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Nanopartículas em vidros óxidos e calcogenetos: não
linearidades ópticas e fabricação de guia de onda com
pulsos de femtossegundos

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pulsos de femtossegundos

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Prof. Dr. Cleber Renato Mendonça

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*To the memory of my grandpa, Mario De Grande,
who I admire for the kindness...
who would be very proud of me...*

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ABSTRACT

ALMEIDA, J. M. P. **Nanoparticles in oxide and chalcogenide glasses: optical nonlinearities and waveguide fabrication by femtosecond laser pulses.** 2015. 107p. Thesis (Doctor of Science) – São Carlos Engineering School, University of São Paulo, 2015.

Femtosecond laser has been an essential tool for nonlinear optics and materials processing at micrometer scale, in which chalcogenide and heavy metal oxide glasses have received special attention not only for their high third-order optical nonlinearities but also due to their transparency up to the infrared regions. Although metallic nanoparticles are expected to improve the optical properties of glasses, there are not enough experimental researches about their influence on the nonlinear refractive index (n_2) and nonlinear absorption coefficient (β), moreover at femtosecond regime. Based on the scientific and technological interests on highly nonlinear glasses, the goal of this thesis was to apply femtosecond laser pulses in two main domains: (i) at the basis of fundamental science, to study the effect of metallic nanoparticles in the third-order nonlinear optical properties of glasses; and (ii) at the field of applied science, aiming the development of photonic devices, performed by the fabrication of 3D optical waveguides containing metallic nanoparticles. This aim was achieved through the techniques of z-scan and femtosecond laser micromachining, which provided the nonlinear optical characterization and waveguides development, respectively. First, we analyzed the third-order nonlinear optical properties of the $\text{GeO}_2\text{-Bi}_2\text{O}_3$ glass containing gold nanoparticles, which promoted saturation of the absorption in the region of the surface plasmon resonance band. On the other hand, these gold nanoparticles did not affect the n_2 that kept constant in the wavelength range of 480 - 1500 nm. The same features were investigated for a $\text{Pb}_2\text{P}_2\text{O}_7\text{-WO}_3$ matrix doped with copper nanoparticles. In contrast to the gold doped ones, these samples showed a slight enhancement of the nonlinear refractive index when the energy of the excitation approaches the surface plasmon band. We also found out that the $\text{Pb}_2\text{P}_2\text{O}_7\text{-WO}_3$ matrix is a good host to grow silver nanoparticles by fs-laser micromachining. Similarly, copper nanoparticles were produced in a borosilicate glass using single-step laser processing. The explanation for metallic nanoparticle formation is addressed in this thesis, as well as, its application in waveguides. Thus, we demonstrated the functionality of optical waveguides containing Cu^0 or Ag^0 nanoparticles. Still based on the technological interests on glasses doped with

nanoparticles, we showed a single-step synthesis of silver sulfide nanoparticles in chalcogenide glass, which was carried in partnership with researches at Princeton University. The materials investigated in this PhD work are of great importance for photonics, in which the synthesis of nanoparticles, fabrication of waveguides and nonlinear optical characterization have been performed.

Resumo

ALMEIDA, J. M. P. Nanopartículas em vidros óxidos e calcogenetos: não linearidades ópticas e fabricação de guia de onda com laser de femtossegundos. 2015. 107p. Tese (Doutorado em Ciências) – Escola de Engenharia de São Carlos, Universidade de São Paulo, 2015.

O laser de femtossegundos tem sido uma ferramenta essencial tanto para a óptica não-linear quanto para o processamento de materiais na escala micrométrica, na qual os vidros calcogenetos e óxidos de metais pesados têm recebido atenção especial, não apenas pelas suas elevadas não-linearidades ópticas de terceira ordem, mas também devido à sua transparência até o infravermelho. Embora seja esperado que nanopartículas metálicas melhorem as propriedades ópticas dos vidros, não existe investigações experimentais suficientes sobre a sua influência no índice de refração não linear (n_2) e no coeficiente de absorção linear (β), sobretudo no regime de femtossegundos. Com base nos interesses científicos e tecnológicos de vidros altamente não-lineares, o objetivo deste trabalho foi aplicar pulsos laser de femtossegundos em dois domínios principais: (i) na campo da ciência fundamental, para estudar o efeito de nanopartículas metálicas nas propriedades ópticas não lineares de terceira ordem destes materiais; e (ii) no domínio da ciência aplicada, visando o desenvolvimento de dispositivos fotônicos, realizado pelo fabricação de guias de onda tridimensionais contendo nanopartículas metálicas. Este objetivo foi alcançado através das técnicas de varredura-z e microfabricação com laser de femtossegundos, que proporcionaram a caracterização óptica não-linear e o desenvolvimento de guias de onda, respectivamente. Primeiramente, foram investigadas as propriedades ópticas não-lineares de terceira ordem do vidro $\text{GeO}_2\text{-Bi}_2\text{O}_3$ contendo nanopartículas de ouro, as quais promoveram saturação da absorção na região da banda de ressonância de plásmon. Por outro lado, essas nanopartículas não afetaram o n_2 , que se manteve constante no intervalo de comprimento de onda 480 - 1500 nm. As mesmas características foram investigadas para uma matriz $\text{Pb}_2\text{P}_2\text{O}_7\text{-WO}_3$ dopada com nanopartículas de cobre. Em contraste com os vidros dopados com ouro, estas amostras apresentaram um ligeiro aumento do índice de refração não linear quando a energia de excitação está próxima da banda de ressonância de plásmon. Observou-se ainda que a matriz $\text{Pb}_2\text{P}_2\text{O}_7\text{-WO}_3$ é ideal para a obtenção de nanopartículas de prata através da microfabricação com laser de femtossegundos. Similarmente, nanopartículas de cobre

foram produzidas em vidro de borosilicato usando somente uma varredura a laser. A explicação para a formação de nanopartículas metálicas é abordada nesta tese, bem como sua aplicação em guias de onda. Deste modo, demonstrou-se a funcionalidade de guias de onda ópticos compostos por nanopartículas de Cu^0 e Ag^0 . Ainda com base nos interesses tecnológicos em vidros dopados com nanopartículas, demonstrou-se uma síntese de nanopartículas de sulfeto de prata em vidro calcogeneto usando o processamento de única etapa, realizada em parceria com pesquisadores da Universidade de Princeton. Os materiais investigados neste trabalho de doutorado são de grande importância para aplicações em fotônica, em que a síntese de nanopartículas, a fabricação de guias de onda e a caracterização óptica não-linear foram realizadas.

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1. Introduction

Amorphous materials do not present long-range order at atomic level, resulting in distinct properties when compared to a crystal of the same composition. Considering the solid state, amorphous networks that present the glass transition phenomenon are classified as glass. According to Shelby, “any material, inorganic, organic, or metallic, formed by any technique, which exhibits glass transformation behavior is a glass”¹. Depending on the chemical elements that act as network former, glassy materials are usually classified as oxide, halide or chalcogenide, besides the organic and metallic ones not addressed in this thesis. Each one owns peculiar features, which can be further modified by the addition of modifier compounds, enabling the preparation of a wide variety of multi-component glasses with optimized properties. The interest on glasses is further intensified by the ability to prepare it in different shapes and sizes, from bulk materials to fibers and thin films, using several methods, such as, melt-quenching, sol-gel and chemical vapor deposition². Despite these attributes, certainly, one of the most relevant features of glasses lies on their optical properties, which makes them important for many applications.

Due to their transparency in a broad spectral range, glasses are useful as passive elements in optical components, including lenses, prisms, mirror substrates, and moreover in optical fibers, that have been crucial for the development of telecommunication systems. Additionally, active functions can also be achieved when, for instance, glasses are doped with rare-earth elements, working as gain media for lasers or light amplifiers³. With exception of lasing action, in all these functionalities glasses are submitted to ordinary levels of light intensity, being therefore in the linear optics regime. However, the development of ultra-short laser pulses allowed to exposed materials to intensities never experimented before, bringing new issues to optical phenomena, in which the branch of nonlinear optics has emerged.

Among the glasses for nonlinear optical purposes, the chalcogenides own the most notable magnitudes on account of the chemical nature of their constituent

elements that are easily polarizable in the presence of intense electromagnetic field. Besides the hyperpolarizability of chalcogenides, they are also interesting because of their photosensitivity and transparency in the mid-infrared region ⁴. Typically, chalcogenide glasses (ChGs) transmit beyond 11 – 20 μm , present high linear index of refraction, $n \approx 2\text{-}3$, and consequently elevated nonlinear index of refraction (n_2), which can be up to thousand times the one of silica ⁴.

In order to ensure those properties, the synthesis of ChGs must be performed in inert atmosphere, once liquid and vapor phases are very susceptible to oxidation and hydrolysis. Thus, the preparation of bulk ChGs is more complex when compared to oxide glasses because the melting is usually carried out inside a silica ampoule sealed under vacuum, and careful must be taken to avoid explosions due to the high vapor pressure ⁵. An alternative to overcoming this issue is the use of solution-based methods, which involve the dissolution of raw materials in amine solvents and the subsequent processing as a liquid through drop cast, spin coat, print or mold cast ⁶. These common procedures result in thin films that have attracted special attention due to the demand of smaller sizes required for all-optical technologies ^{6; 7}. Also, many of the photoinduced effects are more pronounced in thin films than in bulk glasses ⁴.

Although thin films of ChGs are interesting for technological applications, the use of bulk glass is still predominant, mainly for fabrication of tridimensional (3D) devices. Similarly to chalcogenide, heavy metal oxide (HMO) glasses are characterized by high density, high refractive index, low glass transition temperature and excellent infrared transmission ⁸. Nevertheless they have the advantage to be easily prepared by several methods in open atmosphere. At first, oxide glasses have low optical nonlinearities. Nonetheless, their propensity to host large amount of heavy metal elements without reduction of glass forming ability has enable to prepare highly polarizable matrixes, suitable for nonlinear optics. HMO glasses usually contain over than 50 cation percent (cat. %) of lead and/or bismuth ⁸, but the addition of WO_3 and Sb_2O_3 have been the subject of recent researches ^{9; 10; 11}.

Particularly, the presence of lead oxide have been investigated in tellurite, germinate, silicate and borate glass ^{12; 13; 14; 15}. Lead silicate glasses were used on the fabrication of highly nonlinear and low loss fibers ¹³. Studies on binary systems $\text{TeO}_2\text{-PbO}$ and $\text{B}_2\text{O}_3\text{-PbO}$ have shown an enhancement of the third-order optical nonlinearities, with the increased of lead content due to the hyperpolarizability of Pb^{+2} ions ^{12; 14}. In the

same way, bismuth-based glasses have been shown to display high optical nonlinearities, which can achieve values comparable to chalcogenide glasses¹⁶. Comparing Bi^{3+} to Pb^{2+} ions, both have the same electronic distribution, but it has been reported that bismuth leads to higher nonlinear optical properties due to its lower optical band gap, that favors the resonant enhancement effect^{16; 17}. On the other hand, because lead oxide also acts as a glass forming material, it can be employed in higher concentrations than bismuth-based glasses. Given such features, it is usual the association of lead and bismuth in the same matrix^{8; 17}, which is able to support n_2 50-fold higher than silica glass¹⁸.

In addition to heavy metal oxides, a further way to improve the nonlinear optical response of glassy materials is by the incorporation of nanostructures, such as metallic nanoparticles (NPs). These NPs display collective oscillations of electrons in the presence of an external field, originating the surface plasmon resonance (SPR), usually observed in the visible portion of the linear absorption spectrum and called as plasmon band. Since those plasmon resonances induce to strong polarizability in the NP, effects of local field enhancements can result in increases of linear and nonlinear optical properties¹⁹. Nobel-metal NPs have been actively investigated in glasses due to the facility they can be synthesized and also for providing strong and tunable plasmon band by adjusting the particle size^{20 21}.

One of the most ordinary procedures to produce NPs in glasses involves the addition of the compound of interest during the melting, resulting in ions in the glass matrix, which are further reduced to metallic atoms, leading to NPs formation by heat treatment. Methods like ion-exchange and ion implantation followed by annealing have also been employed, however, the formation of NPs in those cases is limited to regions close to the glass surface². Although several methods are available to generate nanoparticles in glass, only femtosecond laser micromachining has allowed controlling it three-dimensionally²². Furthermore, femtosecond lasers are important not only to study the optical nonlinearities at ultrashort pulses regime, but also it has been a powerful tool for materials processing in the microscale.

