focal region ($z \gg 0$), as shown in

Figure 2.3(d), towards the detector, the beam intensity is reduced, and the transmittance has the initial value ($NT = 1$), with negligible nonlinear effect.

The result of scanning the sample with a positive nonlinearity is a Z-scan-signature curve, in which the normalized transmittance as a function of the z position exhibits a minimum of pre-focal transmittance (valley), followed by a maximum of post-focal transmittance (peak)⁷³. For a medium in which the nonlinear refractive index is negative ($n_2 < 0$), the medium will behave as a divergent lens, and the peak-valley configuration in the Z-scan-signature curve is reversed.

The measurements performed with the Z-scan technique allows to determine the value of n_2 . From the Z-scan curve, it is possible to extract some important parameters, such as the peak-valley transmittance variation (ΔT_{PV}) and the peak-valley variation of z (Δz_{PV}). Such quantities are related to important parameters, such that

$$\Delta T_{PV} = 0.406 \Delta \phi_0 \quad (2.18)$$

$$\Delta z_{PV} = 1.7 z_0 \quad (2.19)$$

where z_0 is the Rayleigh parameter of the laser beam ($z_0 = \pi w_0^2 / \lambda$), considering a Gaussian beam with beam waist w_0 , and $\Delta \phi_0$ is the phase change induced by the nonlinearity of the sample, given by

$$\Delta \phi_0 = \frac{k n_2 I_0 L_{eff}}{\sqrt{2}} \quad (2.20)$$

in which k is wave vector ($k = 2\pi/\lambda$), L_{eff} is the effective length of the sample l_0 is the intensity of the beam at the focus given by $I_0 = 2\bar{P}/(\pi)^{3/2}w_0^2f_{rep}t_0$, where, $\bar{P}$ is the average peak power of the laser, f_{rep} is the laser repetition frequency and t_0 is the temporal width of the Gaussian pulse. Finally, n_2 is the nonlinear refractive index that can be obtained by replacing $\Delta\phi_0$ (Eq. 2.20) in ΔT_{PV} (Eq. 2.18) and rearranging to n_2 , which remains in

$$n_2 = \frac{\Delta T_{PV}\lambda\sqrt{2}}{2\pi 0.406 I_0 L} \quad (2.21)$$

Thus, the value of n_2 can be obtained in a relatively simple way, which makes the Z-scan technique of great merit.

The absorptive case (open aperture configuration) is used to measure the variation of absorption as function intensity. Mechanisms such as two-photon absorption, saturated absorption or reverse saturated absorption may contribute to nonlinear absorption. For the measurement, the configuration is similar to the refractive case; however, there is no presence of the aperture before the detector as can be seen in the Figure 2.2 (b). In this configuration, the measured total transmitted power is collected in the far field by a detector, while the sample is scanned along the propagation axis (z-direction) of a focused Gaussian beam. Assuming a medium with a negative two-photon absorption coefficient ($\beta > 0$). Initially, we consider that the sample is at a given position far from the focus ($z \ll 0$ or $z \gg 0$), such that the beam intensity is low and no nonlinear effect occurs; therefore $NT = 1$ (Fig. 2.4 (a) and (d)).

Figure 2.4 - Z-scan technique for a medium with positive nonlinear refractive index ($\beta > 0$) for characterization of nonlinear absorption.

Source: Prepared by the author.

Near the focal region ($z < 0$ and $z > 0$), the increased beam intensity causes the absorption of material to increase, resulting in decreased transmittance (Fig. 2.4 (b) and (c)). Thus, the curve profile obtained by this behavior is a valley centered in $z = 0$, as can be seen in Figure 2.4. For a medium in which the nonlinear coefficient absorption is negative ($\beta < 0$), the curve obtained is a peak centered at $z = 0$.

2.5. Mechanisms involving the femtosecond laser microfabrication

The femtosecond laser was developed in the 1990s, and the first demonstration of the use of femtosecond laser pulses was in the removal of silica and silver that resulted in micrometric size microstructures⁷⁴. A few years later, the femtosecond laser was used for waveguide fabrication and fused silica volume data storage for photonic applications⁷⁵. From these demonstrations, there was an increase in the use of this tool that led to the femtosecond laser microfabrication technique we know today.

The technique consists of the use of ultrashort laser pulses that interact with the material through nonlinear absorption, an interaction capable of producing nanometers to micrometers size structures on the surface of materials and also on the volume of transparent materials⁷⁶. The obtained microstructures do not depend only on the energy absorption processes. The experimental parameters of the laser used in the processing (pulse duration, scan speed, wavelength, and pulse energy), objective lens numerical aperture (NA) and material properties also influence the final result. The absorption of light provided by a femtosecond laser in transparent materials triggers nonlinear processes. For multiphoton absorption to occur, the atoms forming the glass matrix must absorb photons that have enough energy to promote electrons from the valence band to the conduction band. This energy absorbed by the electrons must be greater than the bandgap (E_g) energy of the material. Normally on transparent materials the E_g is generally greater than the photon energy.

For this reason, the absorbed energy is associated with the number of photons. In the case of the samples used in this work, the bandgap energy is between 3.2 and 5.5 eV. When using an 800 nm laser that has a photon energy of 1.5 eV, it is necessary an absorption process between 3 and 4 photons. Furthermore, for this process to occur, the electric field strength in the laser pulse must be equivalent to that of the

interatomic field (of the order of 10^9 V/m)⁷⁷. In order for microfabrication to be viable, it must have a high-intensity laser and high focusing.

2.5.1. Fundamentals processes of femtosecond laser interaction with matter

For a transparent dielectric, there is no linear absorption (when irradiated by a low-intensity laser beam) if the photons incident in the material has energy lower than the bandgap; the light will be completely transmitted through the material. On the other hand, when a high-intensity beam is incident on a material, the processes that govern this interaction are nonlinear. In this case, the absorbed energy is a combination of some mechanisms as photoionization (composed of two processes: multiphoton ionization and tunneling ionization) and avalanche ionization.

Photoionization processes occur because the electrons are excited by a high-intensity field. These processes were described by Keldysh⁷⁸, in which the promotion of the electrons for the conduction band occurs through a combination of multiphoton and tunneling ionization. Multiphoton ionization (shown in Fig. 2.5 (a)) is a nonlinear process in which several photons are simultaneously absorbed by a material to promote the electrons that are in the valence band to the conduction band, such that $E_g < nh\nu$. This process is strongly dependent on the intensity, with probability given by $P(I) = \sigma_n I^n$ where σ_n is the multiphoton absorption coefficient for the absorption of n photons, and I is the intensity of the incident light^{79,80}.

Figure 2.5 - Representation of the promotion of the valence band electron to the conduction band through the processes (a) multiphoton ionization, (b) tunneling ionization and (c) avalanche ionization.

Source: Prepared by the author.

The second photoionizing process is tunneling ionization (Fig. 2.5 (b)), which occurs when the presence of the electromagnetic field is strong enough to alter the structure of the dielectric band, reducing the potential barrier between the valence band and the conduction through the superposition of the Coulomb field with the electromagnetic field of the laser pulse. Electrons can now escape their connected

states by means of quantum tunneling. These two regimes are described by the Keldysh parameter (γ)⁸¹, given by

$$\gamma = \frac{\omega(2m^*E_g)^{\frac{1}{2}}}{eE} \quad (2.22)$$

where ω is the frequency of the laser, m^* is the effective mass of the electron, E_g is the energy of bandgap, e is the charge of the electron and E is the amplitude of the electric field of the laser.

The value of the Keldysh parameter indicates which regime is dominant. For $\gamma \gg 1$, the multiphoton ionization process is dominant, which happens when for lasers with high oscillation frequency. When $\gamma \ll 1$, the oscillation frequency is low, and the tunneling ionization process is dominant, indicating that the electron has a considerable time to tunnel before the optical field changes^{71,82,83}. The photoionization process promotes the electron to the conduction band, which serves as a seed for the avalanche ionization process.

The nonlinear avalanche ionization process may be initiated by states of defects, thermally excited impurities, or prior photoionization processes. Initially, electrons that are in the conduction band (which were previously promoted by the process of photoionization) can successively absorb several photons of the laser. In this way, they are promoted to states of greater energy on their own conduction band, as seen in Figure 2.5 (c). At the moment this energy being absorbed by the electrons exceeds a certain critical value, $E_c > E_g$, such that another electron can be ionized, which is in its bonded state in the valence band, by impact (this process is a transfer of energy that happens by collision), the result will be two electrons in the lower energy state of the

conduction band. Consequently, these two electrons can restart the cycle, which will result in exponential growth of free electrons in the conduction band, while the laser beam is present.

The ionization of a large number of electrons resulting from this absorbed energy leads to a process known as an optical breakdown that occurs through a sequence of events; the formation of free-electron plasma obtained by means of the high-intensity laser pulse, the consecutive absorption of the laser energy by the plasma. Finally, the energy absorbed by the plasma is transferred to the network of the material, which is responsible for structural changes in the material, such as modification in the linear refractive index, local structure, color center formation, etc.

2.5.2. Parameters that influence microfabrication

Experimental laser parameters such as pulse repetition rate, energy intensity, and pulse duration affect the results obtained by the microfabrication process. Laser oscillators (not amplified systems) and amplifiers can be used for such microfabrication. Laser oscillator systems have repetition rates of the order of MHz, and the pulse energy delivered is in the range of nanojoules (nJ). For amplified laser systems, the repetition rates are in kHz and the energy per pulse is given in millijoules (mJ). In the oscillator system the time period between one pulse and the other is less than the thermal diffusion time of the materials, which is of the order of $1\ \mu\text{s}$ ⁸⁴, so a point heat source will be created in the focal volume because the pulses will be accumulated in that region. This accumulated heat can modify an area larger than the focal volume region and causes the local temperature to rise. For the amplified system, the time between pulses is longer than the thermal diffusion time. In this case, the

energy deposited by the pulse has time to propagate and cool before the next pulse arrives, so the modified area is limited to the focal volume region^{77,85,86}.