Femtosecond laser micromachining is a direct laser writing technique that involves nonlinear optical interactions, confining material modification only around the focal volume. Thus, surface damages are avoided by focusing the laser beam into the glass bulk. By moving the sample regarding the laser focus it is possible to change the

material properties with high spatial accuracy. The obtained 3D microstructures may differ from the original material by the refractive index, nonlinear optical susceptibility, crystalline structure, morphology and so on^{23; 24}. Such features can be effectively changed by the formation of metallic nanoparticles during the irradiation process. Once metallic nanoparticles exhibit ultrafast response times and high third-order nonlinearities²⁰, their spatial control in the micrometer scale can be essential for the development of all-optical devices. Although waveguides, splitters, amplifiers and resonators have been demonstrated using different techniques and materials³, 3D-photonic microstructures containing metallic NPs have received little attention despite their importance for integrated optics.

1.1 Objectives

Taking into account the technological interests on glassy materials for nonlinear optics, including heavy metal oxide and chalcogenides glasses, as well as the demand for the fabrication of microdevices for all-optical circuits, the purpose of the research performed on this thesis was to employ femtosecond laser pulses in two main domains: i) at the basis of fundamental science, to study the optical nonlinearities of glasses and evaluate the effect of nanoparticles over these properties; and ii) at the standpoint of applied science, to produce waveguides containing metallic nanoparticles using a single step laser processing.

Considering the fundamental aspect of this research, the goal of this thesis concerned with answering: Do nanoparticles significantly show the resonant enhancement effect for nonlinear optical response by improving the nonlinear refractive index of glassy materials?

1.2 Organization of the thesis

After this introductory section where the main goals of the research has been stated, this thesis presents in the next chapter a brief review of the fundamental concepts in nonlinear optics, emphasizing the properties of amorphous materials, as well as their processing with femtosecond lasers, aiming at the development of optical waveguides (Chapter 2). Then, Chapter 3 encompasses the experimental methods employed for characterization and processing of the samples. Emphasis is given to the z-

scan technique, which affords the refractive and absorptive nonlinearities. By using an amplified fs-laser along with an optical parametric amplifier, it was possible to investigate those properties in a wide range of wavelengths (approximately from 400 to 1500 nm). Details about the experimental setup for femtosecond laser micromachining for the production of 3D waveguides containing metallic nanoparticles are also presented in Chapter 3.

In the following, the thesis is split in two parts, which displays and discuss the results obtained for oxide (Part I) and chalcogenide glasses (Part II). Most of the work has been devoted to oxide glasses. Thus Part I include the next four chapters (Chapters 4 to 7), which investigate the nonlinear optical properties of a $\text{GeO}_2\text{-Bi}_2\text{O}_3$ glass matrix containing gold nanoparticles (Chapter 4) and $\text{Pb}_2\text{P}_2\text{O}_7\text{-WO}_3$ with copper nanoparticles (Chapter 5). We found out that this latter matrix, when doped with silver ions, is a good target for the fabrication of silver NPs into the core of waveguides using femtosecond laser micromachining, as presented in Chapter 6. Similarly, in Chapter 7 we show the simultaneous production of waveguides and copper NPs in a borosilicate glass (BSi) that is particularly important for being the origin of the studies of fs-laser processing of glassy materials in the Photonics Group at IFSC-USP ²⁵.

Finally, Part II focuses on the synthesis of nanoparticles chalcogenide glass, which was developed thanks to the partnership with Prof. Craig B. Arnold - Princeton University. Chapter 8 was carried out at Arnold's Group during the one-year internship supported by FAPESP – BEPE program. In this chapter we describe the synthesis of nanoparticles in arsenic sulfide films using a solution-based method. The initial idea was to obtain metallic silver nanoparticles using a methodology simpler than laser ablation of a metal target, as reported in ref. ²⁶. However, such approach led to the production of silver sulfide nanoparticles, as shown in the results of Chapter 8. Additionally, Chapter 9 presents a general conclusion of the whole research work.

2. Theoretical foundation and literature review

2.1 Nonlinear optical properties

It is usual to relate optical properties of materials with light refraction, absorption, reflection and scattering. These properties originate from a polarization induced in the medium by an electromagnetic field. When such polarization ($\vec{P}$) responds linearly to the applied electromagnetic field ($\vec{E}$), through the relationship $\vec{P} = \epsilon_0 \chi^{(1)} \vec{E}$ - where $\chi^{(1)}$ is the linear susceptibility and ϵ_0 is the permittivity of free space - the induced optical phenomena are encompassed in the linear optical regime. However, if the material properties do not respond in such a linear way, which occur when very intense electromagnetic fields are used, the regime of nonlinear optics comes to actuate and the polarization is described by ²⁷

$$\vec{P} = \epsilon_0 (\chi^{(1)} \vec{E} + \chi^{(2)} \vec{E}^2 + \chi^{(3)} \vec{E}^3 + \dots) \equiv \vec{P}^{(1)} + \vec{P}^{(2)} + \vec{P}^{(3)} + \dots \quad (2.1)$$

in which $\chi^{(2)}$ and $\chi^{(3)}$ are the second- and third-order nonlinear optical susceptibilities, respectively. Such behavior is observed when the intensity of radiation is comparable to interatomic electric field, being only provided by lasers.

Although the concept of multiphoton absorption was predicted by Maria Goppert-Mayer in 1931, the first experimental demonstration of a nonlinear optical effect took place thirty years later, right after the developed of the laser in 1960 by Maiman. Such first demonstration, specifically the second-harmonic generation (SHG) in a quartz crystal, was carried out by Peter Franken et al.. This is an example of second-order nonlinear polarization, $\vec{P}^{(2)}$, which also include the effects of sum- and difference-frequency generations. The observation of second-order optical nonlinearities depends on material symmetry conditions, being absent in isotropic media and centrosymmetric crystals. On the other hand, the third-order nonlinear optical interactions are observed in isotropic materials when irradiated with enough light intensity. In this way, the lower

order nonlinear optical properties of glasses are related to third-order optical susceptibility and, at first, they do not display second-order nonlinearities.

2.1.1 Third-order nonlinear optical processes

Considering the electric field provided by a laser, $\vec{E} = \mathcal{E} \cos \omega t$, the third-order polarization can be written as

$$\vec{P}^3 = \frac{1}{4} \epsilon_0 \chi^3 \mathcal{E}^3 \cos 3\omega t + \frac{3}{4} \epsilon_0 \chi^3 \mathcal{E}^3 \cos \omega t \quad (2.2)$$

As it can be observed in eq. 2.2 there is a term that oscillates at frequency 3ω and another one at ω , the same frequency of the applied field. The first one is responsible for third-harmonic generation (THG), represented in Fig. 2.1a, in which three photons of frequency ω are destroyed and one photon at 3ω is created. The second term in eq. 2.2 disturbs the polarization at the frequency of the incident field, ω , leading to effects of two-photon absorption (TPA), shown in Fig 2.1b, and also to the intensity dependent refractive index, called as optical Kerr effect. Those processes are the most studied nonlinear optical phenomena of glassy materials, and are the properties investigated in this thesis.

Fig. 2.1: Nonlinear optics effects associated with the third-order optical susceptibility. a) Third-harmonic generation and b) two-photon absorption.

Source: By Robert W. Boyd ²⁷

Optical Kerr effect and two-photon absorption are respectively related to real and imaginary part of third-order susceptibility ($\chi^{(3)} = \chi_R^{(3)} + i\chi_{Im}^{(3)}$), as expressed by eqs. 2.3 and 2.4 ^{27; 28}:

$$\chi_R^{(3)} = \frac{4}{3}n_0^2\epsilon_0cn_2 \quad (2.3)$$

$$\chi_{Im}^{(3)} = \frac{2}{3}\frac{n_0^2\epsilon_0c^2}{\omega}\beta_{TPA} \quad (2.4)$$

from where one obtains the nonlinear index of refraction – n_2 (m²/W) – and the two-photon absorption coefficient – β_{TPA} (m/W), being c the speed of light in a vacuum and n_0 the linear index of refraction. We use SI (mks) system, which can be changed to gaussian units through $\chi_{SI}^{(3)} = 160\pi^2\epsilon_0\chi_{esu}^{(3)}$ [†].

In this sense, glass polarizability is modified by third-order optical effects and its optical properties become dependent on intensity and the global refractive index (n) and absorption coefficient (α) are written as:

$$n = n_0 + n_2I \quad (2.5)$$

$$\alpha = \alpha_0 + \beta I \quad (2.6)$$

It is worth mentioning that the nonlinear absorption coefficient (β) is not always related to two-photon absorption process. Saturation effects are also encompassed in nonlinear optical regime, since they are observed at high light intensity regime. Saturable absorption results in the decrease of absorption coefficient on account of the depletion of ground state associated with intense resonant excitation. Even under nonresonant conditions eq. 2.1 loses its validity if the applied laser field intensity is close to the characteristic atomic field (comparable to 3.5×10^{16} W/cm²), because of the photoionization that can occur under these conditions ²⁷. In fact, photoionization is the central effect behind femtosecond laser micromachining, enabling to produce optical devices, such as waveguides, into the bulk of transparent materials, as will be described in the next section.

[†] It is usual to report the nonlinear index of refraction in gaussian units: $n_2(m^2/W) = \frac{40\pi n_2(esu)}{n_0 c(ms^{-1})}$

2.2 Laser-induced optical breakdown in glasses

Laser-induced breakdown in optically transparent materials refers to the permanent damage caused by tightly focused laser pulses, in a process that transforms the material into an absorbing plasma ²⁹. Considering a pulse duration of 100 fs (10^{-13} s) and a pulse energy of only one-third of 1 mJ focused to a 20 μm diameter spot ($2w_0$), the peak intensity - $I_\infty = E_p/\pi w_0^2$ - achieves 10^{15} W/cm². When such high irradiance interacts with the target a sequence of nonlinear optical reactions is initiated and a permanent damage is produced. The damage region can differ from the original material in a number of properties, including refractive index, absorption coefficient, structure and morphology ²⁴, which has provided new opportunities for laser material processing and aggregating new issues to fundamental sciences.

In a transparent dielectric, the bound valence electrons have an ionization potential or bandgap (E_g) greater than the photon energy, thus the bound electrons do not absorb the laser light at low intensities ²⁹. However at the intensities provided by ultrashort laser pulses, a nonlinear absorption mechanism promotes electrons from valence band (VB) to the conduction band (CB). Current investigations claim that such process can occur by photoionization or avalanche ionization ³⁰.

Depending on laser frequency and intensity, photoionization mechanism is achieved through multiphoton ionization or tunnelling ionization, represented on Fig. 2.2. At high laser frequencies, but still in a nonresonant region, nonlinear ionization is a consequence of multiphoton absorption, in which several photons are absorbed at the same time by an electron in VB promoting it to CB. On the other hand, tunnelling ionization prevails at lower laser frequencies and higher intensities. In this process, the band structure of dielectric is distorted due to the intense field, so that the potential is suppressed and band to band transition can occur, whereby a bound electron tunnels out to become a free electron at CB ^{30; 31}. The transition between multiphoton and tunnelling ionizations has been analyzed through the Keldysh parameter, defined by

$$\gamma = \frac{\omega}{e} \left[\frac{mc n \epsilon_0 E_g}{I} \right]^{1/2} \quad (2.7)$$

and plotted in Fig. 2.3, where m and e are the reduced mass and charge of the electron. Keldysh proposed that the photoionization is predominated by the multiphoton absorption for $\gamma > 1.5$ and by tunneling ionization for $\gamma < 1.5$.

Fig. 2.2: Nonlinear photoionization processes underlying femtosecond laser machining. (a) Tunneling ionization, (b) multiphoton ionization, and (c) avalanche ionization: free carrier absorption followed by impact ionization. VB, valence band; CB, conduction band.

Source: By Martin Ams et al. ³¹

Fig. 2.3: Keldysh parameter (γ) as a function of laser intensity (for a 800 nm light in fused silica). When γ is larger (smaller) than about 1.5 photoionization is a multiphoton process (tunnelling).

Source: Reprinted from ³⁰

Avalanche ionization, also illustrated in Fig. 2.2, requires a seed electron already in the CB. Although glasses are dielectric materials, there are always some free or conduction electrons in any real material system, which can come from impurities. Those electrons in CB linearly absorb several laser photons sequentially, moving to higher energy levels. When the energy of this electron exceeds the conduction band minimum by more than the E_g , by collision it transfers energy to an electron in VB, resulting on two electrons at the conduction band minimum. Each of these electrons keep absorbing energy through free-carrier absorption as long as the laser field is present, leading to an exponential growth on electron density. Thus, a plasma of free electron is created, been responsible for the further material modification, as alteration of the refractive in confined regions.

2.2.1 Optical waveguides in glasses[†]

The origin of 3D waveguides in glass is related to studies on laser-induced breakdown in dielectrics. Investigating the damage produced by fs-pulses tightly focused inside fused silica, Hirao's team observed a local change in the refractive index, Δn , of approximately 0.015³³. The nature of this Δn was discussed considering effects on the glass network resulting from localized melting or defects formation, as peroxy radicals, Si E' and nonbridging oxygen hole centers. Moreover, multiphoton processes were associated with laser-induced damage³³. In the following year, the functionality of those damage lines for waveguide was demonstrated and the role of fs-laser became clearer³⁴. Due to the high intensity in the focal volume, multiphoton absorption occurs, confining material ionization and plasma formation in the focused region inside the glass. The further interactions can lead to a local heating, and therefore structural densification during cooling and increase of the refractive index^{33; 35}.

The guided modes are mainly determined by the shape, size and Δn of the waveguide, which can be controlled by the writing conditions, including the average power and repetition rate of the fs-laser, as well as sample scan speed and numerical aperture of the objective ^{34; 36}. Moreover, the direction of sample movement defines the waveguide geometry. Elliptical or roughly cylindrical cross sections are obtained when

[†] This section was recently published as part of a Review paper, please see in J. Braz. Chem. Soc.³² or DOI: [dx.doi.org/10.5935/0103-5053.20150238](https://doi.org/10.5935/0103-5053.20150238)

the sample is translated transversal or longitudinally to the laser beam, respectively³³. Although cylindrical waveguides favor the light coupling and guiding, their length is limited by the work distance of the employed objective, usually shorter than 10 mm for $NA > 0.25$. Thus, at the beginning of 20th century one of the first issues to be solved dealt with the asymmetry of the waveguides when produced by transversal writing. Such asymmetry follows the beam intensity profile where nonlinear interactions take place. Therefore, it is feasible that the waveguide cross-section is equivalent to the confocal parameter ($b = 2\pi w_0^2/\lambda$) along the beam propagation direction, corresponding to the beam diameter $2w_0$ when observed perpendicularly to it. In order to control the beam diameter without affecting the focal length, Osellame et al.^{37; 38} developed the astigmatic beam-shaping technique, in which a telescope with cylindrical lenses is employed so that the size and symmetry of the waveguide can be adjusted. A modification on the experimental setup made the micromachining of cylindrical waveguides simpler. Similar beam shaping can be achieved by using a slit, positioned before the objective lens and oriented parallel to the sample translation direction^{39; 40}. Figure 2.4 (a) shows a nonfunctional waveguide and its elliptical cross-section, produced by a fs-laser (800 nm, 120 fs, 1kHz) in a phosphate glass, using a 20× objective lens ($NA=0.46$) and scan speed of 40 $\mu\text{m/s}$ without slit. Using a slit of 500 μm , cylindrical waveguide is performed, as shown in Fig. 5 (b), enabling the light confinement. To obtain a waveguide with a symmetrical profile the ratio between the beam waist at directions perpendicular to the laser propagation must be $\frac{w_y}{w_x} = \frac{NA}{n} \sqrt{\ln 2/3}$ at the objective entrance, where n is the refractive index and x is the waveguide axis, according to ref.³⁹.

Fig. 2.4: Differential interference contrast microscopy showing waveguides and their cross-sections, when micromachined (a) without and (b) with a slit before the objective lens³⁹.

Source: By M. Ams et al.³⁹.

Other drawback of laser processing of materials is related to the processing speed of the waveguides. The amplified laser systems employed own repetition rate on the order of kHz, which restricted the increase of the processing rate. Thus, the development of long cavity Ti:sapphire oscillator provided fs-pulses at MHz rate, with enough energy per pulse for such task. Although the pulse energy decreased from mJ to nJ, the time interval between two consecutive pulses is also reduced typically from ms to ns, bringing not only faster laser scan speed, but also new issues concerning the heating accumulation. Given that the heat diffusion time out of the focal volume of a high numerical aperture lens is about 1 μ s, there is not enough time for the irradiated region to cool down, resulting on the increase of the temperature and consequently melting/material modification in a dimension much larger than the focal volume⁴¹. Structures composed by concentric rings are commonly seen when fs-lasers with repetition rate of MHz are used, as illustrated on the top-view microscope image of Fig. 2.5.

Fig. 2.5: Dependence of laser-induced damage in a borosilicate glass (AF45) with the repetition rate, number of pulses and fluence of a 1045 nm- femtosecond laser. Beam direction is normal to the image plane ⁴².

Source: By Shane M. Eaton et al.⁴²

The inner rings in Fig. 2.5 represent the region achieved laser pulses, where nonlinear effects initiated by multiphoton absorption and followed by multiphoton- and avalanche ionization take place⁴³. Part of the energy absorbed by the electrons is transferred to the lattice, and the central region acts as a heat source outward the focal volume. The local temperature can reach values as high as a few thousand °C (around

7000° C). Then, the melted glass resolidifies according to the temperature and pressure gradients, leaving stress-strain zone that affects the inner region, giving rise the outer rings^{42; 44}. The magnitude of the heat affected zone, and therefore the waveguide size, depends on the number of laser pulses, thermal diffusion coefficient and the material's optical bandgap, which defines the nonlinear interactions. Furthermore, in general, 200 kHz can be defined as the onset of repetition rate for heat accumulation generated by laser in glass. Because of its high bandgap energy and melting temperature, pure fused silica is a particular case, requiring wavelength closer to the bandgap and greater pulse energy and repetition rate⁴². Nevertheless, waveguides can be micromachined in fused silica by using fs-lasers of low repetition rate (1 kHz), in which the change of refractive index is controlled by the laser scan speed³⁶.

In this sense, the choice of MHz or kHz laser systems substantially affects the resulting photo-written structure. If thermal effects are adverse, as in the obtainment of sub-micrometric structures, low repetition rate are appropriate, whereas high repetition rate lasers can play as a heat source, being beneficial for the reduction of waveguide loss, induced crystallization and ionic diffusion^{42; 45; 46}. Combining diffusion and crystallization with nonlinear optical processes, caused by fs-laser pulses, it has been possible to control the formation of metallic nanoparticles three-dimensionally at micrometer scale^{22; 25; 47; 48; 49}, as it will be discussed in Chapter 6.

We have discussed the effects of longitudinal and transversal laser writing, as well as the influence of repetition rate on the fabrication of waveguides in glass. Among the experimental parameters, pulse duration also affects the laser-induced damage in transparent materials. Experiments and modeling on fused silica are studied in references⁵⁰ and⁵¹, for regimes of short and ultra-short pulses respectively, in which contributions from multiphoton, tunnel and avalanche ionizations are thoroughly described. Also investigating fused silica, Mazur group found a dependence of NA with the damage caused by fs-laser pulses⁵². For $NA \geq 0.10$ there is a sharp threshold energy that indicates the onset of multiphoton ionization. Such threshold energy is well below the critical power for self-focusing for a regime of high NA (greater than 0.25), resulting in structures that matches the confocal parameter, whereas lower NAs cause broken filaments, suggesting multiple refocusing of the femtosecond laser beam^{52; 53}.

Most of the key works concerning laser-induced damage and waveguides are performed using standard or commercial glasses, moreover fused silica. Nevertheless,

studies on optical nonlinearities demonstrate the importance of tailoring material properties through the composition, stimulating the use of multicomponent glasses for direct laser writing. For instance, quantitative measurements on fs-laser induced Δn have shown a strong dependency on glasses composition, its structure and thermal properties^{33; 54}. Positive, negative and nonuniform variations of Δn result not only from the glass composition but also from the laser writing parameters^{55; 56}. The waveguide shape is also affected by composition, as in the case of heavy metal oxide glasses, which have high n_2 and hence self-focusing effect¹⁵. Even so, Y-splitters, directional couplers, supercontinuum and second harmonic generation have been demonstrated in those glasses using fs-laser micromachining⁵⁷. In addition, heavy metal oxide glasses are excellent hosts for earth-rare elements, enabling the development of active waveguides^{58; 59}.

3. Experimental procedures

Two different Ti:sapphire laser systems were employed in this work. For the measurements of nonlinear optical spectroscopy we used an amplified system with repetition rate of 1 kHz and pulses of 150 fs and 400 μ J at 775 nm (Clark-MXR), which is used to pump an optical parametric amplifier (OPA-Quantronix) that provides 120-fs pulses from 460 up to 2000 nm. Femtosecond laser micromachining experiments were mainly carried out with an oscillator system operating at 5 MHz with pulses of 50 fs and 100 nJ, centered at 800 nm (Femtsource-XL). However, in some occasions the amplified laser was also used for micromachining. Details about the experimental setups and techniques are presented in the following sections, while preparation of the samples is described individually in the corresponding chapter.

3.1 Nonlinear optical spectroscopy

3.1.1 Z-scan technique

The third-order nonlinear optical properties of glass samples were obtained through the z-scan technique^{60; 61}, that consists in measuring sample transmittance in the far field while it is scanned along the propagation (z direction) of a focused Gaussian beam. Depending if there is/is not an aperture (iris) in front of the detector, it is possible to obtain the refractive or absorptive nonlinearities, called respectively close and open aperture z-scan. In the close aperture z-scan configuration, see Fig. 3.1a, as the sample approaches the focus the induced self-phase modulation diverge the beam into the far field, assuming $n_2 > 0$, leading to a decrease in the transmission through the iris. After the focus, the effect is to converge the beam, which in turn increases the light transmitted through the iris. Thus, the technique is based in a self-phase modulation acquired by a laser when propagates throughout a nonlinear medium, resulting in a distortion of the beam wave front. The phase shift $\Delta\phi_0$ at the exit of the sample is:

$$\Delta\phi_0 = \frac{k \cdot n_2 \cdot I_0 \cdot L}{\sqrt{2}} \quad (3.1)$$

where k is the wave vector and L is the sample effective length. By plotting the normalized transmittance as a function of the z position $T(z) = P(z)/P(z_\infty)$, one obtain the z -scan signature represented by a prefocal valley followed by a posfocal peak (Fig. 3.1a), featuring a positive refractive nonlinearity, in which pick-valley variations are given by ³⁰:

$$\Delta z_{P-V} = 1.7 z_0 \quad (3.2)$$

$$\Delta T_{P-V} = 0.406 \cdot \Delta\phi_0 \quad (3.3)$$

where $z_0 = \pi w_0^2 / \lambda$, enabling to figure out the laser intensity, $I_0 = 2P / \pi w_0^2$, and the nonlinear refractive index:

$$n_2 = \frac{\Delta T_{P-V} \cdot \lambda \cdot \sqrt{2}}{2\pi \cdot 0.406 I_0 \cdot L} \quad (3.4)$$

The sensitivity to the nonlinear refraction is due to the aperture, and its removal makes the technique sensitive to nonlinear absorption, including multiphoton absorption or saturation of absorption effects, configuring open z -scan measurements. In this case, the z -scan trace is symmetric with respect to the focus ($z=0$), showing a minimum (e.g. multiphoton absorption) or maximum transmittance (saturation of absorption). Figure 3.1b exemplifies the multiphoton absorption process, in which changes in transmittance is associated with the nonlinear absorption coefficient through:

$$\Delta T_{P-V} = \left| 1 - \frac{1}{q_0} \ln(1 + q_0) \right| \quad (3.5)$$

with $q_0 = \beta I_0 L$. For the nonlinear absorption spectra of samples reported in Chapter 5 we used the white-light continuum (WLC) z -scan technique ^{62; 63}, which uses as excitations source the WLC generated by pumping of a distilled water cuvette with the amplified laser system. Thus, the WLC spectrum, from 450-750 nm, is collected in a single scan without the need of using the OPA, as in all other experiments.

Fig. 3.1: Representation of z-scan measurements for close (a) and open (b) configurations to obtain, respectively, the nonlinear refractive index and nonlinear absorption coefficient through normalized transmittance as a function of z position (z-scan signature).

Source: By Joel Hales-Georgia Tech, available in www.photonicswiki.org

We have employed a spatial filter placed before the z-scan setup to ensure a Gaussian profile for the laser beam. The laser pulse energies ranged from 10 to 200 nJ, and the beam waist sizes at the focus varied from 12 to 28 μm , depending on the excitation wavelength. The experimental errors for nonlinear refraction and absorption measurements are estimated within $\pm 20\%$ and $\pm 10\%$, respectively. Fused silica has been used as standard calibration for closed aperture z-scan, where the approximate value of $n_2 \sim 1.9 \times 10^{-20} \text{ m}^2/\text{W}$ was obtained at visible and infrared regions, being in accordance with results from the literature ⁶⁴.