The threshold energy/fluence, as well as the magnitude of change of the refractive index, are different for each type of material. For different amounts of energy per pulse several changes in material have been observed. For low, medium and high energies, consequences such as mild change in refractive index, birefringent modification, and voids produced by microexplosions, respectively, have been observed⁸⁷. Pulse duration is another parameter that has been investigated and shows an influence on the damage threshold. Damage from longer laser pulses is due to heat accumulation and eventual failure. For short pulses, on the other hand, there is an interval between the modification limit and the damage threshold, which allows the production of smooth microstructures.

The parameters mentioned before are defined by the laser. However, other experimental parameters, such as the numerical aperture, which is independent of the laser, play a fundamental role in the microfabrication process. Proper focusing provides sufficient intensity for the nonlinear interaction of the material with the laser pulse, delivering energy in a well-localized manner over a small region in the sample bulk. In general, laser beam focusing is achieved using objective microscope lenses. The numerical aperture is one of the variables that determine the optical breakdown and the beam waist. For low NA, two nonlinear processes dominate energy deposition before damage occurs. One of them is self-focusing and white light generation, the latter being responsible for causing a spectral widening of the pulse as it propagates. For high NA is the multiphoton process that induces bulk damage (NA above 0.6) and the microstructures produced are approximately symmetrical spheres, but below this value, the microstructures become larger and asymmetric⁷⁷.

2.5.3. Optical waveguides

With appropriate parameters and comprehension of nonlinear absorption processes, the waveguides produced by laser microfabrication can be categorized according to geometry, mode structure, refractive index distribution, and material. All femtosecond laser microfabrication systems of waveguides present similar principles. They basically consist of a femtosecond laser that is focused on the bulk of a transparent material through an objective microscope lens. The sample is scanned and for the focal point where the laser intensity exceeds the threshold modification process takes place, causing a permanent local change of the refractive index.

Microfabrication can be obtained in two directions: longitudinal (Fig. 2.6 (a)) and transversal (Fig. 2.6 (b)), where each direction causes different forms of geometry. In the longitudinal writing, the sample is scanned along the beam propagation direction, which produces structurally cylindrical cross-sections. However, the length of the waveguide is physically restricted to the working distance of the microscope objective^{88,89}. On the other hand, the transversal writing occurs when the sample is scanned perpendicular to the direction of laser beam propagation. In this configuration the waveguide length is limited by the stages of translation. However the writing depth is limited by the working distance of the objective lens, and the cross-section is elliptical^{88–90}.

Figure 2.6 - Representation of longitudinal (a) and transversal (b) writing direction in transparent materials. The arrows indicate the scanning direction of the material.

Source: Prepared by the author.

The modifications that occur in the femtosecond laser-induced refractive index in a material result from the nonlinear absorption process. The induced modification of the laser interaction with the material is normally characterized as types I, II, III, and VI. The type I waveguide (Fig. 2.7(a)) shows a positive refractive index change (Δn) induced by the laser in the irradiated focal volume leading to a change of the order of 10^{-4} to 10^{-3} ^{91,92}. This type of waveguide can be obtained with low intensity and low focal volume damage, causing a smooth modification of the refractive index, preserving uniformity and optical quality. Type II (Fig. 2.7(b)) is a waveguide known as a double-line; these waveguides are located in the border regions of the produced tracks. These tracks present a negative refractive index change induced by the laser, which causes a dilatation in the nucleus of the track and is usually followed by a reduction in the refractive index. Thus, the border regions may present a high refractive index due to the stress-driven effect. A waveguide of this type is typically obtained from

the production of two parallel tracks with an appropriate distance, so the core of the waveguide will be in the region between the two tracks. This type of guide is most commonly produced in crystals⁹².

Type III waveguide is known as cladding waveguide as show in Figure 2.7(c). This waveguide consists of a core formed by several tracks that behave as a cladding and that have a low refractive index. These tracks are adjacent to each other in such a way that they produce an almost constant barrier of low refractive index. In this way, it provides the confinement of light within the core that consists of a higher refractive index⁹².

Figure 2.7 - Representation of the types of waveguide configurations that can be obtained by fs-laser microfabrication technique, type I (a), type II (b), type III (c) and type IV (d). In the insets are illustrated the cross-sections for each type and the dotted lines the spatial modes of the waveguide cores.

Source: Prepared by the author

Finally, type IV waveguides (Fig. 2.7(d)) consist of the use of high-intensity ultrashort pulses for the production of planar waveguides through the ultra-fast ablation mechanism. This mechanism is employed to remove the material from the surface in the focal volume resulting in a shallow cavity. A disadvantage of this type of guide is the roughness produced at the edges which leads to significant losses and decreases the quality of the waveguides⁹².

A core region forms an optical waveguide of step index with a high refractive index (n_a) that is surrounded by a low refractive index (n_b) region, called cladding, in which the index profile that suddenly changes on the interface n_a and n_b . These devices allow conducting light in a controlled manner and along the direction in which it was produced. From a ray optics point of view, the phenomenon that enables the confinement of light is known as total internal reflection (TIR), as illustrated in Figure 2.8. The refractive index of layer 1 is higher than that of the layers surrounding it. By Snell's Law it can be shown that for angles of incidence greater than the limit angle ($\theta_L = n_b/n_a$) total internal reflection will occur. The light beam will travel within the core (n_a) and will be fully reflected internally at the upper and lower interfaces of the structure⁹³.

Figure 2.8 - Scheme illustrating the concept of total internal reflection in a waveguide.

Source: Prepared by the author.

A guided mode can be obtained from the moment light is confined to the core. The amount of guided modes depends on the wavelength refractive index contrast, the geometry and the wavelength of the light. Therefore, single or multimode waveguides can be fabricated, which will exhibit different field intensity distributions.

As light propagates in the waveguide, a decrease in amplitude can be observed over the entire length of the waveguide. This decrease is caused by losses that are related to intrinsic characteristics of the guide, which may be caused by factors related to the material and the process of microfabrication. Optical attenuation in the

waveguide may come from different sources, one of which is the loss in radiation intensity, which involves the probability that some photons will escape at the waveguide interface. Coupling losses are usually related to Fresnel reflections at the input interface of the waveguide, as well as mode mismatch. Imperfections on the surface or inside of the material, presence of defects and variations in material composition are characteristics that lead to scattering losses. Finally, absorption losses occur in materials that absorb part of the light being guided. In most transparent materials absorption losses can be neglected.

Chapter 3. Experimental

3.1. Characterization of samples

The characterization measurements carried out in this work were performed with the purpose of both complementing and understanding the results obtained. Optical properties were analyzed using a UV-vis spectrophotometer (Shimadzu, model UV-1800). Luminescence properties were determined using two types of equipments: (i) a Fluorescence spectrophotometer (FL 7000 – Hitachi), and (ii) Horiba Fluorolog spectrofluorimeter (model FL-1050).

The linear refractive index was obtained using two types of equipments: (i) the refractometer Pulfrich (Carl Zeiss Jena Pulfrich Refractometer *PR2®*) using Hg and He lamps as spectral sources and (ii) prism coupling M-line technique (Metricon – model 2010) that was performed at the Chemistry Department of USP Ribeirão Preto. Density measurements were performed using the Archimedes method (Density accessory kit Mettler Toledo), using absolute ethanol as the immersion liquid.

The microstructures produced on the surface and volume of the samples were analysed by optical microscopy. For the microstructure width measurements, we used a Zeiss optical microscope model LSM 700, with a coupled CCD camera.

3.2. Nonlinear optical spectroscopy

The Z-scan technique with femtosecond pulses was used to measure the third-order nonlinear optical properties of glass samples. The experimental configuration consists of a Ti:Sapphire laser amplifier system (Clark-MXR) centered at 775 nm, with pulse duration of 150-fs and a repetition rate of 1 kHz. Such laser was used as the excitation source to an optical parametric amplifier that emits pulses of approximately 120 fs and allows selecting the wavelength between 460 to 2600 nm. A spatial filter is used to

obtain a Gaussian beam profile before the Z-scan setup, as required for method. An illustration of the Z-scan setup is displayed in Figure 3.1. The apparatus is composed of a converging lens, a translation stage for moving the sample, followed by a beam splitter. A portion of the beam is directed to a lens that is responsible for focusing the transmitted beam in the detector 1; this detector collects the signal for the nonlinear absorption. The other part of the transmitted beam is collected by detector 2, which is responsible for the nonlinear refractive index signal. Finally, the signals obtained by the detectors are connected to a lock-in amplifier and sent to the computer for collection of the normalized transmittance as a function of the position of the sample. No nonlinear absorption signal was observed in open-aperture Z-scan measurements for both vitreous systems studied in this work.

Figure 3.1 - Experimental configuration used in the determination of the nonlinear refractive index by the refractive Z-scan technique.

Source: Prepared by the author.

In order to control the intensity of the excitation beam in the sample, both intensity filters and polarizers were used. In addition, intensity filters were also used to prevent saturation effects on the detectors. To confirm the validity of the values of n_2 , a sample of fused silica was used as reference material.