3.1.2 Optical Kerr gate (OKG)

It is possible to analyze the response time of the refractive optical nonlinearity by using measurements of Kerr gate. This experiment is very similar to pump-probe technique that allows studying the dynamics of the excited state. However, in the case of OKG, the dynamic is associated with the induced birefringence in the Kerr medium. The experimental setup, represented in Fig. 3.2, consists in placing the isotropic sample between two crossed polarizers. An intense pump beam induces the refractive nonlinearity, responsible for generating anisotropy, affecting the propagation of a second weaker laser beam - probe, which is overlapped spatially and temporally (delay line) with the pump beam, both focused on the sample. The signal generated in probe beam is checked in a photodetector connected to a lock-in amplifier after passing through the sample and the analyzer, from which the response time is obtained taking into account the original pulse time.

Fig. 3.2: Experimental setup used for optical Kerr gate measurements.

Source: By the author.

The earlier mentioned amplified laser system and the OPA were used as excitation sources to perform measurements at different wavelengths, depending on the interest region for each sample. The laser beam was split into pump and probe (4 % of the pump) beam by a glass slide. Transient transmittance measurements were performed for the samples of Chapter 6 by removing the analyzer from the OKG setup, featuring a traditional pump-probe experiment. We have calibrated the laser pulse width, after passing through lenses, glass plates and polarizers using a thin BBO crystal, thus obtaining a pulse of 200-220 fs.

3.2 Femtosecond laser micromachining

Femtosecond laser micromachining was employed in order to produce 3D waveguides, as well as to grow spatially controlled metallic nanoparticles in glasses. The experimental setup, schematically displayed in Fig. 3.3, basically requires an objective lens, a xyz translational stage and a camera to follow the processing, besides the femtosecond laser. The sample is placed over a computer-controlled x - y - z stage, which moves it at constant speed in the plane perpendicular to the laser propagation, while the objective lens that focus the beam into the glass remains fixed. The numerical aperture (NA) of the objective lens determines the focal volume, so that its variation (kept within 0.65 - 0.25) enables to control the micromachined region, featuring the size and shape of waveguides. Figure 3.4 is a picture of the built apparatus.

Fig. 3.3: Representation of experimental setup for femtosecond laser micromachining used to produce waveguides and generate nanoparticles into the glassy samples.

Source: By the author.

Fig. 3.4: Picture of the experimental setup used for femtosecond laser micromachining.

Source: By the author.

3.3 Coupling and optical losses of waveguides

In order to evaluate the functionality of the waveguides containing metallic nanoparticles, we performed coupling measurements using a standard system, based on a He-Ne laser (632.8 nm) and microscope objectives, as illustrated in Fig. 3.5. Near-field propagation mode was collected onto a CCD camera.

Waveguide losses were determined by measuring the input and output power at the entrance of the first objective and right after an iris placed at the exit of the second objective, taking into account the transmission of all components of the system. In order to distinguish coupling from propagation losses, the transmittance was obtained for the whole length of the waveguide ($\sim 5 - 6$ mm) and then for half of such length.

Fig. 3.5: Representation of experimental setup used for coupling 632.8 nm-light in the waveguides and analyze propagation modes and optical losses.

Source: By the author.

Oxide Glasses

4. Ultrafast third-order optical nonlinearities of heavy metal oxide glasses containing gold nanoparticles[†]

This chapter reports on the third-order nonlinear properties and the response time of GeO₂-Bi₂O₃ glass, as well as the effect of gold nanoparticles on these properties. The nonlinear refractive index spectrum and the nonlinear absorption coefficient were determined by the Z-scan technique, and the response time was obtained through Kerr gate measurements, using femtosecond pulses. The results show that the presence of gold nanoparticles causes a saturable absorption effect that is overcome by the two-photon absorption process at higher light intensities, for wavelengths within the plasmon band. We measured a constant value for the nonlinear refractive index (n_2) for the visible and infrared regions, which was not affected by the presence of gold nanoparticles in the sample. However, the n_2 value is one order of magnitude higher than the one for fused silica and 1.5 times better than PGO (PbO-GeO₂) glasses. In addition, the response time of the induced birefringence for the samples with and without gold nanoparticles is faster than the pulse duration (220 fs), indicating an ultra-fast electronic process.

4.1 Introduction

Heavy-metal oxide glasses are promising materials for photonic applications due to their high third order nonlinearities, which are fundamental to the development of all-optical devices¹². Among heavy metals, lead has been widely investigated because it can be incorporated, in the form of lead oxide, in large amounts to glasses, resulting in high third-order nonlinear optical susceptibilities (χ^3)^{12; 62; 66}. Nonetheless, it has been reported that bismuth oxide leads to 1.5 times larger χ^3 than lead oxide, both in borate matrix¹⁷. Although Pb²⁺ and Bi³⁺ have the same electronic structure [(Xe) 4f¹⁴ 5d¹⁰ 6s²

[†]Already published, please see in Optical Materials⁶⁵ or DOI: [10.1016/j.optmat.2013.12.012](https://doi.org/10.1016/j.optmat.2013.12.012).

6p⁰] and optical transition mechanism (¹S₀→³P₁), the higher susceptibility associated to the bismuth glass is due to its smaller optical band gap ¹⁷. For the same reason, germanium dioxide is an important glass former in this research field. In fact, the band gap energy of vitreous germania is smaller than other common oxide glass formers ¹.

Beside the hyperpolarizability of the glass constituents, addition of metallic nanoparticles is also expected to improve the optical nonlinearities of glasses. Due to the local field enhancement effect, Au, Ag and Cu nanoparticles have been incorporated in several materials in order to obtain a better performance of both linear and nonlinear optical properties ^{67; 68; 69; 70}. Enhancement of rare-earth ions emission on glasses containing metallic nanoparticles have been demonstrated ^{69; 71; 72}; a growth of ~1000% in the photoluminescence intensity of Eu³⁺ doped GeO₂-Bi₂O₃ glass containing gold nanoparticles was reported in Ref. ⁶⁹, for example.

Despite such significant effects on the linear optical properties, considerable enhancement on nonlinear optical properties of glasses containing metallic nanoparticles has not been obtained. Therefore, this work reports on the effect of gold nanoparticles in the third-order nonlinear optical susceptibility of the GeO₂-Bi₂O₃ glass. Because a strong enhancement of the photoluminescence was observed in the GeO₂-Bi₂O₃ glass doped with Eu³⁺ ⁶⁹, such sample was also chosen to be studied in this work. The nonlinear absorption coefficient at wavelengths within the plasmon resonance band and the nonlinear refractive index at visible and near-infrared regions (480-1500 nm) were obtained using the wavelength-tunable femtosecond Z-scan technique. In addition, the response times of the nonlinearity have been evaluated at 780 nm by the optical Kerr gate technique.

4.2 Materials and methods

The 58.4 GeO₂ – 41.6 Bi₂O₃ (wt%) glass matrix and the 3Au₂O₃ – 0.5Eu₂O₃ (wt%) doped sample (GB and GB-Au respectively), were prepared by the melt-quenching method as described in Ref. ⁶⁹. The Au nanoparticles were obtained by adequate annealing of the GB-Au sample at 420 °C for 3h. Spherical shaped nanoparticles, with size distribution around 5 nm, were observed in the transmission electron microscopy (TEM) images. The third-order nonlinearities and response times were obtained using z-scan and optical Kerr gate measurements, as described in section 3.1.

4.3 Results and discussions

The linear absorption spectra of GB (a) and GB-Au (b) samples, displayed in Fig. 4.1, reveal that both samples are transparent for wavelengths longer than 600 nm. The two narrow absorption peaks observed for GB-Au (b) at 395 and 465 nm are due to the $\text{Eu}^{3+} 4f-4f$ electronic transitions originated from the ground state (7F_0)⁶⁹. Moreover, this sample presents a broad absorption band centered at 500 nm, which is related to the surface plasmon resonance of Au-nanoparticles, indicating that nanoparticles formation occurs after the annealing at 420 °C during 3h. Such nanoparticles have spherical shape with diameter around 5 nm, according to TEM images as reported in Ref.⁶⁹.

Fig. 4.1: Linear absorption spectrum of (a) GB and (b) GB-Au samples.

Source: By the author.

In order to evaluate the effect of the gold nanoparticles on the third-order optical nonlinearities of germanium-bismuth glass, open and closed aperture Z-scan measurements were carried out. In Fig. 4.2, typical Z-scan results for nonlinear absorption (open aperture) are depicted for GB and GB-Au at 500 nm. Table 1 presents the values of nonlinear absorption for GB and GB-Au samples for wavelengths from 500-580 nm. According to the Z-scan signature displayed in Fig. 4.2, which features a valley at the focal region ($z = 0$), a two-photon absorption (2PA) process is observed for the GB matrix. Although GB sample presents a tail associated to the interband transition at 500 nm in the linear absorption spectrum, the reverse saturable absorption can be discarded

once the excitation photon energy (2.48 eV) is far from the band gap energy of the glassy matrix ($E_g = 3.2$ eV). In this case, the two-photon absorption coefficient (β_{2PA}) value of 0.08 cm/GW is obtained by fitting the experimental curve. On the other hand, the sample containing gold nanoparticles (GB-Au) presents a normalized transmittance (NT) curve with values higher than one at pre- and post-focal positions, and values lower than one for the focal position, as shown in Fig. 4.2. This indicates that two opposite nonlinear absorption effects are competing: the 2PA already observed on the glass matrix GB ($NT < 1$) and saturable absorption (SA) of the Au-nanoparticles ($NT > 1$)⁷³. Because the excitation energy is resonant with the gold plasmon band at 500 nm, the nonlinear absorption process of GB-Au presents SA (pre- and post-focal positions) that overlaps the two-photon absorption at low intensity regimes. At this region, SA overcomes 2PA because the former is a one-photon process. However, as the intensity increases when the sample approach the focus, 2PA starts to compete with SA, decreasing considerably the transmittance at the focal position ($z = 0$)⁷⁴. To obtain the 2PA and SA magnitudes from the experimental result presented in Fig. 4.2 (GB-Au), the 2PA and SA theoretical curves (doted lines) were added and the corresponding absorption coefficients were adjusted until a good fit to the experimental data was obtained (solid line in Fig. 4.2). Through this procedure, we found a SA coefficient $\beta_{sat} = -0.14$ cm/GW and $\beta_{2PA} = 0.11$ cm/GW. The same behavior observed in Fig. 4.2 at 500 nm was also obtained for wavelengths between 500 and 560 nm, within the plasmon band. Nevertheless, only 2PA occurs for GB-Au at 580 nm. Therefore, the SA is related to the plasmon resonance of the gold nanoparticles, since it is observed only when the excitation is performed with wavelengths whitin the plasmon band. Concerning the values of β_{sat} , we observed a decrease of their magnitude as the excitation wavelength moves away from the plasmon band, while β_{2PA} of both samples stays nearly constant considering the estimated error. For longer wavelengths ($\lambda > 580$ nm) we were not able to observe any signal.

Fig. 4.2: Open aperture Z-scan signature at 500 nm for GB and GB-Au. Open symbols represent the experimental results, while solid lines are the fitting curves. In the GB-Au, the dotted lines correspond to the individual theoretical curves for SA (normalized transmittance higher than one) and 2PA (normalized transmittance lower than one), while the solid curve represents the sum of both processes.

Source: By the author.

Table 4.1: Nonlinear absorption values of GB and GB-Au sample. β_{2PA} and β_{sat} represent the two-photon and saturable absorption coefficients respectively.

λ (nm)	β_{2PA} (cm/GW) ± 0.01		β_{sat} (cm/GW) ± 0.01
	GB	GB-Au	
500	0.08	0.11	-0.14
520	0.06	0.11	-0.12
540	0.08	0.11	-0.10
560	0.06	0.05	-0.08
580	0.09	0.05	0

Figure 4.3 shows the spectra of the nonlinear refractive index (n_2) for GB and GB-Au glasses. The insets display typical closed aperture Z-scan signatures for each sample. For wavelengths between 480 and 580 nm the division between close and open aperture Z-scan curves was performed in order to isolate the effects of the nonlinear absorption and refraction⁶¹. One can notice a constant behavior of n_2 as a function of the wavelength for both glasses. Moreover, the average values of n_2 for GB and GB-Au samples are very similar, being respectively 1.7 e $1.8 \times 10^{-19} \text{ m}^2/\text{W}$. Therefore, no effect of the gold nanoparticles has been observed for the refractive nonlinearities of germanium-bismuth glass. Although it has been reported the influence of the metallic nanoparticles in the third-order nonlinear optical susceptibilities for excitation with nano or picosecond laser pulses excitations^{67; 68; 75}, the nonlinear refractive index for femtosecond regimes seems to be not sensitive to the presence of nanoparticles for wavelengths within and far from the plasmon band. Such independence was observed

for silver nanoparticles in lead-germanium glass ⁷⁶. An explanation for this result is based on the low concentration of the metallic nanoparticles, once the filling factor has been reported to be an important parameter for the enhancement effect of the optical nonlinearities ⁷⁷. In this sense, the magnitude of the nonlinear refractive index shown in 4.3 is directly related to the highly polarizable atoms in the glass matrix, being one order of magnitude larger than the average value of the fused silica for the same wavelength range ^{62; 64}. The results obtained show that for GB glasses n_2 is 1.5 times higher when compared to PGO (PbO-GeO_2) glasses containing silver nanoparticles ⁷⁶, This result is in agreement to the improvement on the χ^3 caused by the bismuth oxide in borate glass when compared to lead oxide and it is related to the coordination states around the heavy metal ion ¹⁷. It has been reported that Pb^{2+} have fourfold or threefold coordinations in many oxygenated compounds (forming PbO_3 trigonal and/or PbO_4 square pyramids), while Bi^{3+} configure polyhedrals with higher coordination numbers (5 - 6), being in most cases $[\text{BiO}_6]$ octrahedral units. Such difference in the coordination states causes changes in the glass polarizability which results in a decreasing of their band gap energy and consequently in the increasing of the nonlinear optical susceptibilities ^{17; 78; 79}.

Fig. 4.3: Spectra of nonlinear refractive index (n_2) of GB and GB-Au glasses. The insets show the closed Z-scan signature for each sample at 780 nm, which are representatives for the whole spectrum.

Source: By the author.

In the same way, the presence of gold nanoparticles does not affect the Kerr gate signal, as shown in Fig. 4.4 for excitation at 780 nm. The fused silica signal was added in Fig. 4.4 for the sake of comparison. The optical Kerr gate signal is related to the nonlinear birefringence induced in the samples by a pump beam. The change in the polarization of the probe beam can be determined as a function of the delay time between both beams (pump and probe), resulting in the response time of the nonlinear birefringence⁸⁰, in the present case directly related to n_2 . As one can notice, samples with and without Au-nanoparticles presented a symmetric Kerr gate signal, indicating that the response time is shorter than the pulse duration. Using a Gaussian fit, we have found a pulse duration of 220 fs which is in agreement with our calibration using a BBO crystal. Although the optical nonlinearity of GB and GB-Au glasses has been limited by the pulse duration and no effect of the nanoparticles could be observed, the result displayed in Fig. 4.4 indicates an ultra-fast electronic process (less than 220 fs).

Fig. 4.4: Kerr gate signal of the GB and GB-Au samples excited at 780 nm. The result of fused silica is shown in order to check the signal on the nonlinear glasses. Open symbols are the experimental data while the solid line represents the Gaussian fit.

Source: By the author.

4.4 Conclusions

We have investigated the third-order nonlinear optical properties and the response times of $\text{GeO}_2\text{-Bi}_2\text{O}_3$ glass, as well as the effect of gold nanoparticles in this glassy matrix. The nonlinear absorption coefficient and the nonlinear refractive index spectra were obtained using a tunable fs Z-scan technique, while the optical Kerr gate was carried out to obtain the response time of the optical nonlinearity. Our results show that the presence of gold nanoparticles affects the nonlinear absorption process only within the plasmon band region (centered at 500 nm), in which, at low light intensities, the saturable absorption effect overlaps the two-photon absorption that becomes dominant for higher intensities. For the sample without gold nanoparticles, only two-photon absorption was observed, indicating that SA is caused by the plasmon resonance associated to the gold nanoparticles. On the other hand, the nanoparticles do not affect the nonlinear refractive index spectrum, once a constant behavior from 480 to 1500 nm was observed for both samples. In this region, the average value of n_2 is $1.8 \times 10^{-19} \text{ m}^2/\text{W}$ and it is one order of magnitude larger than that of fused silica. When compared to the PGO glass, the $\text{GeO}_2\text{-Bi}_2\text{O}_3$ sample has a n_2 1.5 times higher. Therefore, the use of Bi_2O_3 is a better alternative when compared to PbO regarding the improvement of third-order nonlinearities. In addition, such optical nonlinearity exhibits an ultra-fast response time, being shorter than the laser pulse duration ($< 220 \text{ fs}$). In summary, the GB glasses analyzed in this work have low nonlinear absorption coefficient, high nonlinear refractive index and ultra-fast response times, which are interesting for photonic applications, as all-optical switching.

5. Nonlinear optical properties of tungsten lead-pyrophosphate glasses containing metallic copper nanoparticles[†]

We have prepared heavy metal oxide glasses containing metallic copper nanoparticles with promising nonlinear optical properties which were determined by Z-scan, and pump-probe measurements using femtosecond laser pulses. For the wavelengths within the plasmon band, we have observed saturable absorption and response times of 2.3 ps. For the other regions of the spectrum reverse saturable absorption, and lifetimes shorter than 200 fs were verified. The nonlinear refractive index is about $2.0 \times 10^{-19} \text{ m}^2/\text{W}$ from visible to telecom region, thus presenting an enhancement effect near the plasmon and Cu^{+2} bands.

5.1 Introduction

Oxide glasses, such as phosphate glasses, have been used as host material for heavy metal elements due to their wide range of applications in photonics, and on account of their interesting properties, such as low glass transition temperature, T_g , high thermal expansion coefficient, (allowing easy optical fibers fabrication), transparency from the ultraviolet up to 5 μm , and their high vitrifying ability and unusual capability to dissolve large amounts of other glass formers, modifiers, and intermediate compounds without reduction of glass forming ability ^{82; 83; 84}. Glasses containing heavy-metal-oxides (HMO), such as PbO , WO_3 , Bi_2O_3 and Sb_2O_3 , are the subject of research because of their nonlinear (NL) optical properties that can be tailored by using appropriate concentration of hyperpolarizable elements, and by extended infrared transmittance ^{2; 85; 86; 87}, which are the main features to develop NL photonic devices for all-optical switching, optical limiters and infrared technologies.

[†]Already published, please see in Plasmonics ⁸¹ or DOI: [10.1007/s11468-013-9585-z](https://doi.org/10.1007/s11468-013-9585-z).

Furthermore, glasses containing metallic nanoparticles (NP) are also promising photonic materials for nonlinear optics due to their wide range of resonant absorption frequencies, ultrafast response times and large third-order nonlinear optical coefficients associated to the surface plasmon resonance (SPR) of metallic NP^{88; 89}. Generally, these nanocomposites glasses contain noble metallic NP, such as Ag, Au and Cu, are prepared by the introduction of metal ions into the optically transparent glass matrix, and followed by metal reduction processes that can be achieved by heat treatment, or laser irradiation, both promoting the NP precipitation within the glass host^{2; 90; 91}. However, the majority of the researches done in this field has aimed at synthesizing silver and gold NP owing to their unique electrical and optical properties^{76; 92}. Glasses containing copper NPs are also very promising materials for optical application because they are less expensive, and show many similar properties compared to other noble metals^{48; 93}. Nowadays, there are several reports concerning the nonlinear optical properties of Cu NPs embedded in silicate glasses²⁵, ceramic matrix^{94; 95} and sapphire matrix⁹⁶. The most widely used techniques to precipitate Cu are ion implantation, femtosecond laser irradiation and sol-gel methods, followed by heat treatment to reduce and grow nanoparticles^{93; 97; 98}.

Considering the scenario above, and knowing that there are still many unsolved fundamental questions around the origin of optical nonlinearities, in spite of the numerous studies of glasses containing metallic nanoparticles, the actual task is to develop methods to synthesize NP with controlled optical properties according to their size and nature. The present work has the purpose of showing the growth of metallic Cu nanoparticles into an unusual and transparent binary glass system, based on lead pyrophosphate and tungsten oxide doped with copper ions, using heat treatment close to the glass transition temperature, T_g , for the NP nucleation and growth. The nanoparticles nature and morphology were confirmed by HR-TEM (high resolution transmission electron microscopy) and selected area electron diffraction (SAED). To investigate the influence of heat treatment on copper NP precipitation within the matrix, the samples were optically characterized by ultraviolet-visible absorption, and Z-scan technique to investigate the effect of copper NPs in the third-order nonlinear optical properties. The nonlinear refractive index (n_2) and the excited state absorption spectrum were determined by close-aperture, and white-light continuum (WLC) Z-scan techniques^{63; 99} using ~ 150 fs pulses at 1 kHz repetition rate.

5.2 Materials and methods

Glass preparation

Glass samples were synthesized by the conventional melt-quenching method using tungsten oxide WO_3 (Aldrich 99.8% pure), lead pyrophosphate $\text{Pb}_2\text{P}_2\text{O}_7$ and copper oxide CuO (99% pure), prepared according to the molar composition $(70\text{Pb}_2\text{P}_2\text{O}_7\text{-}30\text{WO}_3)$: 0.5CuO . Preparation started with the heat treatment of raw materials at 150°C for 1 h to reduce adsorbed gases. Then, chemicals were mixed together at an appropriate molar ratio, and the batch mixture was melted at 980°C for 1 h to ensure homogenization and fining. Finally, the melt was cooled in a stainless steel mold pre-heated at 80°C below the glass transition temperature - to prevent the nanoparticles precipitation during the synthesis process - and annealed at this temperature for 2 h to minimize the mechanical stress resulting from thermal gradients upon cooling. Before performing the optical characterizations, the bulk sample was optically polished and cut in 5 pieces, each of them undergoing different heat treatment times at 410°C , in order to obtain metallic Cu nanoparticles inside the glass matrix. The annealing conditions and characteristic temperatures of the samples are shown in Table 3.1.

Table 5.1: Annealing conditions and characteristic temperatures of PW glasses doped with CuO. Note that all samples were annealed at 410°C for different times.

Samples	Annealing conditions		Characteristic temperatures	
	$T_{\text{ht}} (^\circ\text{C})$	$t_{\text{ht}} (\text{min})$	$T_{\text{g}} (^\circ\text{C})$	$T_{\text{x}} (^\circ\text{C})$
PW-0		0		
PW-5		5		
PW-20	410	20	410	575
PW-60		60		
PW-120		120		

Characterization techniques

The glass samples with different heat treatment times were characterized by X-ray diffraction (XRD). A Siemens D 5000 equipment and $\text{CuK}\alpha$ radiation were used in 2θ range of $10 - 70^\circ$. Characteristic temperatures (T_{g} for glass transition and T_{x} for onset

crystallization) were determined by DSC using a TA 2910 instrument. The estimated error in the temperature measurement is $\pm 2^\circ \text{C}$ for T_g and T_x (obtained from tangent intersections). Powered samples were set in aluminum pans under N_2 atmosphere and heated at 10°C/min .

The linear absorption spectra of the glasses were recorded from 400 to 1600 nm with a Perkin Elmer Lambda 900 spectrophotometer. To confirm the nanoparticles precipitation and their nature, high resolution transmission electron microscopy (HR-TEM) and selective area electron diffraction (SAED) were obtained from powdered glasses suspended in ethanol, and deposited on grids using a FEI, Model Tecnai G2 F20 (200 kV) microscope equipped with a field emission gun (FEG). The third-order nonlinearities and response times were obtained using z-scan and optical Kerr gate measurements, as described in section 3.1 of this thesis.

5.3 Results and discussions

For all samples (Table 5.1), the typical amorphous halo was observed by X-ray diffraction. No diffraction peaks were observed regardless the time of treatment because the copper concentration was below the detection limit of this technique. DSC measurements were carried out in the temperature range from 150°C to 600°C . The thermograms showed the same thermal behavior for all samples, with a T_g temperature around 410°C and a T_x of approximately 575°C , resulting in a thermal stability parameter ΔT ($T_x - T_g$) of 165°C . Based on XRD and DSC analyses, it is clear that no abrupt changes were observed on the structural or thermal properties independently of the heat treatment undergone by the samples. Such results could be attributed to the low copper concentration into the glass host. However, the heat treatment at 410°C for different times caused significant changes on the color of the glasses. The sample $\text{Pb}_2\text{P}_2\text{O}_7\text{-WO}_3$ doped with 0.5 mol % of CuO , without heat treatment, presented a homogeneous yellowish color, transparent and free of strains. On the other hand, the glass pieces heat treated during 5, 20, 60 and 120 min exhibited a mix of brown and dark green homogeneous color, as shown in Fig. 5.1. In general, materials containing metallic nanoparticles show an intense color and their optical properties strongly depend upon the particle size, shape, concentration and the surrounding medium ^{22; 100}.