3.3. Femtosecond laser microfabrication

Femtosecond laser microfabrication was used to produce optical waveguides in the samples. The experimental configuration consists of a Ti:Sapphire laser oscillator

(Femtosome-100XL) centered at 800 nm, with pulses duration of 50-fs and a repetition rate of 5 MHz. After the laser beam passes through a mirror, the beam reaches the microscope objective which focuses the beam on the sample, as illustrated in Figure 3.2.

Figure 3.2 - Experimental setup for the microfabrication used for the production of waveguides.
Source: Prepared by the author.

The sample is fixed to support connected to three-dimensional translation stages (x-y-z), which are driven by computer controlled step motors to move the sample

perpendicularly to the direction of propagation of the beam. To accompany the microstructure process in real time a CCD camera and lighting were used.

3.4. Waveguide coupling system

The waveguides produced with femtosecond lasers were characterized in a coupling system consisting of a laser and microscope objective lens. In the configuration employed, an input objective lens focuses the laser beam on the waveguide entrance; the transmitted light is collected by an objective output lens, as shown in Figure 3.3. The image of the modes of propagation was collected on a CCD camera. According to the properties of the waveguides and rare-earth ions present on the sample, different types of laser were used for coupling. The standard characterization laser employed for all samples was the line tunable helium-neon laser system (632.8 nm; 612 nm; 594 nm and 543 nm) (model LSTP-1010). Other specific lasers were also used to analyze the emission of rare-earth ions for each glass system as: HeCd (325 and 442 nm) and diode laser (405 nm).

To obtain efficient coupling, both the input and output microscope objectives and the sample with the waveguides are aligned using three-dimensional (x-y-z) positioning stages. In addition, the waveguide must be positioned parallel to the propagation of the laser beam, and the entrance and exit faces must be in the focal plane of the objective lenses of input and output at the same time.

Figure 3.3 - Representation of the experimental configuration of the coupling system.
Source: Prepared by the author.

In the waveguide optics, the transmitted light intensity will be gradually reduced by various types of losses. These losses can originate from the characteristics of the produced waveguides, which can be associated with the material and with the microfabrication process. Scattering losses occur due to volume and/or surface irregularities as an example of the presence of defects and variation in material composition. Absorption losses occur in materials that absorb part of the radiation employed in propagation, as well as material processing imperfections, the last being responsible for a large part of the absorption. Losses caused by Fresnel reflections should also be taken into account since they occur at the air-glass interfaces at the input and output ends of the waveguides. Finally, the input coupling losses occur at the interface between the radiation source and the input face of the waveguide, this type of loss is composed of the incompatibility between the areas of the light source and the waveguide and the effect of the numerical aperture, which is determined by the acceptance angle that defines a light acceptance cone that satisfies the condition for the total internal reflection⁹⁴.

The total losses (α_{total}) of waveguides are characterized by coupling (α_{coupl}) and propagation (α_{prop}) losses. The presence of defects, imperfections, and impurities in

glass are some of the reasons for propagation losses⁹⁵. The losses are commonly expressed in decibels (dB) and can be calculated by using:

$$\alpha_{total}(dB) = -10 \log_{10} \left(\frac{P_{input}}{P_{output}} \right) \quad (3.1)$$

in which P_{input} is the power measured before the input objective lens, and P_{output} is the power measured after the output objective lens. In this way, it is considered the transmission of all components of the system.

Chapter 4. Third-order optical nonlinearity and fs-laser fabrication of waveguides in barium borate glass doped with Dy³⁺ and Eu³⁺

This chapter reports, initially, a study on the nonlinear refraction (n_2) of (mol%) 60B₂O₃-40BaO (designated here as BBO) and (42.5B₂O₃-42.5BaO-15SiO₂):0.1Dy-0.05Eu (BBS-DyEu) glasses through femtosecond Z-scan technique. The results were modeled using the BGO approach, which showed that oxygen ions are playing a role in the nonlinear optical properties of the glasses studied here. In this chapter, it is also demonstrated the fabrication of three-dimensional waveguides with broad emission in the visible spectrum. Such performance was achieved through the co-doping with Dy³⁺ and Eu³⁺ ions, which together provide broad emissions at 488 nm (blue), 579 nm (yellow) and 616 nm (red), along with the glass processing with femtosecond laser pulses.

4.1. Introduction

The study of nonlinear optical properties of materials has been pushed by the need to develop novel technologies in optics and photonics, such as all-optical switching⁵⁹, optical limiting⁹⁶, and amplifiers⁹⁷. Different types of solid-state materials, from polymers to crystals^{16,98–100}, have been developed and investigated as feasible candidates for such purposes^{101,102}. In this direction, glasses have received considerable attention because of their excellent optical properties and flexibility to be produced with different compositions and shapes, aside from their mechanical stability, ease of handling and fast production process, which make them useful for several purposes¹⁰³. Moreover, glasses can exhibit significant optical nonlinearities depending on the chemical nature of their constituents that can be easily manipulated in order to meet specific needs for a given application. At the same time, femtosecond laser

micromachining has been shown as an important method for the fabrication of optical devices in transparent materials, being useful for processing glassy materials, allowing obtaining gain waveguides and amplifiers^{43,65,90,104}.

Boron-based glasses are one of the major glass-forming matrices, which present low production cost, thermal stability, wide range of transparency, ease of incorporating oxides modifier, and rare-earths ions^{105,106}. Thus, the composition of boron-based glasses can be easily changed to achieve specific properties targeting different applications. Since borate glasses in its pure form are hygroscopic, their physical and optical properties are usually improved by the addition of modifiers, such as alkaline and earth alkaline ions. As an example, the barium borate ones can be designed to have second harmonic generation by submitting it to crystallization or polling process^{107,108}. Particularly, the glass system based on B_2O_3 -BaO has attracted interest for nonlinear optics¹⁰⁹, because when subjected to a proper heat-treatment, the barium metaborate (β -BaB₂O₄ β -BBO) phase is crystallized, configuring an important material for frequency-doubling devices¹¹⁰.

Over the years, the interest in exploring rare-earth doped or co-doped ions in glassy materials has increased. In particular, borate glasses have been extensively studied because of their high rare-earth ions solubility¹¹¹, which is interesting for the development of the photonic and optoelectronic devices^{66,112–116}. There are several applications of borate glasses containing alkaline and earth alkaline ions such as, for example, vacuum ultraviolet optics, radiation dosimetry, solar energy conversion, optoelectronics, nonlinear optics^{50,109,117}, new light sources, display devices, UV sensors, and tunable visible lasers^{105,118}. Depending on the rare-earth ion, different functionalities can be accomplished; for example, the incorporation of Nd³⁺ ions in barium borate matrix was demonstrated to be promising for broadband laser

amplification in the infrared region¹¹⁹. Also, energy applications were demonstrated in barium borate glasses co-doped with Eu^{3+} - Tb^{3+} , being efficient as photon downshifting cover glass for solar cells¹²⁰. Among the lanthanide ions, dysprosium has unique luminescence properties. The glass-doped Dy^{3+} ion exhibits two dominant emission bands in the blue (470-500 nm) and yellow (560-600 nm) regions, with applications as radiation dosimetry measurement and solid-state lasers^{121,122}. Also, Eu^{3+} ion has been used as a dopant for glass matrix targeting at several applications, such as white OLEDs, LED and plasma display^{123–125} due to its characteristic red emission around 616 nm. The combination of emissions from Dy^{3+} and Eu^{3+} ions can result in white light generation, which is promising for photonic devices¹²⁶. Although the co-doping of Dy^{3+} and Eu^{3+} is interesting for luminescent glasses, its incorporation in barium borate glasses for the development of optical devices is still scarce.

4.2. Materials and methods

The glass compositions studied are (mol%) $60\text{B}_2\text{O}_3$ - 40BaO (designated here as BBO) and $(42.5\text{B}_2\text{O}_3$ - 42.5BaO - $15\text{SiO}_2)$: 0.1Dy - 0.05Eu (BBS-DyEu). The BBO samples were first prepared by mixing appropriate amounts of high purity (>99.99%) materials, that were melted in a platinum crucible in an electrically heated furnace for 3 h at 1100 °C. The melt was quenched on a steel plate and annealed in a furnace at 450 °C for 1 h¹²⁷. For the BBS-DyEu sample, a homogeneous mixture of BaCO_3 , SiO_2 and B_2O_3 reagents were melted for approximately 3 h in an electric furnace at 1200 °C in air. The liquid was then quenched by pouring it on a steel plate and heat-treated in a conventional electric furnace at 500 °C for 24 h to remove thermal stress. Then, Dy_2O_3 and Eu_2O_3 were incorporated into this matrix by melt-quenching¹²⁸. Polished flat samples with ~1 mm of thickness, free of inclusions or cords were used for the optical

measurements. These samples were prepared at the Group of Nanomaterials and Advanced Materials (NaCA) of the São Carlos Institute of Physics (IFSC - USP) by Prof. Dr. Valmor Roberto Mastelaro team.

The absorption spectrum of the glasses was measured in the range of 200–1000 nm with a UV-vis spectrophotometer. A Pulfrich refractometer (*Carl Zeiss Jena Pulfrich Refractometer PR2®*) was employed to measure the linear refractive indices (n_0) using Hg and He lamps as spectral sources. The emission and excitation spectrum of the BBS-DyEu was measured in the range of 470–750 nm, excited at 325 and 442 nm, and the excitation spectrum in the range of 315–600 nm monitoring the emission at 616 nm.

Third-order nonlinear optical characterization (nonlinear refraction (n_2) and nonlinear absorption) were performed using closed and opened aperture Z-scan technique, respectively^{72,129}. An optical parametric amplifier (OPA) was used as the excitation light source, which provided pulses of 120-fs from 460 to 1500 nm. The OPA is pumped by a Ti:Sapphire laser amplified system (*CPA 2001, Clark MXR®*) at 775 nm with 150-fs pulses at 1 kHz repetition rate. Fused silica has been used as reference material, whose nonlinear refractive index was found to be approximately $2.1 \times 10^{-20} \text{ m}^2/\text{W}$ from visible to infrared, which is in accordance with the literature¹³⁰. Waveguides were written throughout the length of the sample BBS-DyEu by using a Ti: Sapphire laser oscillator (50-fs, 800 nm, the maximum energy of 100 nJ and 5 MHz of repetition rate). Femtosecond laser pulses were focused by a microscope objective (NA= 0.65) in the sample, while it was displaced by a translational xyz stage moved at 10 $\mu\text{m/s}$ in the plane perpendicular to the laser beam. The guiding properties of the produced waveguides were determined by using an objective-lens coupling system; standard and UV-coated microscopy objectives (NA= 0.65) were used to coupled light from a HeNe (632.8 nm) and a HeCd (325 and 442 nm), respectively¹³¹.

4.3. Results and discussion

The linear absorption spectra of BBO and BBS – DyEu are shown in Figure 4.1. While the BBO sample is transparent for wavelengths longer than 400 nm, the spectrum of BBS-DyEu presents narrow absorption peaks that are characteristic of Dy^{+3} and Eu^{+3} . For Dy^{+3} , eight absorption bands, related to electronic transitions from the ground state ($^6\text{H}_{15/2}$) to excited states, can be identified; at 349 nm ($^6\text{H}_{15/2} - ^6\text{P}_{7/2}$), 386 nm ($^6\text{H}_{15/2} \rightarrow ^4\text{F}_{7/2}/^4\text{I}_{13/2}/^4\text{M}_{19/2,21/2}/^4\text{K}_{17/2}$), 424 nm ($^6\text{H}_{15/2} \rightarrow ^4\text{G}_{11/2}$), 454 nm ($^6\text{H}_{15/2} \rightarrow ^4\text{I}_{15/2}$), 747 nm ($^6\text{H}_{15/2} \rightarrow ^6\text{F}_{1/2}/^6\text{F}_{3/2}$), 797 nm ($^6\text{H}_{15/2} \rightarrow ^6\text{F}_{5/2}$) and 890 nm ($^6\text{H}_{15/2} \rightarrow ^6\text{H}_{5/2}/^6\text{F}_{7/2}$). For Eu^{3+} , one absorption band from ground state ($^7\text{F}_0$), can be identified at 393 nm ($^7\text{F}_0 - ^5\text{L}_7$). The absorption band at 364 nm is an overlap of the bands of the ions Dy^{+3} ($^6\text{H}_{15/2} \rightarrow ^6\text{P}_{5/2}$) and Eu^{+3} ($^7\text{F}_0 \rightarrow ^5\text{D}_4$)¹³².

Figure 4.1 - Linear absorption spectrum of samples BBO and BBS-DyEu. The absorption spectrum of BBS-DyEu sample was vertically shifted for better visualization of the Dy⁺³ and Eu⁺³ absorption peaks.

Source: Prepared by the author.

The linear refractive index is an important optical parameter for the development of optical devices, as well as for understanding the nonlinear index of refraction of materials. In Figure 4.2, we present the dispersion curve for the samples BBO and BBS–DyEu, along with the fitting obtained using the two-pole Sellmeier dispersion equation, given in Eq. 4.1¹³³

$$n^2 = \sqrt{A + \frac{B\lambda^2}{\lambda^2 - C} + \frac{D\lambda^2}{\lambda^2 - E}} \quad (4.1)$$

where λ is the wavelength in micrometers, and A , B , C , D , and E are the dispersion parameters of the material absorption¹³⁴. The Sellmeier coefficients obtained through the fitting are listed in Table 4.1, for both samples. To complement the results obtained from the linear refractive index for the BBO sample, we added the value of n_0 measured at wavelength at 1.014 μm as reported by Mito and collaborators¹³⁵. The introduced value is illustrated by an empty circle symbol, as seen in Figure 4.2.

Figure 4.2 - Linear refractive index of (a) BBO and (b) BBS-DyEu glasses. The solid line represents the fitting with the Sellmeier equation (Eq. 4.1), whose coefficients are shown in Table 4.1. The open symbol in spectrum (a) corresponds to n_0 at 1.014 μm obtained from MITO¹³⁵ for the same glass composition and was added to improve the fitting.

Source: Prepared by the author.

Table 4.1 - Sellmeier coefficients for the BBO and BBS–DyEu glasses obtained from the fitting shown in Figure 4.2.

Samples glass	R-squared	A	B	C	D	E
BBO	0.96	2.4 ± 0.4	0.3 ± 0.4	0.06 ± 0.05	0.01 ± 0.03	50 ± 30
BBS - DyEu	0.99	2.1 ± 0.4	0.5 ± 0.4	0.04 ± 0.02	0.07 ± 0.02	90 ± 40

Source: Prepared by the author.

The Figure 4.3 shows typical closed-aperture (refractive) Z-scan signatures for BBO (a) and BBS–DyEu (b) samples, at 800 and 750 nm, respectively. From Z-scan curves, similar to the ones displayed in Figure 4.3, obtained at various wavelengths, we are able to obtain the dispersion of n_2 (nonlinear refraction spectrum).

Figure 4.3 - Closed-aperture Z-scan measurements for (a) BBO sample at 800 nm and (b) BBS-DyEu at 750 nm.

Source: Prepared by the author.

The spectra of n_2 obtained for both samples are shown in Figure 4.4, and exhibit a nearly constant behavior as a function of the wavelength, considering the experimental error. For comparison purposes, we determined the mean values of n_2 for BBO and BBS – DyEu as 3.43 and $5.27 \times 10^{-20} \text{ m}^2/\text{W}$, respectively. Such values are 1.63 and

2.51, respectively, higher than the ones reported for fused silica¹³⁰. No nonlinear absorption signal was observed in open-aperture Z-scan measurements, indicating that two-photon absorption is absent in the analyzed wavelength range.

Figure 4.4 - Spectra of the nonlinear refractive index (n_2) of BBO (a) and BBS – DyEu (b). The solid lines along the symbols represent the fit obtained with the BGO model, with parameters given in the text.

Source: Prepared by the author.

In order to further understand the optical nonlinearities of the studied glasses, we modeled the experimental n_2 spectra using the BGO model¹³⁶, which describes the interaction of electromagnetic radiation with matter through a classical nonlinear oscillator. In this model, the second hyperpolarizability is assumed to be proportional to the linear polarizability squared, and the incident light field frequency is considered to be far from any resonance ($\omega \ll \omega_0$), in such a way that the nonlinear refractive index is written in SI units (m^2/W) as¹³⁶,

$$n_{2(BGO)} = \frac{5(n_0^2 + 2)^2(n_0^2 - 1)^2(gs)}{6n_0^2 c \hbar \omega_0 (Ns)} \quad (4.2)$$

where c is the speed light in (m/s), g is an anharmonicity parameter, s is the effective oscillator strength, N is the density of nonlinear oscillators, $2\pi\hbar$ is the Planck's constant and n_0 is the linear refractive index of light at the wavelength λ . The product Ns as well as the resonance frequency ω_0 are obtained from Eq. 4.3.

$$\frac{4\pi}{3} \frac{(n_0^2 + 2)}{2(n_0^2 - 1)} = \frac{m(\omega_0^2 - \omega^2)}{e^2(Ns)} \quad (4.3)$$

where e and m are the electron charge and mass, respectively. The product Ns and ω_0 in Eq. 4.3 can be obtained from the linear index of refraction n_0 (Fig. 4.2), for each sample. The dispersion of n_0 in the BGO model is included by using the Sellmeier equation (Eq. 4.1), with the parameters given in Table 4.1.

By using the BGO model, the mean nonlinear refractive index ($\bar{n}_2$) of BBO and BBS-DyEu was calculated as $3.4 \times 10^{-20} \text{ m}^2/\text{W}$ and $5.2 \times 10^{-20} \text{ m}^2/\text{W}$, being in good agreement with the mean values of n_2 measured experimentally. The parameter g ,

obtained through the fitting, was found to be (0.43 ± 0.02) and (0.62 ± 0.03) for BBO and BBS-DyEu, respectively. The effective oscillator strength, estimated from the ratio between the density of nonlinear oscillators (N_s) and the density of oxygen ions in the samples, matched the typical value obtained for oxide glasses ($s \cong 3$), which suggests that oxygen is playing a role in the nonlinearities of the glasses analyzed herein¹³⁶.

Studies on the nonlinear refractive index on the BaO-ZnO-B₂O₃ system doped with Sm³⁺⁴⁶ demonstrated an increase of n_2 from 0.77 up to 1.22×10^{-20} m²/W when the dopant concentration varies from 0.5 mol% to 2.0 mol%. EEVON et al⁵⁹ also observed an increase of the n_2 value from about 6.3×10^{-19} m²/W to 9.4×10^{-19} m²/W when the concentrations of the rare-earth ion Gd³⁺ is increased from 1 mol% to 5 mol% in a zinc borotellurite glass. Such observation is in agreement with our results, which revealed larger nonlinear refractive index values for the glass containing RE ions, thus confirming the influence of the polarizability of Dy³⁺ and Eu³⁺ ions on the nonlinear optical properties of the BBS-DyEu glass.