Fig. 5.1: Pictures of glass samples of the system $(\text{Pb}_2\text{P}_2\text{O}_7\text{-WO}_3):0.5 \text{ CuO}$ mol % heated at 410°C for 5, 20, 60 and 120 min, respectively.

Source: By the author.

Such color change was analyzed by the linear absorption spectrum, as displayed in Fig 5.2a. The sample without heat treatment (i) presents a broad absorption band centered at 840 nm, and attributed to the superposition of $^2\text{B}_{1g} \rightarrow ^2\text{A}_{1g}$ and $^2\text{B}_{1g} \rightarrow ^2\text{B}_{2g}$ transitions of the Cu^{2+} ions¹⁰¹. For the samples that were subjected to the heated treatment, an additional band at approximately 560 nm is observed on the linear absorption spectra (ii, iii and iv). Such band corresponds to the surface plasmon resonance (SPR) of Cu^0 nanoparticles and, therefore, indicates the formation of metallic copper inside the glass matrix by different times of heat treatment. The position of the SPR band, observed in Fig. 5.2a, is in agreement with the values reported in the literature for metallic Cu nanoparticles produced in silicate^{93; 102; 103} and borosilicate glasses^{48; 98}. The presence of the SPR band has almost no effect on the absorption related to Cu^{2+} ions, thus indicating that not all copper ions were reduced to Cu^0 , but rather remained in the oxidized state. As it can be seen in Fig. 5.2a, the increase of the heat treatment time leads to an increase of the SPR band up to 20 minutes, after which, the process seems to get saturated, as it has been verified by the similar absorption spectra observed in the samples treated for 20 (iii) and 120 minutes (iv). It is important to point out that the appearance of the SPR band is directly related to metallic nanoparticles¹⁰⁴. Most of the works regarding the growth of copper nanoparticles inside glasses matrix uses some physical nucleation processes, such as ion implantation and infrared laser irradiation before the heat treatment. However, in this work, the growth of nanoparticles is achieved just by heat treatment, carried out at the glass transition temperature. Such result can be confirmed by the TEM micrograph in Fig. 5.2b, in which quasi spherical Cu-NPs measuring around 15 nm are observed.

Fig. 5.2: a) Absorption spectra of the tungsten pyrophosphate glasses containing 0.5 mol % of CuO (i) no thermally treated and thermally treated for (ii) 5 minutes, (iii) 20 minutes, and (iv) 120 minutes at 410° C; b) High magnification TEM micrographs of the PW-120 sample.

Source: By the author.

To verify and confirm the growth of nanoparticles, as well as their chemical nature, a high resolution transmission electron microscopy (HRTEM) was performed for the sample PW-120. Fig. 5.3a presents a HRTEM image showing the nanoparticles synthesized by heat treatment at 410 °C for 120 min. The images show the formation of quasi spherical nanoparticles with different sizes, ranging from 5 to 15 nm in diameter. The Fig. 5.3b displays the selected area electron diffraction (SAED) pattern, in which the crystallographic planes (111), (311) (200) and (220) could be identified (JCPDS – 04-0836), thus confirming the formation of a cubic copper structure.

Fig. 5.3: a) High resolution TEM micrograph of the PW-120 sample; b) SAED pattern containing the crystallographic planes of cubic Cu structure related to the NPs.

Source: By the author.

As it is known, the formation of nanoparticles involves two distinct processes: (i) reduction of the metal ions followed by a (ii) heat treatment at temperatures up to T_g . At these temperatures the glass viscosity greatly decreases, allowing for the diffusion and aggregation of metallic atoms due to their mobility through the glass network, which leads to nanoparticles formation. In our case, however, we have not used a nucleation process before the heat treatment, and not even annealing temperatures above glass transition. Thus, we suggest that the nucleation occurs during the cooling time of the melt into the pre-heated mold. In the short time interval of cooling, the copper ions have enough time to diffuse inside the host, reduce and create small clusters of metallic Cu from divalent copper ions used as raw material.

The direct dependence of Cu-NP nucleation on the temperature of the pre-heated mold is clear. When the mold is cold, or heated at temperatures below the glass transition, T_g (e.g. $T_g = 410\text{ }^\circ\text{C}$), the annealing with $T = 410\text{ }^\circ\text{C}$ used in this work is not enough to change the color of the samples and to create the SPR band at the visible range (which indicating the presence of metallic copper nanoparticles). On the other hand, when the mold is pre-heated at temperatures very close to T_g (e.g. $T_g - 20\text{ }^\circ\text{C}$ from $T_g - 80\text{ }^\circ\text{C}$), the obtained sample presents the same color than those obtained using cold mold, plus the fact that no SPR band appears. However, after annealing at $410\text{ }^\circ\text{C}$ for different times, the changes in the color of the samples and the appearance of the metallic copper SPR absorption band centered at 560 nm are clearly observed.

This process can be understood when considering that the melt temperature is high enough to lead a range of different phenomena producing free electrons, e.g. oxygen losses and/or redox reaction, and structural holes which trap these electrons inside the random glass network after cooling. By raising the temperature of the glass sample at T_g , the nucleus, which was already formed during cooling can grow or accrete, favoring the formation of larger secondary nanoparticles (clustering). Thereby, due to their mobility at T_g , the unreduced Cu^{2+} ions can capture free electrons caged to form reduced Cu^0 atoms, which are also thermally induced clustering to form metallic nanoparticles ². We must also consider the large amount of valence electrons in Pb atoms.

Glasses containing metallic nanoparticles are expected to be promising materials for photonic applications on account of the ultrafast response times, and the high nonlinear optical properties associated to the SPR ¹⁰⁵. In Fig. 5.4, we present the

nonlinear refractive index (n_2) spectrum of the copper doped $\text{Pb}_2\text{P}_2\text{O}_7\text{-WO}_3$ glass without nanoparticles (0 min), and for those thermally treated during 5 and 120 min. The results obtained for the PW-20 glass are not shown because they are similar to the one obtained for PW-120. The solid line in Fig. 5.4 (right axis) displays the linear absorption spectrum of each sample to aid the interpretation of the n_2 data. For all the samples and wavelength range analyzed, we have obtained a positive n_2 with magnitude on the order of $2.0 \times 10^{-19} \text{ m}^2/\text{W}$, which is in the same order of the values found for the lead borate and the lead germanate glasses^{62; 76}. However, the n_2 values obtained for the samples containing Cu nanoparticles and Cu^{2+} are almost three times higher than the ones reported for the pure $\text{Pb}_2\text{P}_2\text{O}_7\text{-WO}_3$ glassy matrix at 800 nm¹⁰. Such an increase is not directly associated to the presence of the metallic nanoparticles, once a similar n_2 value was obtained for the copper doped sample without nanoparticles (Fig. 5.4 a). As it can be seen in Fig. 5.4, the values of n_2 follow the spectral profile of the linear absorption spectrum. This behavior is more evident in Fig. 5.4a (sample without Cu nanoparticles). Therefore, we have attributed the enhancement of the n_2 to the presence of Cu^{2+} ions, whose higher polarizability at the near infrared region favors the optical nonlinearity of the sample. On the other hand, the effect of the Cu^0 nanoparticles on n_2 can be verified for wavelengths near the SPR band, in which an increase of n_2 is observed at 660 nm for the samples treated for 5 and 120 min. Such enhancement can be understood by the local field enhancement effect, provided by the Cu nanoparticles, on the nonlinear optical response. It is worth mentioning, that for the sample without nanoparticles (0 min), there is no increase of the n_2 values at around 660 nm. Nonetheless, when the excitation wavelength is tuned within the plasmon band (at 580 nm), the value of n_2 presents a small decrease of its magnitude compared to the one at 660 nm, but it is still higher compared to the sample without nanoparticles. This decrease of n_2 inside the SPR band can be related to the inversion of the nonlinear absorption processes, as it will be shown later. Furthermore, the polarization induced by the SPR may lead to a negative contribution for n_2 , decreasing the positive values observed in Fig. 5.4 b and c for wavelengths shorter than 660 nm.

Fig. 5.4: Nonlinear refractive index (left axis - symbols) and linear absorption (right axis - solid line) spectra of a) copper doped glass and; for the samples containing Cu^0 nanoparticles obtained by the heat treatment at 410 °C for b) 5 min and c) 120 min.

Source: By the author.

The behavior of n_2 in the SPR band region can be better understood by the analysis of the nonlinear absorption data shown in Fig. 5.5. The normalized transmittance, obtained from the open-aperture WLC Z-scan measurements at the focus, is shown in Fig. 5.5a as a function of the wavelength. The normalized transmittance values obtained for the sample without nanoparticles are lower than 1, indicating a reverse saturable absorption (RSA) in the whole spectrum. However, for PW-5 and PW-120 (squares and triangles in Fig. 5.5a), we have verified values of normalized transmittance higher than 1 at the plasmon band region (520 – 620 nm), featuring a saturable absorption process (SA) that it is probably related to a depletion of the ground state. In the other regions of the spectrum, a RSA was obtained¹⁰⁵. Thus, the inversion of the nonlinear absorption effect is associated to a saturation of the surface plasmon band absorption⁷³. From the fitting of the normalized transmittance as a function of the z position (Z-scan signature), we were able to obtain the effective nonlinear absorption coefficient (β_{eff}) in the white light spectrum, in intervals of 5 nm, as shown in 5.5b. It is important to remark that, the so called β_{eff} presented herein is associated to the excited state absorption processes. As one can see, the copper doped glass devoided of nanoparticles has positive β_{eff} values that are increased when the excitation energy approaches the linear absorption, as a consequence of the resonant enhancement. Because of the plasmon band, the samples PW-5 and PW-120 presented negative nonlinear absorption coefficient between 520 – 620 nm.

Fig. 5.5: a) Experimental (line) and fitting (symbols) of the normalized transmittance spectra at the focus position ($z=0$) for glass with (5 and 120 min) and without (0 min) CuO nanoparticles. b) Spectra of excite state absorption coefficient for the analyzed samples. The PW-20 spectrum was omitted because it is very similar to the PW-120 one.

Source: By the author.

Another interesting feature of the copper doped $\text{Pb}_2\text{P}_2\text{O}_7\text{-WO}_3$ glasses is related to the response time of the optical nonlinearity. Fig. 5.6a shows the temporal evolution of the normalized transmission for all samples at 780 nm, in which it was observed an OKG signal of 200 fs, similar to the pulse duration. Thus, the lifetime of the nonlinear process associated to the Cu^{+2} absorption band is faster than the pulse duration, so as to indicate an ultrafast electronic process. A similar behavior was obtained for the excitation at 500 and 620 nm. Conversely, no OKG signal was detected at 560 and 580 nm, which are wavelengths within the plasmon band. Fig. 5.6b presents the results of transient transmittance (pump-probe configuration) for excitation at 560 nm. In this case, no signal was detected for the sample without nanoparticles (circles), while a

mono-exponential behavior was observed for the samples thermally treated during 5 and 120 min (squares and triangles), thus indicating that the lifetime of the electrons associated to Cu^0 nanoparticles is of 2.3 ± 0.4 ps. Such response time corresponds to the electron-phonon interaction, and it is in agreement with the ones reported for metallic copper nanoparticles ¹⁰⁶.

Fig. 5.6: a) Optical Kerr Gate signal of Cu doped tungsten pyrophosphate glasses without heat treatment (0 min) and thermally treated for 5, 20, and 120 min excited at 780 nm. b) Transient transmittance of the samples excited at 560 nm, within the plasmon band. The inset displays the linear behavior for a logarithmic scale of the 5 and 120 min samples.

Source: By the author.

5.4 Conclusions

We have synthesized copper doped tungsten pyrophosphate glasses containing Cu^0 nanoparticles and analyzed their nonlinear optical properties. Metallic copper nanoparticles are easily grown in the doped matrix by heat treatment at 410 °C during 5 minutes or longer times. The presence of Cu^{2+} improves the nonlinear refraction in the visible and near infrared region. Samples containing Cu nanoparticles also present an enhancement of the nonlinear refractive index when the energy of the excitation source approaches the surface plasmon resonance band. However, the decrease observed on the n_2 values within the plasmon band may be associated to a negative contribution of n_2 , on account of the surface plasmon absorption. In fact, we have observed that the Cu^0 nanoparticles promote saturation of the absorption in the region of the surface plasmon resonance band, while the reverse saturation of the absorption was obtained for the other spectral regions, as well as for the sample without nanoparticles. Furthermore, the

energy exchange from the excited electron of the nanoparticles to the matrix occurs in a time interval of 2.3 ps, featuring an electron-phonon interaction, while the dynamics of the optical nonlinearity associated to Cu^{+2} displays a response time shorter than 200 fs. Despite any future applications, the glasses analyzed in this chapter are interesting materials for all-optical devices, since they exhibit a high nonlinear refractive index, low nonlinear absorption coefficients and ultrafast response times.