Figure 4.5 (a) presents the emission spectra of the BBS-DyEu glass sample, excited at 442 nm. The two major emission bands, located at 488 nm and 579 nm are attributed to the transitions $^4F_{9/2} \rightarrow ^6H_{15/2}$ (blue color characteristic of the emission) and $^4F_{9/2} \rightarrow ^6H_{13/2}$ (yellow color characteristic of the emission) of the Dy³⁺ ions, respectively. The inset in Figure 4.5 (a) highlights the lowest emission band centered at 616 nm, which is attributed to the $^5D_0 \rightarrow ^7F_2$ transition of Eu³⁺ (red color characteristic of the emission)^{127,132}. Another weak transition at 667 nm (red color characteristic of the emission) can also be observed in the emission spectrum, being assigned to the $^4F_{9/2} \rightarrow ^6H_{11/2}$ transition of Dy³⁺¹³⁷. The same behavior was observed for excitation at 325 nm.

Figure 4.5 - (a) Emission spectra of the BBS-DyEu glass sample excited at 442 nm. The inset shows a zoom in of the lowest emission band centered at 616 nm, which is attributed to the $^5D_0 \rightarrow ^7F_2$ transition of Eu^{3+} . (b) Excitation spectrum of the sample monitored at 616 nm.

Source: Prepared by the author.

Glassy systems co-doped with Dy^{3+} and Eu^{3+} ions are known to support energy transfer process of non-radiative nature^{138,139}, which can be inferred through the

excitation spectrum in Figure 4.5 (b), while monitoring the Eu^{3+} emission at 616 nm. Besides the expected excitation bands of Eu^{3+} , it is possible to observe a shoulder at 454 nm (marked with a rectangle), which is related to the characteristic excitation of the Dy^{3+} ion¹⁴⁰. Such result indicates the energy transfer from Dy^{3+} to Eu^{3+} and it is likely to occur given the partial overlap between the emission bands at 488 nm ($^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$) and 579 nm ($^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$) of Dy^{3+} ions with the absorption bands of Eu^{3+} at 467 nm ($^7\text{F}_0 \rightarrow ^5\text{D}_2$) and 580 nm ($^7\text{F}_0 \rightarrow ^5\text{D}_0$), not assigned in the absorption spectrum (Fig. 4.1) due to its low intensity^{132,141}. A schematic model is presented for the energy transfer from Dy^{3+} to Eu^{3+} in Figure 4.6. When the energy level of Dy^{3+} ($^4\text{I}_{15/2}$) is excited by 454 nm, the initial population relaxes without radiation until it reaches the lowest energy level ($^4\text{F}_{9/2}$) and consequently transfers to the energy levels $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ (483 nm) and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ (575 nm). Also, part of the energy of level $^4\text{I}_{15/2}$ of the Dy^{3+} is transferred to level $^5\text{D}_2$ of the Eu^{3+} and subsequently without radiation relaxes to the energy level $^5\text{D}_0$, which transfers to the other levels $^7\text{F}_J$ ($J = 0, 1, 2$) of Eu^{3+} emitting fluorescence.

Figure 4.6 - Energy level scheme of Dy^{3+} and Eu^{3+}

Optical microscopy images show the top (Fig. 4.7) and cross-section (Fig. 4.8 (a)) views of a waveguide produced by fs-laser micromachining in the BBS-DyEu sample. The 7.8-mm long waveguides were produced at approximately $70 \mu\text{m}$ below the sample surface, using pulse energy of 32 nJ at a scanning speed of $10 \mu\text{m/s}$. Such images display that the fabricated waveguides are homogeneous along their length and present a slightly elliptical cross-section, sizing approximately $5 \mu\text{m}$.

Figure 4.7 - Optical microscopy images (top view) of waveguides produced in the BBS-DyEu sample. The inset illustrates the schematic layout of the waveguide.

Source: Prepared by the author.

A typical mode profile of light guided at 632.8 nm is shown in Figure 4.8 (b), demonstrating that the produced waveguide supports single-mode guiding with a nearly Gaussian intensity profile. By fitting such intensity distribution, assuming the fundamental mode of a step-index waveguide, a refractive index change on the order of 9.0×10^{-4} was determined, in agreement with other results reported in the literature^{142–145}.

Figure 4.8 - (a) Optical microscopy images (cross-section view) of waveguides produced in the BBS-DyEu. (b) Near-field output profile of the light guided at 632.8 nm with its horizontal and vertical profiles.

Source: Prepared by the author.

Transmission measurements performed in the waveguides (7.8 mm long) show that the overall loss, including coupling and propagation losses, is (7 ± 1) dB at 632.8 nm. By calculating the mismatch coefficients using the method described in Ref.^{146,147}, a propagation loss of (3 ± 1) dB/cm can be determined, which is in agreement with other ones reported by fs-laser written waveguides^{148,149}.

Using the objective lens coupling system previously described¹³¹ light from the HeCd laser was coupled into the waveguide. Figure 4.9 displays the spectra of the light collected at the waveguide output, for excitation at 442 nm (black) and 325 nm (gray). The peaks observed correspond to the emission of Dy^{3+} and Eu^{3+} ions, in agreement with Figure 4.5 (a).

Figure 4.9 - Emission spectra obtained at the waveguide output when coupling light at 442 nm (black line) and 325 nm (gray line).

Source: Prepared by the author.

Figure 4.10 shows the near field output profile of the guided sample emission when light at 325 nm (a) and 442 nm (b) were coupled in the waveguide. The intensity profile observed, in both cases, exhibits a nearly Gaussian distribution. While the 325 nm light is completely absorbed at the beginning of the sample (~ 1.9 mm), for 442 nm the interaction length is on the same order of the fabricated waveguide. For both cases, filters were used to block the excitation wavelength. Therefore, the observed spectrum and profile correspond to the guided emission.

Figure 4.10 - The near-field output profile of the light guided at 325 (a) and 442 nm (b).

Source: Prepared by the author.

4.4. Partial conclusion

The nonlinear refractive index of BBO and BBS-DyEu glasses were characterized by the Z-scan technique and modeled using the BGO empirical method. Both glasses exhibited a nearly constant nonlinear refractive index for the 460 - 1500 nm spectral window, within the experimental error. This behavior was confirmed by the BGO model, which also showed that the oxygen ions present in the glass matrix play a role in its third-order nonlinearities. Furthermore, the n_2 value of BBS-DyEu glass was found to be larger than that of the BBO, indicating that polarizability of the rare-earth ions

contributed to the nonlinear increase. This study represents an advance towards the understanding of the nonlinear properties of borate glasses, mainly the ones related to the third-order susceptibility, thereby meeting the needs for the development of new optical devices based on the optical Kerr effect. The femtosecond laser micromachining enables the fabrication of homogeneous waveguides in barium borate glass co-doped with rare-earth ions (Dy^{3+} and Eu^{3+}), which are relevant for white light generation. The results demonstrate that the waveguides are able to support single-mode guiding with the additional propagation of glass fluorescence when coupling UV light. The waveguide characterization performed with a HeNe laser at 632.8 nm showed that the refractive index change is on the order of 9.0×10^{-4} , able to guide a Gaussian intensity profile with propagation loss of (3 ± 1) dB/cm. Moreover, those waveguides act as active optical elements, being able to guide the emission of Dy^{3+} and Eu^{3+} , resulting in an optical device with broad visible spectrum.

Chapter 5. Third-order optical nonlinearities and fs-laser fabrication of waveguides in CaLiBO glasses doped with Tb³⁺ and Yb³⁺

This chapter describes a study on the linear and nonlinear optical properties in a series of lithium-calcium tetraborate (CaLiBO) glasses doped with two rare-earth ions, Tb³⁺ and Yb³⁺. The nonlinear index of refraction (n_2) was determined in a wide wavelength range (470 - 1500 nm) through the femtosecond Z-scan technique. Such results were modeled by the BGO approach, in which the optical nonlinearity was related to the oxygen present in the glasses. In addition, the molar electronic polarizability evidenced that there is a strong influence of the polarizability of the rare-earth ions in the nonlinear optical properties. Thus, we can infer that the cooperation of oxygens and the polarizability of rare-earth ions are responsible for the nonlinearity present in the investigated vitreous system. It has also been demonstrated the fabrication of three-dimensional waveguides by femtosecond laser pulses. In most waveguides, almost elliptical cross-sections, with diameter of approximately 6 μm and 7.0 mm long, were inscribed into the bulk of the glass by direct laser writing. Such waveguides were shown to support single-mode operation at 632.8 nm, 612 nm, 594 nm, 543 nm, and 405 nm (tunable helium-neon laser system), with propagation loss of (2 ± 1) dB/cm.

5.1. Introduction

Research in nonlinear optics is fundamental for the development of new photonic devices with applications in areas of specific interest, such as optical limiting^{32,150}, all-optical switching^{151–153} and photodetectors^{154,155}. It has been reported a variety of studies evaluating the nonlinear optical properties of silicate¹⁵⁶, germanate¹⁵⁷, phosphate¹⁵⁸, borate¹⁵⁹ and tellurite⁵⁸. Among these kinds of glasses, the borate ones

are known for having low melting point, good thermal stability, and easiness in the manufacturing process^{122,160}. Due to their high hygroscopicity, the incorporation of modifying ions, such as alkaline, alkaline earth, and transition metals, helps to reduce this problem, without changing its properties significantly^{112,161}. Furthermore, they are matrices that have excellent solubility of rare-earth ions because they present a set of borate groups that constitute the three-dimensional random network^{22,162}. In particular, Calibo glasses (calcium-lithium tetraborate glass) activated with rare-earth are considered effective luminescent matrices for energy transfer studies^{163–166}. Rare-earth ions present high luminescence efficiency from the visible to the infrared in a variety of host materials and can be used luminescent materials and as activation center laser^{167–169}. Among the rare-earths, the Tb^{3+} ion is known to emit light blue and green light under UV excitation. Due to this characteristic, it has been reported applications as X-ray scintillators, medium for green solid-state lasers and white light-emitting device^{170–173}. Glassy materials activated by Yb^{3+} ions exhibit wide near infrared (NIR) absorption, being suitable for diode lasers pumping. They present emission between 900 and 980 nm, which makes them favorable to the generation of ultrashort laser pulses, targeting applications that include solid-state lasers, light-emitting diodes, athermal laser, upconversion, and downconversion processes^{174,175}.