6. Metallic nanoparticles grown in the core of femtosecond laser micromachined waveguides[†]

Tridimensional-waveguides containing silver nanoparticles have been fabricated in tungsten lead–pyrophosphate glass by femtosecond laser micromachining. Nucleation and growth of nanoparticles occur in a single step process when high repetition rate laser (MHz) is employed, while an additional annealing is required for the irradiation using kHz laser system. The presence of nanoparticles locally changes the refractive index and, therefore, the elliptical structures produced by direct laser writing were able to guide light. By increasing the pulse energy applied during the micromachining, the waveguide size increased from 2 to 30 μm , while their propagation loss decrease from 1.4 to 0.5 dB/mm at 632.8 nm.

6.1 Introduction

Glasses are promising candidates for the development of technological applications on the account of their relatively easy manipulation, which makes it possible to fabricate them in different sizes, shapes and compositions. Among these features, the ability of change the glass composition can be pointed out as one of the most relevant, once it determines the material properties and performance ². Thus, several glass-formers and modifiers have been exploited for new technologies in optics and photonics. For instance, tungstate-phosphate glasses have been demonstrated to be a promising material due to their attractive linear and nonlinear optical properties. Their P–O–W bond results in a highly connected network, which is also favorable for further addition of WO_3 that increases the polarizability, and consequently the optical nonlinearities of the glass matrix ⁹. In the same direction, the addition of heavy metal oxide also increases the material's nonlinearity, a desirable feature for photonic devices.

[†] Already published, please see in Journal of Applied Physics ¹⁰⁷ or DOI: [10.1063/1.4875485](https://doi.org/10.1063/1.4875485).

Lead oxide has been a great glass modifier, providing suitable figures of merit for all-optical switching, $n_2/\beta\lambda > 1$, in which n_2 is the nonlinear index of refraction and β the two-photon absorption coefficient^{10; 62; 108}. Tungsten lead–pyrophosphate glasses have demonstrated an ultra-fast electronic (100-200 fs) third-order nonlinearity with a nonlinear index of refraction one order of magnitude higher than fused silica^{10; 109}. Furthermore, this glass matrix can be successfully used to form metallic nanoparticles, upon adding the desired metal to the matrix, affecting its nonlinearities at the plasmon band region¹⁰⁹.

Despite the good features displayed by tungsten lead–pyrophosphate glasses, they have not yet been exploited for the development of device applications. To accomplish this task, the choice of the proper material processing method is crucial. Among the techniques for the fabrication of photonic devices, femtosecond laser micromachining has unique advantages that enable processing the material's bulk within the micrometer scale, without damaging its surface²³. In addition, as a consequence of the nonlinear interaction during micromachining, the optical properties can be locally changed, resulting in different absorption coefficient, refractive index and structure²⁴. For instance, the spatially controlled growth of metallic nanoparticles in glass using femtosecond laser irradiation has been demonstrated^{22; 25; 110; 111}. The control of such properties in a confined region makes possible the development of photonic devices, as waveguides, splitters, resonators and microfluidic channels^{23; 24}.

Fabrication of waveguides in materials with promising optical nonlinearities has been the subject of several studies aiming at integrated photonic devices. Most of these studies, however, concern planar structures, in which three or more layers of thin films are deposited on substrates by conventional methods, such as chemical vapor deposition, ion-exchange and sol-gel¹¹². On the other hand, by using fs-laser micromachining direct writing of 3D-waveguides in glass can be realized. Glass composition, laser parameters and experimental settings, i.e., wavelength, repetition rate, numerical aperture and scan speed, affect the waveguide features. Hence, depending on the experimental conditions, fs-laser micromachining can lead to waveguides with refractive index changes from 10^{-4} - 10^{-2} , resulting in propagation of fundamental or higher-order modes, and loss ranging from 0.7 to 4.0 dB/cm^{15; 23; 24; 113; 114}. In this direction, the purpose of this chapter is to study the nonlinear optical properties of tungsten lead–pyrophosphate glass and femtosecond laser

micromachining to produce waveguides containing metallic nanoparticles in its core, using one-step laser processing.

6.2 Materials and methods

The preparation method, structure, thermal and optical properties of the $70\text{Pb}_2\text{P}_2\text{O}_7 - 30\text{WO}_3$ (mol %) glass were recently described in ref. ⁹. Its refractive index at 633 nm, glass transition and crystallization temperatures are 1.9, 432 °C and 520 °C, respectively. This sample was doped with 1 mol% of AgCl during the melting, in order to obtain metallic silver nanoparticles (Ag NPs) by fs-laser micromachining.

The two Ti:Sapphire lasers described in Chapter 3, amplifier (1 kHz, 400 μJ , 150 fs) and oscillator systems (5 MHz, 100 nJ, 50 fs), were used in this study. Experimental procedure related to sample micromachining and light coupling/losses of waveguides were reported in sections 3.2 and 3.3, respectively.

The formation of Ag NPs was verified using linear absorption spectroscopy (Shimadzu UV-1800) and transmission electron microscopy – TEM (Tecnai G2 F20 - 200 kV) performed in a grating pattern (160 lines, 3 mm long, separated by 15 μm) produced by direct laser writing using pulse energy of 30 nJ and an scan speed of 100 $\mu\text{m/s}$.

6.3 Results and discussions

The absorption spectrum of the as prepared silver doped glass, displayed in Fig. 6.1 (curve A), shows that the sample is transparent at the visible and near infrared, where fs-laser excitation is performed. The UV absorption edge corresponds to a band gap energy of 3.2 eV. A color change was observed after the fs-laser irradiation using the oscillator system (5 MHz repetition rate), as shown in the inset of Fig. 6.1. Such color corresponds to a broad absorption band, centered at 470 nm (spectrum B), that corresponds to the surface plasmon resonance of metallic nanoparticles. It is known that the frequency, bandwidth and intensity of the plasmon band are affected by the size, shape and dielectric environment surrounding the nanoparticles ¹⁹. In general, the surface plasmon resonance of silver nanoparticles in oxide glass is located at 450 nm ¹¹¹. Thus, the absorption band at 470 nm in the spectrum B of Fig. 6.1 indicates that Ag^0 NPs have been generated during fs-laser irradiation. Nonetheless, we used TEM and electron diffraction to verify the presence and composition of the NPs, as illustrated in Fig. 6.2.

Quasi-spherical NPs, with diameter around 10 nm, were observed and the (111), (200), and (311) crystallographic planes of silver were indexed (crystmet database, #35881).

Fig. 6.1: Linear absorption spectrum of (A) as prepared 70 $\text{Pb}_2\text{P}_2\text{O}_7$ – 30 WO_3 : 1 AgCl (mol %) glass; and (B) after the irradiation with fs-laser (oscillator system – $E_p = 30 \text{ nJ}$, 50 fs and 5 MHz of repetition rate), using a scan speed of $100 \text{ }\mu\text{m/s}$ to produce a grating pattern of 160 lines with 3 mm, separated by $15 \text{ }\mu\text{m}$. The inset shows the difference between the irradiated and no irradiated regions of the sample.

Source: By the author.

Fig. 6.2: TEM image and electron diffraction pattern obtained from the sample after fs-laser irradiation.

Source: By the author.

The silver doped tungsten lead–pyrophosphate glass was also micromachined using an amplified laser system, with repetition rate of 1 kHz (150 fs, $E_p = 380 \mu\text{J}$). In this case, showed in Fig. 6.3, the irradiation resulted in an increase of the absorbance for the visible region of the spectrum ($\alpha=1.6 \text{ cm}^{-1}$) due to the formation of color center and reduction of silver ions ^{25; 111; 115}. A small plasmon band was observed at 485 nm only after a heat treatment, performed at 400 °C for 1h, as displayed in the inset of Fig. 6.3. The effect of color centers caused by the irradiation using the MHz laser can be ruled out, since the plasmon band overcomes any absorption caused by the color center.

Fig. 6.3: Linear absorption spectrum of (A) as prepared 70 $\text{Pb}_2\text{P}_2\text{O}_7$ – 30 WO_3 : 1 AgCl (mol %) glass; and (B) after the irradiation with fs-laser (amplifier system – 380 μJ , 150 fs and 1 kHz of repetition rate), using an scan speed of 100 $\mu\text{m/s}$ to produce a grating pattern of 160 lines with 2.5 mm, separated by 15 μm . The inset shows the absorption spectrum after irradiation and further annealing at 400 °C for 1h along with the samples picture.

Source: By the author.

It is known that high power laser and ionizing radiation result in photoelectrons in oxide glasses, which move through the solid at high speed leading to secondary electrons and holes ¹¹⁶. These secondary electrons and holes are trapped by defects in the glass matrix producing new electronic configurations that are understood as color centers ^{115; 117}. In the case of femtosecond lasers in transparent glasses, free electrons are generated due to nonlinear optical interactions, as photoionization and avalanche

ionization^{23; 24}. The former directly promotes electrons from the valence to the conduction band by multiphoton absorption, while avalanche ionization requires seed electrons already in the conduction band, which keep absorbing energy from the photons until it has enough energy to transfer an electron from the valence to the conduction band by collision⁴³. In this way, the generated electrons can be trapped (color center), or interact to the ions in the glass matrix, resulting on the photoreduction of the Ag^+ , which is fundamental for the nanoparticle nucleation. Finally, its growth happens due to atomic mobility promoted by some heating process¹¹¹.

Although fs-lasers are known for avoiding thermal effects during the light-matter interaction, depending on the repetition rate local heating can occur due to the cumulative effect⁴¹. For the oscillator system (5 MHz), the time interval between two subsequent laser pulses is 200 ns, that is shorter than the heat diffusion time out of the focal volume – generally 1 μ s for high numerical aperture lenses. Therefore, metallic nanoparticles are generated in an one-step laser processing, since the heat promotes aggregation of the reduced metal atoms into nanoparticles. On the other hand, for the amplified system, pulses are delivered every 1 ms, resulting on enough time to the lattice cool down before the next pulse arrives, preventing the cumulative heat effect. Thus, when lasers with kHz repetition rate are employed, a further annealing is required to promote the growth of nanoparticles.

The process of nanoparticle formation in glass by femtosecond laser exposure can be summarized according to the eqs. (1-3), which describe the free electron generation due to nonlinear optical interactions (eq. 1); the photoreduction of silver ions (eq. 2); and the agglomeration of the neutral atoms as a consequence of heat caused by high repetition rate lasers or thermal treatment (eq. 3)¹¹⁸.

It has been reported that the presence of silver NPs in silicate glasses leads to increase of the refractive index in 4.6% (or $\Delta n = 7.10^{-2}$)¹¹⁹. Thus, the micromachined structures containing Ag NPs should be able to act as waveguide. Furthermore, recent studies have suggested that high repetition rate lasers present some advantages over the low repetition rate systems, for providing more symmetric and circular structures on account of the heat deposited by successive pulses^{41; 113}. For this reason we have

performed the light coupling experiments only in the structures fabricated with the oscillator. Images of the waveguides fabricated with $E_p = 35$ nJ and 60 nJ, as well as their near-field distribution of the light guided at 632.8 nm are shown in Fig. 6.4 and 6.5, respectively. A representative top view image of the waveguides is illustrated in Fig. 6.4a. We observed an increase of the waveguide size from 2 to 30 μm , when the pulse energy used for the micromachining was increased. The waveguide shape also depends on the pulse energy; for the lower pulse energy (Fig. 6.4b) we obtained an elliptical shape, with a dark region at the center, and a more circular structure with the dark region at the bottom for the higher energy (Fig. 6.5a). The dark region reveals a preferential aggregation of the NPs in such positions. The preferential accumulation of metallic NPs at the lower region has already been observed for silicate and borosilicate glasses shined with fs-lasers^{25; 119}. Such behavior might be due to the non-uniform laser intensity distribution, as a consequence of the spherical aberration caused by high numerical aperture of the focusing lens¹¹⁰, or because of the self-focusing effect, that happens when materials with $n_2 > 0$ are exposed to high laser intensities²⁵. However, although the dark regions present a higher amount of nanoparticles, it is reasonable to assume that in the rim outside such region nanoparticles are also present, but in a smaller concentration, since Ag atoms could diffuse to the boundary regions due to fs-laser induced temperature gradient^{42; 120}.