Despite the scientific and technological interests on rare-earths doped borate glasses, little attention has been given to their optical nonlinearities. Although, borate glasses generally display the lowest optical nonlinearities among the different classes of glass, in this study we show that the addition of rare-earth ions can improve such properties, favoring their use in nonlinear optical devices. The investigation was carried out with a lithium calcium tetraborate (CaLiBO) glass system, containing ytterbium and terbium ions, which showed to be relevant as down-converter material for the near-

infrared region and applications in solar cells^{176,177}. The nonlinear refraction spectra of the glass with different Tb^{3+} content were investigated in a wide wavelength range (470 - 1500 nm) at femtosecond regime. Experimental data obtained through the Z-scan technique were further modeled by BGO approach, in which the optical nonlinearity is related to the oxygen ions present in the glasses. The molar electronic polarizability given by the Lorentz-Lorenz relation showed that there is a strong influence of the polarizability of the rare-earth ions on the nonlinear optical properties. We infer that the cooperation of both oxygen ions and the polarizability of rare-earth ions are responsible for the nonlinearity present in this vitreous system.

On the other hand, femtosecond laser writing has already proven to be an important tool for processing glassy materials as waveguides with broad emission in the visible spectrum, as demonstrated in barium borate glass containing dysprosium (Dy^{3+}) and europium ions (Eu^{3+})¹⁷⁸. The combination of Tb^{3+} and Yb^{3+} ions can result in energy transfer, which is promising for optoelectronic devices. Although the co-doping of Tb^{3+} and Yb^{3+} is interesting in luminescent glasses, its incorporation in borate glasses for the development of optical devices is still unexplored.

5.2. Materials and methods

The glasses studied here have the composition (99% - x) CaLiBO + 1% Yb_2O_3 + x% Tb_4O_7 with x = 0.1; 1.0 and 2.0 (mol %) and were synthesized by melt-quenching technique, using platinum crucible and electric furnace open to the atmosphere. These samples were prepared at the Group of Nanomaterials and Advanced Materials (NaCA) of the São Carlos Institute of Physics (IFSC - USP) by Dr. Juliana Mara Pinto de Almeida under the supervision of Prof. Dr. Antonio Carlos Hernandez. High purity B_2O_3 (Alfa Aesar 97.5%), Li_2CO_3 (Carlo Erba 99%), CaCO_3 (Alfa Aesar 99.5%), Tb_4O_7

(Alfa Aesar 99.9%) and Yb_2O_3 (Alfa Aesar 99.9 %) were used as raw materials. Initially, CaLiBO glass matrix, composed by $60\%\text{B}_2\text{O}_3 + 30\%\text{CaO} + 10\%\text{Li}_2\text{O}$ (mol%) (CaLiBO), was prepared. Its reagents were heated at $850\text{ }^\circ\text{C}$ for 40 min to allow decarbonation. The temperature was slowly increased to $1100\text{ }^\circ\text{C}$, and after 2 h the melt was quenched into a stainless-steel mold at room temperature. Terbium and Ytterbium codoped glasses were obtained by melting of the CaLiBO matrix together with rare-earth oxides at $1100\text{--}1300\text{ }^\circ\text{C}$ during 30-100 min, depending on the composition. The samples were quenched at the same conditions that CaLiBO matrix and annealing at $590\text{ }^\circ\text{C}$ for 9 h. Polished flat samples with $\sim 1.4\text{ mm}$ of thickness, free of inclusions or cords were used for the optical measurements.

The absorption spectrum of glasses was measured in the range of $200\text{--}1200\text{ nm}$ with a UV-vis spectrophotometer. The emission spectrum exciting at 405 nm was measured in two equipments: in the range of $430\text{--}700\text{ nm}$ it was determined using a Fluorescence spectrophotometer and from 900 nm to 1150 nm it was measured using a Horiba Fluorolog spectrofluorimeter with a Hamamatsu photomultiplier. The excitation spectrum when monitored at 977 nm in the range of $300\text{--}550\text{ nm}$ was collected by a photodiode detector using the Horiba Fluorolog spectrofluorimeter.

The nonlinear refractive index (n_2) and the two-photon absorption (β) spectra were analyzed using closed- and open-aperture Z-scan technique, respectively⁷². An optical parametric amplifier (OPA) was employed as excitation light source and provides 120-fs pulses from $470\text{ to }1500\text{ nm}$. The OPA is pumped by a Ti:Sapphire laser amplified system (*CPA 2001*, *Clark MXR*[®]) at 775 nm with 120-fs pulses at 1 kHz repetition rate. Fused silica has been used as reference material, whose nonlinear refractive index was found to be approximately $2.1 \times 10^{-20}\text{ m}^2/\text{W}$ from visible to infrared, which is in accordance with the literature¹³⁰. The experimental error associated with the n_2

determination is 20 %, being related to the pulse intensity fluctuation, and experimental error on the determination of pulse duration and beam waist. A Pulfrich refractometer (*Carl Zeiss Jena Pulfrich Refractometer PR2®*) using Hg lamps as spectral sources and m-line technique were employed to measure the linear refractive index.

Femtosecond laser writing was performed with a Ti:sapphire laser oscillator centered at 800 nm, with a maximum energy of 100 nJ and operating at a repetition rate of 5 MHz, delivering 50-fs pulses throughout the length of the sample. Femtosecond laser pulses were focused by a microscope objective (NA = 0.65) within the sample, while it was moved perpendicularly to the laser beam by a translational xyz stage moved at 10 and 200 $\mu\text{m/s}$. The guiding properties of the produced waveguides were determined by using an objective-lens-based coupling system; standard (NA = 0.40 and 0.17) and UV-coated microscopy objectives (NA = 0.40 and 0.50) were used to coupled light from multi-line tunable helium-neon lasers (model LSTP-1010) (632.8, 612, 594 and 543 nm) and diode laser (405 nm), respectively. The guided modes were observed with the aid of a CCD camera. Waveguide losses were determined by measuring the input and output laser power, considering the transmission of all optical components in the system¹³¹. The characterization of the produced waveguides was characterized using a Carl Zeiss model LSM 700 microscope that has a camera attached that allows the monitoring of the images in real time.

5.3. Results and discussion

Absorption spectra of the samples are shown in Figure 5.1. CaLiBO presents a wide transmission window, from 350 nm to $\lambda > 1100$ nm. Besides that, it is possible to observe absorption peaks that are characteristic of the Yb^{3+} and Tb^{3+} ions in the doped

samples. The transitions of Tb^{3+} ion are located at 317 nm ($^7\text{F}_6 \rightarrow ^5\text{D}_1$); 338 nm ($^7\text{F}_6 \rightarrow ^5\text{D}_0$); 350 nm ($^7\text{F}_6 \rightarrow ^5\text{L}_9$); 368 nm ($^7\text{F}_6 \rightarrow ^5\text{L}_{10}$); 377 nm ($^7\text{F}_6 \rightarrow ^5\text{G}_6 + ^5\text{D}_3$) and 484 nm ($^7\text{F}_6 \rightarrow ^5\text{D}_4$)^{179,180}, and the transition at 975 nm ($^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$) is due to Yb^{3+} ion^{181,182}.

Figure 5.1 - Linear absorption coefficient spectra of CaLiBO (a), $x = 0.1$ (b), $x = 1.0$ (c) and $x = 2.0$ (d) samples. They were vertically shifted for better visualization of the Yb^{3+} and Tb^{3+} absorption peaks.

Source: Prepared by the author.

The linear refractive index (n_0) is an important optical characteristic of the glass which is related to the electronic polarizability¹⁸³, as well as the nonlinear index of refraction. In Figure 5.2, we present the linear refractive index values measured at 404.7, 435.8, 546.1, 632.8, and 1538 nm (symbols) for all samples. These

experimental values were fitted using the bipolar Sellmeier (Eq. 5.1) dispersion equation¹³³,

$$n_0^2 = \sqrt{A + \frac{B\lambda^2}{\lambda^2 - C} + \frac{D\lambda^2}{\lambda^2 - E}} \quad (5.1)$$

where A , B , C , D , and E are Sellmeier's coefficients and λ is the wavelength in micrometers, in order to obtain the spectra of the linear refractive index (continuous line). The Sellmeier coefficients obtained through the fitting are presented in Table 5.1.

Figure 5.2 - Linear refractive index of CaLiBO (a), $x = 0.1$ (b), $x = 1.0$ (c) and $x = 2.0$ (d) glasses. The solid lines represent the fitting with Sellmeier equation (Eq. 5.1), while symbols are the experimental data with error of the order of 1×10^{-4} .

Source: Prepared by the author.

Table 5.2 - Sellmeier coefficients for CaLiBO glasses obtained from the fitting shown in Figure 5.2.

Samples glass	R-squared	A	B	C	D	E
CaLiBO	0.97	2.27 ± 0.06	0.24 ± 0.02	0.056 ± 0.008	0.6 ± 0.6	80 ± 30
x = 0.1	0.99	2.43 ± 0.01	0.123 ± 0.007	0.085 ± 0.005	0.9 ± 0.5	100 ± 20
x = 1.0	0.98	2.49 ± 0.09	0.11 ± 0.08	0.09 ± 0.03	1.2 ± 0.3	100 ± 10
x = 2.0	0.98	2.56 ± 0.02	0.095 ± 0.008	0.093 ± 0.007	1.3 ± 0.5	100 ± 20

Source: Prepared by the author.

Figure 5.3 shows typical closed-aperture (refractive) Z-scan signatures for CaLiBo (a), x = 0.1 (b), x = 1.0 (c), and x = 2.0 (d), at 950, 700, 750, and 600 nm, respectively. From Z-scan curves, similar to the ones displayed in Figure 5.3, obtained at various wavelengths, we are able to obtain the dispersion of n_2 (nonlinear refraction spectrum).

Figure 5.3 - Typical Z-signature measured for (a) CaLiBO at 950 nm, (b) $x = 0.1$ at 700 nm, (c) $x = 1.0$ at 750 nm and (d) $x = 2.0$ at 600 nm. The line is the adjustment from which n_2 is extracted.

Source: Prepared by the author.

The spectra of n_2 (nonlinear refraction spectrum) for the samples CaLiBO, $x = 0.1$, $x = 1.0$, and $x = 2.0$, obtained from closed-aperture (refractive) Z-scan technique are shown in Figure 5.4 (a), (b), (c) and (d), respectively. The nonlinear refraction spectra show a nearly constant behavior as a function of the wavelength, within the experimental error. The mean values of n_2 obtained for CaLiBO, $x = 0.1$, $x = 1.0$, and $x = 2.0$ are 4.2, 4.5, 4.6 and $4.7 \times 10^{-20} \text{ m}^2/\text{W}$, respectively. Such values are about twice higher than the ones reported for fused silica¹³⁰. In addition, for open-aperture Z-scan measurements, no nonlinear absorption signal was observed, indicating the absence of two-photon absorption in the wavelength range analyzed.

Figure 5.4 - Spectra of the nonlinear refractive index (n_2) of CaLiBO (a), $x = 0.1$ (b), $x = 1.0$ (c) and $x = 2.0$ (d). The symbols correspond to the experimental data and solid lines represent the fit obtained with the BGO model, with parameters given in the text.

Source: Prepared by the author.

The nonlinear refraction spectra displayed in Figure 5.4 were modeled using the BGO (Boling, Glass, and Owyong) approach¹³⁶, which is a semi-empirical model based on a classical nonlinear oscillator. It assumes that the second hyperpolarizability is proportional to the square of the linear polarizability, and considers that the incident light frequency is far from resonance ($\omega \ll \omega_0$). According to this model, the nonlinear refractive index, in SI (m^2/W), is written as¹³⁶,

$$n_{2(BGO)} = \frac{5(n_0^2 + 2)^2(n_0^2 - 1)^2(gs)}{6n_0^2 c \hbar \omega_0 (Ns)} \quad (5.2)$$

in which g is a dimensionless anharmonicity parameter, s is the effective oscillator strength, c is the speed light, $2\pi\hbar$ is the Planck's constant, N is the composition-dependent ion density, and n_0 is the linear refractive index of light at the wavelength λ . The product Ns , as well as the resonance frequency ω_0 can be obtained by using,

$$\frac{4\pi}{3} \frac{(n_0^2 + 2)}{2(n_0^2 - 1)} = \frac{m(\omega_0^2 - \omega^2)}{e^2(Ns)} \quad (5.3)$$

in which m and e are the mass and electron charge, respectively. By evaluating Eq. 5.3 at two frequencies ω , at which the linear index of refraction n_0 is known (through the results in Fig. 5.2), one are able to determine the parameters Ns and ω_0 for each sample. Furthermore, the dispersion of n_0 can be included in the BGO model (Eq. 5.2) using the Sellmeier equation (Eq. 5.1), with the corresponding coefficients displayed in Table 5.1.

The effective oscillator strength, s , was estimated from the ratio between the density of nonlinear oscillators (Ns) and the density of oxygen ions in the samples (N_{ox}),

considering that oxygen plays the major role in the nonlinearities of oxide glasses³⁵. From such procedures, we determined $s = 2$. Therefore, the only free parameter to be obtained by fitting the experimental data with the BGO model is the anharmonicity parameter g .

The red line along the data points in Figure 5.4 corresponds to the fitting obtained with the BGO model, according to the procedure described previously, from which the parameter g was determined as being (0.82 ± 0.04) , (0.84 ± 0.04) , (0.85 ± 0.04) , and (0.86 ± 0.05) for CaLiBO, $x = 0.1$, $x = 1.0$ and $x = 2.0$, respectively. As it can be seen, there is a good agreement between the experimental data and the model. The mean nonlinear refractive index values obtained from the BGO model to CaLiBO, $x = 0.1$, $x = 1.0$ and $x = 2.0$ are 4.2 , 4.5 , 4.6 and $4.7 \times 10^{-20} \text{ m}^2/\text{W}$ are in good agreement with the experimental ones. Therefore, according to the BGO model, the major contribution for the nonlinear index of refraction of the samples studied here are related to the glass matrix, whose main electronic transitions are located in the UV region of the spectrum, reason why an almost flat behavior is observed for the n_2 dispersion, as seen in Figure 5.4.

Studies on the n_2 of SAL ($\text{SiO}_2\text{-Al}_2\text{O}_3\text{-La}_2\text{O}_3$) glasses were investigated as a function of the content of the earth-rare La^{3+} ion by using the Z-scan technique. In such work, it was observed an increase of n_2 with the concentration of the rare-earth, which is also related to the oxygen ions¹⁸⁴. Similarly, the nonlinear refractive index of zinc borotellurite glass was studied for different concentrations of Gd^{3+} . The authors observed an increase in n_2 with the rare-earth ion concentration, which was attributed to Gd^{3+} ion inducing high polarizability of the glass network⁵⁹.

The electronic polarizability is another important property that influences optical nonlinearities¹⁸⁵. The electronic molar polarizability in ($\text{\AA}^3$) is given by

$$\alpha_M = \left(\frac{3}{4\pi N_A} \right) R_M \quad (5.4)$$

in which N_A is Avogadro's number, and R_M is the molar refraction value, given by the Lorentz -Lorenz equation as^{186–188}:

$$R_M = \left[\frac{n_0^2 - 1}{n_0^2 + 2} \right] \frac{M}{\rho} \quad (5.5)$$

where n_0 is the linear refractive index, M is the molecular weight, and ρ is the density (see Table 5.2).

Table 5.3 - Density (ρ), molecular weight (M) and molar electronic polarizability (α_M) for the CaLiBO glasses.

Samples glass	M(g/mol)	$\rho(\text{g/cm}^3)$	$\alpha_M(\text{\AA}^3)$
CaLiBO	61.6	2.5743 ± 0.0009	3.27 ± 0.07
x = 0.1	65.6	2.732 ± 0.002	3.32 ± 0.07
x = 1.0	72.3	2.9269 ± 0.0008	3.49 ± 0.08
x = 2.0	79.8	3.131 ± 0.002	3.65 ± 0.08

Source: Prepared by the author.

The values for the molar electronic polarizability determined using Eq. 5.4 are shown in Table 5.2. In Figure 5.5, it can be observed that the mean values of the nonlinear refractive index display a clear increasing tendency, with the molar electronic polarizability, which in turn is related to the increase in the concentration of Tb^{3+} ion.

Figure 5.5 - Nonlinear refractive index as a function of the electronic molar polarizability, evidencing that the increase depends on the addition of the rare-earth ions.

Source: Prepared by the author.

The increase of the electronic polarizability values is probably due to the presence of Yb^{3+} ($0.86 \text{ \AA}^3$) ions, as well as the addition and increase of the Tb^{3+} ($1.04 \text{ \AA}^3$) ion concentration, whose polarizabilities are greater than B^{3+} ($0.003 \text{ \AA}^3$), Ca^{2+} ($0.47 \text{ \AA}^3$) and Li^+ ($0.024 \text{ \AA}^3$) ions^{189,190}. The same behavior has been observed in $\text{BiCl}_3\text{-Li}_2\text{O-B}_2\text{O}_3\text{-Er}_2\text{O}_3$ glasses, in which the polarizability presented a gradual increase with the increase of the Er^{3+} content⁴⁴. A study of the $\text{CaO-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-CaF}_2$ system doped with Nd^{3+} revealed that the electronic polarizability increased as a function of the rare-earth concentration, which was attributed to an increase of nonbonding oxygen caused by the rare-earth addition since these are more polarizable than the oxygens that are connected¹⁹¹. The comparison of the reported observations are in agreement with our

results, which demonstrated an increase in both, the nonlinear refractive index and the electronic polarizability values for glasses containing rare-earth ions. Therefore, our results indicate a cooperative effect between the glass matrix (major effect) and the electronic polarizability of the rare-earth contributions to the optical nonlinearity of CaLiBO glasses.

Figure 5.6 (a) shows the emission spectrum of the CaLiBO system samples, excited at 405 nm. The emission bands belonging to the Tb^{3+} ion are at 492 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_6$), 547 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_5$), 588 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_4$) and 624 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_3$). The Yb^{3+} ion presents emission bands at 977 nm ($^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$). Glassy systems co-doped with Tb^{3+} and Yb^{3+} ions are known to support energy transfer process of down-conversion^{50,192–194}. This process can be verified through the excitation spectrum shown in Figure 5.6 (b). As can be seen, the excitation spectrum shows the absorption structure of the Tb^{3+} ion, which can be seen in Figure 5.1, when monitoring the Yb^{3+} ion emission at 977 nm. This result indicates downconversion process from Tb^{3+} to Yb^{3+} 50.

Figure 5.6 - (a) Emission spectra of the CaLiBO (black curve), $x = 0.1$ (dark gray curve), $x = 1.0$ (gray curve), and $x = 2.0$ (light gray curve) excited at 405 nm. (b) Excitation spectrum of the sample monitored at 977 nm.

Source: Prepared by the author.

For the production of waveguides, an energy study was initially performed on the sample surface to determine the threshold energy (E_{th}). This study was performed by varying the energy and scanning speed. Figure 5.7 shows the dependence of the squared of ablation line width (L^2) changes with the pulse energy (log-scale). The line width values in all samples demonstrated a slight increase with pulse energy, varying from approximately 0.8 – 2.1 mm when the pulse energy increases from 46 to 62 nJ, for the scanning speeds used (10, 50 and 200 $\mu\text{m/s}$). Results were adjusted using the model presented in Ref.¹⁹⁵, and the threshold energy (E_{th}) values were obtained for each sample at the three mentioned speeds. The threshold energy value obtained are: (41.0 ± 2.0) nJ, (37.0 ± 2.0) nJ, (36.0 ± 7.0) nJ and (32.0 ± 4.0) nJ for CaLiBO, $x = 0.1$, $x = 1.0$ and $x = 2.0$, respectively.

Figure 5.7 - Squared line width as a function of the pulse energy (E-log scale) for CaLiBO (a), $x = 0.1$ (b), $x = 1.0$ (c), and $x = 2.0$ (d) for three translation speeds 10 $\mu\text{m/s}$ (black circles), 50 $\mu\text{m/s}$ (red circles), and 200 $\mu\text{m/s}$ (blue circles).

Source: Prepared by the author.

Figure 5.8 shows optical microscopy images of the top (b) and cross-sectional (a) views of waveguides produced by fs-laser micromachining in the CaLiBO system. The waveguides are 7.0-mm long and were produced approximately 100 μm below the sample surface. For the production of waveguides with good optical quality and homogeneity, the energies and scanning speeds for the samples were respectively, CaLiBO – 52 nJ and 10 $\mu\text{m/s}$, $x = 0.1$ – 48 nJ and 200 $\mu\text{m/s}$, $x = 1.0$ and $x = 2.0$ where the same energy value and scan speed of 52 nJ and 200 $\mu\text{m/s}$. The images show that the waveguides are homogeneous along their length and the cross-sections have a slightly elliptical majority, measuring approximately 6 μm .

CaLiBo

$x = 0.1$

$x = 1.0$

$x = 2.0$

Figure 5.8 - Optical microscopy images of the cross-section (a) of the input face of each sample and top view (b) of the produced waveguides.

Source: Prepared by the author.

Typical mode profiles of light guided at 632.8, 612, 594 and 543 nm are shown in Figure 5.9, demonstrating that these waveguides support the single-mode guiding with a nearly Gaussian intensity profile. By adjusting such intensity distribution, assuming the fundamental mode of a step-index waveguide, a refractive index change on the order of 1.0×10^{-3} was determined, according to other results reported in the literature^{62,196}.

Figure 5.9 - Near-field output profile of the light guided at 632.8 nm, 612 nm, 594 nm and 543 nm for rare-earth ion-doped samples.

Source: Prepared by the author.

Transmission measurements performed in the waveguides (7.0 mm long) show that the overall loss, including coupling and propagation losses at 632.8 nm is (5 ± 1) dB for the three samples which contains rare-earths. By calculating the mismatch coefficients using the method described in Ref.^{146,147}, a propagation loss of (3 ± 1) dB/cm can be determined, which is in agreement with other ones reported by fs-laser written waveguides^{148,149}. A fine-tuning of the fabrication parameters, such as pulse energy, repetition rate, and focalization can lead to an improvement in the waveguide propagation loss.

Employing the objective lens coupling system described in Chapter 3, the light from a laser diode with a wavelength of 405 nm was coupled into the waveguide for the

three samples. Figure 5.10 shows the intensity profile distribution. However, it was not possible to collect the guided emission spectra at the waveguide output. One possible explanation for that may be the low intensity of the emission when excited/coupled at this wavelength, and/or the intensity of the diode laser that was not enough to allow the observation of such emissions.

Figure 5.10 - Near-field output profile of the light guided at 405 nm for samples $x = 0.1$, $x = 1.0$ and $x = 2.0$.

Source: Prepared by the author.

Typical guided light mode profiles at 632.8 and 405 nm are shown in Figure 5.11 for the CaLiBO sample. These profiles also demonstrate that these waveguides support single-mode guiding with an approximately Gaussian intensity profile. By adjusting this intensity distribution, assuming the fundamental mode of a step-index waveguide, a refractive index change was determined in the order of 1.0×10^{-3} .

Figure 5.11 - Near-field output profile of the light guided at 632.8 nm (a) and 405 nm (b) for CaLiBO.

Source: Prepared by the author.

Transmission measurements were also performed on the waveguides (7.0 mm long) of the CaLiBO sample and showed that the total loss, including coupling and propagation losses at 632.8 nm was (5 ± 1) dB. By calculating the mismatch coefficients, a propagation loss of (2 ± 1) dB/cm can be determined.

5.4. Partial conclusion

The nonlinear refractive index of CaLiBO glasses containing different concentrations of rare-earth ions was characterized by the Z-scan technique and interpreted using the empirical BGO model. The addition of Tb^{3+} and Yb^{3+} ions do not affect the spectral behavior of the nonlinear refractive index, which exhibited a nearly constant value for the spectral window between 470 - 1500 nm, within the experimental error, for all investigated samples. This behavior was confirmed by the BGO model, which also showed that the oxygen ions present in the glass matrix play a role in its third-order nonlinearities. Nonetheless, the n_2 of CaLiBO glasses increased with the addition of Tb^{3+} and Yb^{3+} , indicating that the combination of oxygen ions present in the

matrix and the polarizability of the rare-earth ions contributed to the increase of the nonlinear response. This study presents the progress on the understanding of the nonlinear properties of borate glass and the influence that rare-earth ions have on these properties, especially those related to third-order susceptibility, contributing to the development of new optical devices.

By using femtosecond laser micromachining, we have been able to demonstrate the fabrication of homogeneous waveguides in the CaLiBO system doped with Tb^{3+} and Yb^{3+} ions. The results showed that the waveguides are capable of supporting simple guiding mode when coupled at visible wavelengths. The characterization of waveguides at 632.8 nm showed that the refractive index change is of the order of 1.0×10^{-3} , capable of guiding a Gaussian intensity profile with loss varying from (2 ± 1) dB/cm to (3 ± 1) dB/cm for CaLiBO glasses. In addition, these waveguides were unable to guide Tb^{3+} and Yb^{3+} emission probably due to low emission intensity and insufficient laser intensity.

Chapter 6. Conclusions and perspectives

The main objective of this dissertation was to demonstrate the use of the femtosecond laser as an instrument in the characterization of rare-earth doped glassy materials. This study focused on investigating the influence of rare-earths on the nonlinear optical properties and on the production of waveguides.

The third-order optical properties were analyzed in two glass systems: the first one are the BBO and the BBS-DyEu (the last doped with the rare-earth ions Dy^{3+} and Eu^{3+}), and the second is the CaLiBO system that presents Tb^{3+} and Yb^{3+} ions as dopants. The nonlinear refractive index (n_2) showed almost constant values around $4.5 \times 10^{-20} \text{ m}^2/\text{W}$ for the visible and infrared regions. This behavior was modeled and confirmed by the BGO approach, which revealed that the main contribution to the nonlinear refractive index is related to the vitreous matrix. Samples doped with the rare-earth ions showed higher n_2 values when compared to samples without these doping ions, indicating a cooperative effect of the glass matrix and the electronic polarizability from the rare-earths to the optical nonlinearity of the glasses.

The ability to produce waveguides using one-step laser processing has been demonstrated in rare-earth ion doped glass samples. For the BBS-Dy sample, waveguides were produced with 32 nJ pulse energy, homogeneous along their length and with slightly elliptical cross-section operating in the single-mode regime. Propagation losses were determined to the order of $(3 \pm 1) \text{ dB/cm}$ at 632.8 nm. When coupled with UV laser light, they were able to operate in single-mode guided emission of Dy^{3+} and Eu^{3+} ions, being relevant in the generation of white light as an optical device with a wide visible emission. In the CaLiBO set, the waveguides were produced with pulse energy above the ablation threshold, presented full-length homogeneity and elliptical and circular cross-sectional dimensions of $\sim 6 \mu\text{m}$, operating in a single mode

at 632.8 nm. Propagation losses at this wavelength were (2 ± 1) dB/cm and (3 ± 1) dB/cm for the undoped sample and the Tb^{3+} and Yb^{3+} doped samples, respectively. Coupling with UV laser light has demonstrated single-mode guidance; however, it was not possible to observe rare-earth emissions that may be due to the low intensity of ion emissions or laser intensity.

The works described here demonstrate the potential of borate glasses as a nonlinear optical material. Moreover, the addition of rare-earth ions helps to improve the nonlinearity, as described in this study. However, it is important to mention that the investigation of optical nonlinearities was observed in samples that have common concentrations of rare-earth ions. Therefore, new designs may be suggested to optimize optical nonlinearities as a function of the amount of rare-earth ion concentration in the matrix. Additional studies can be proposed regarding the dependence of the effect of n_2 with other types of rare-earth ions, and the combination of rare-earth and transition metals ion, aiming to investigate the influence on the increase of the optical nonlinearity. Other issues could be raised in the investigation of other types of glasses matrices containing rare-earth ions for nonlinear optical characterization, as well as laser microstructuring for photonic devices.

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