Independently on the NP distribution, both structures were able to guide light at 632.8 nm, indicating a positive refractive index change at the irradiated regions. As waveguides have been demonstrated in different glass due to structure modification after femtosecond laser exposure²⁴, it is reasonable to assume that the light confinement observed in Fig 6.4c and 6.5-b,c results from a combination of the presence of nanoparticles and structural modification. Because the nanoparticle formation happens in a single step process, it is not possible to distinguish the contribution of each process on the refractive index change. Nonetheless, based on the literature, we suggest that the main contribution is caused by the nanoparticles, once $\Delta n = 1.4 \times 10^{-3}$ ¹¹³ has been observed on account of structural modification whereas 7×10^{-2} ¹¹⁹ when silver nanoparticles are produced by direct laser writing in silicate glasses.

Fig. 6.4: Optical microscopy images of the waveguide fabricated with the oscillator laser (5 MHz of repetition rate), using pulse energy of 35 nJ, scan speed of 10 $\mu\text{m/s}$ and $\text{NA} = 0.65$. a) and b) show the top and end views respectively, while c) displays the near-field output profile of the light guided at 632.8 nm.

Source: By the author.

Fig 6.5: a) End view of the waveguide fabricated with pulse energy of 60 nJ, focused 200 μm below the sample's surface using $\text{NA} = 0.65$, scan speed of 10 $\mu\text{m/s}$ and 5 MHz of repetition rate; and b) different light guided profiles at 632.8 nm obtained by changing the coupling alignment.

Source: By the author.

In general, the light propagation occurs at the periphery of the structures, as seen on the near-field output pattern of Fig. 6.4c and 6.5b. Nonetheless, in the case of the waveguide fabricated with $E_p = 60$ nJ the light coupling also happens at the head of the structure, as shown in Fig. 6.5c, indicating a non-uniform refractive index distribution. Such feature seems does not agree to the expected result, once the region with high nanoparticle contraction should present an enhancement of Δn and, therefore higher

light confinement. However, the light guided (632.8 nm) can be absorbed and scattered by nanoparticles. Thus according to the increase of nanoparticles there is a decrease of the transmittance. This trade-off between higher index of refraction and raise of absorption and scattering defines if there will be light guiding in a specific region. That is the main reason why the guiding was not observed at those regions of preferential accumulation of nanoparticles and the light confinement happens in the structure's rim, where the refractive change overcomes the absorption and scattering.

We have analyzed the optical loss of those waveguides measuring their transmittance at 632.8 nm for the whole (5.7 mm) and half-length waveguide. It is difficult to report the losses with accuracy due to the high dispersion of the transmittance values, given the nature of the waveguides. Nonetheless, for the waveguide fabricated with $E_p = 35$ nJ we obtained a propagation loss of 1.4 dB/mm and coupling loss of 9 dB, while for the waveguide fabricated with $E_p = 60$ nJ we found 0.5 dB/mm and 11 dB, respectively. Such values correspond to an average of at least ten measurements. The differences between both waveguides are related to their sizes and refractive index distributions. Waveguides fabricated in silicate glass slides (Corning 0215) using the same method have propagation loss of about 0.3 dB/mm at 632.8 nm¹¹³. It is important to point out that at 632.8 nm, the glass containing silver nanoparticles has an absorption coefficient of 0.8 cm^{-1} (corresponding to an absorption loss 0.35 dB/mm) associated to the plasmon band (see Fig. 6.1). Thus, the optical losses can be attributed not only to the light scattering due to the roughness of the waveguide, but also to absorption at 632.8 nm. In spite of those losses, the waveguides reported herein are still interesting for photonic applications, since short optical path are required. In addition, the waveguide efficiency is expected to be better for the infrared wavelengths, where there is no absorption and scattering are minimized.

6.4 Conclusions

Femtosecond laser micromachining has already been used to fabricate 3D waveguide in glass, as well as to grow metallic nanoparticles in controlled regions. In this chapter we have shown how both features can be encompassed to produce waveguides containing nanoparticles using one-step laser processing. We have also

characterized the propagation mode and losses of those waveguides when low and high pulse energy is applied for the fabrication. Nucleation and growth of silver nanoparticles in lead–pyrophosphate glasses arise from the photoreduction of the Ag ions and their aggregation, as a consequence of the free electron generation and the local heat, provided by the irradiation with femtosecond laser pulses with repetition rate of MHz. When amplified laser system with kHz of repetition rate is employed, a subsequent annealing is required to grow the nanoparticles, since there is no local heating during the laser exposure to aid metal agglomeration. By increasing the pulse energy from 37 to 60 nJ the waveguide size increased from 2 to 30 μm , while their propagation loss decreased from 1.4 to 0.5 dB/mm at 632.8 nm. Optical microscopy images showed a preferential accumulation of nanoparticles in the center of the smaller waveguide and at the bottom of the bigger one. Such behavior is associated with the light intensity distribution profile, which can be affected by the self-focusing. Therefore, the light guiding was observed at the peripheral regions of the structures, suggesting a non-uniform refractive index distribution.

7. Fs-laser induced copper nanoparticles and waveguides in borosilicate glass

In the previous chapter we showed how to obtain waveguides containing metallic silver nanoparticles by fs-laser direct writing. Herein, we demonstrated the same achievements for copper NPs in a borosilicate matrix. Due to the similarities on the physical mechanism behind nucleation and growth of NPs by ultrashort laser pulses discussed in Chapter 6, the current chapter focuses on the experimental results, based on the waveguides features. Roughly cylindrical core waveguides with diameters around 5 μm and multimode profile at 632.8 nm have been obtained. Also, elliptical monomode waveguides have been produced, which revealed the best propagation loss, 1.3 ± 0.1 dB/mm.

7.1 Introduction

Femtosecond laser micromachining has been proved to be a powerful method for fabricating microscopic structures inside transparent materials with high spatial resolution, due to its nonlinear optical interaction. Moreover, it is possible to achieve the spatial control of nanoparticles precipitation in very confined regions of amorphous materials. Glasses containing metal nanoparticles have been considered promising for several technological applications in the fields of optics and photonics. Recently, several studies on the production of metallic nanoparticles in glass by femtosecond laser excitation have been carried out ^{22; 47; 111}. Most of the papers, however, have been focused on gold and silver nanoparticles, and little attention has been given to copper, which has shown high optical nonlinearities ⁷⁰. For example, K. Uchida and co-authors reported that the third-order nonlinear susceptibility of copper nanoparticles (χ_m^3) is three order of magnitude higher than silver, while it is two orders of magnitude higher than gold ^{20; 70}. It is worth to point out that these optical susceptibilities are from the NPs themselves, and lower third-order nonlinearities are observed when dispersed in glass

matrix²⁰ Even so, copper NPs in glass are interesting because they are cheaper, and show many similar properties compared to other noble metals. Also its plasmon band lies in a red-shifted region of visible spectrum, being important for optical spectroscopy.

We previously investigated the ability to produce and control copper NPs in a borosilicate glass, called BSi-Cu, using fs-laser micromachining, as reported in reference²⁵. In this study, an amplifier laser system (1kHz, 150 fs, 400 μ J and 775 nm) was employed, requiring an additional step of heat-treatment to obtaining the NPs. This was the pioneer work developed by Photonics Group-IFSC on fs-laser micromachining in glassy materials, which motivated us to proceed using BSi-Cu sample in investigations about copper NPs into the core of waveguides. For this purpose, we have used the oscillator fs-laser (5 MHz, 50 fs, 100 nJ, 800nm) that enabled to achieve this goal in a single step processing, according to the results described in section 7.3.

7.2 Materials and methods

The copper doped borosilicate glass (50SiO₂ - 17B₂O₃ - 11.5MgO - 10Na₂O - 11.5Al₂O₃):0.1CuO mol% was synthesized by conventional melting-quenching technique, using high purity metallic oxides and sodium carbonate as raw material. A batch of 100 g was melted, using a platinum crucible, in an electric furnace open to the atmosphere during 1 h at 1400° C. The resulting melt was quenched into a preheated stainless-steel mold and annealing at 400° C for 12h to minimize the mechanical stress²⁵.

Glass transition temperature (T_g) was determined by Differential Scanning Calorimetry (DSC), using a Netzsch STA 409C, in Al₂O₃ pans, within a range of 20 to 700° C with a heating rate of 10° C/min, and in a synthetic air atmosphere. From DSC curve we obtained $T_g = 495 \pm 2^\circ \text{C}$ and no exothermic peak was found, indicating that there is no formation of crystalline phases during the heating up to 700° C²⁵.

The optical setup used to produce the NPs was shown in section 3.2, and the results obtained using both laser systems (amplifier and oscillator) are presented herein for comparison purpose. However, the functionality and characterization of optical losses (section 3.3) have been only studied for waveguides produced using the laser with repetition rate of 5 MHz, since no annealing is required for nanoparticle growth.

7.3 Results and discussions

Figure 7.1 displays the absorption spectra of pristine sample (solid line) and after the irradiation using fs-lasers of 5 MHz and 1 kHz of repetition rate, represented respectively by dotted and dashed curves[†]. Copper doped glass originally presents a wide absorption band from 550-1000 nm due to the presence of Cu^{+2} ions, which confer the bluish color to the sample ²⁵. The plasmon band associate with copper NPs is readily observed at 570 nm, after the irradiation with the oscillator laser (dotted line). On the other hand, the dashed spectrum exhibits an increase of the absorbance for wavelengths smaller than 700 nm, caused by irradiation with amplified laser. Such increase is related to electronic states created by the photoionization. They represent color center formations as well as photoreduction reactions, which lead to a preferential light absorption ^{22; 115; 121}. Particularly, Cu^0 atoms cause a broad absorption band around 450 nm, indicating that the irradiation with 1kHz laser induced the nucleation but not the growth of copper nanocrystals. The diffusion and aggregation of Cu^0 species was further achieved by a heat treatment at 600° C during 1h. Then, surface plasmon resonance was observed only in the irradiated region, resulting in an absorption spectrum quite similar to the dotted curve in Fig. 7.1.

Fig. 7.1: Absorption spectra of the copper-doped borosilicate glass. Solid line represents the glasses as prepared, while dotted and dashed lines are the spectra after the irradiation with fs-lasers of 5 MHz and 1 kHz repetition rate respectively[†]. Surface plasmon resonance of Cu^0 is seen at 570 nm. The inset shows the formation of copper NPs only in the irradiated regions by oscillator laser.

Source: By the author.

[†] The irradiation with amplified laser was carried out using $v = 100 \mu\text{m/s}$ and $E_p = 470 \mu\text{J}$ ($P_{av} = 470 \text{ mW}$), while for oscillator laser $v = 10 \mu\text{m/s}$ and $E_p = 74 \text{ nJ}$ ($P_{av} = 370 \text{ mW}$), both using $\text{NA} = 0.65$.

As previously discussed (Chapter 6), the formation of metallic NPs is a consequence of the free electron generation and photoreduction of ions in the matrix (in this case Cu^{2+}) caused by nonlinear optical interactions, featuring the nucleation process. The growth is further achieved due to a heating, provided by the cumulative effect from MHz laser or additional annealing, as performed when using repetition rate of kHz. Taking advantage of the ability to produce and to control NPs in very confined regions in the glass matrix using a single-step processing, we have fabricated waveguide structures containing the core composed by copper NPs. Figure 7.2 shows the cross-section and top view optical images of a representative waveguide, micromachined using the laser oscillator, pulse energy of 74 nJ and 10 $\mu\text{m}/\text{s}$ of scan speed. The near-field profile at 632.8 nm is displayed on the right-hand side of Fig. 7.2, where is clearly noticed multimode propagations, similar to LP_{21} .

Fig. 7.2: Cross- and longitudinal sections (top view) of the waveguide produced 200 μm deep into BSi-Cu glass using the oscillator laser ($v=10 \mu\text{m}/\text{s}$, $E_p=74 \text{ nJ}$, $\text{NA} = 0.65$), which results in the precipitation of Cu^0 NPs. Right-hand panel is the near field image, showing the multimode propagation (LP_{21}) at 632.8 nm.

Source: By the author.

It is worth remembering that we have applied transversal laser writing, which usually in elliptical cross-sections (see literature review in section 3.1.2). Nonetheless, the waveguide in Fig 7.2 has an approximately elliptical shape with diameter close to 5 μm . We could not evaluated the guided modes as a function of the waveguide size by increasing the pulse energy, as performed in Chapter 6, because the production of Cu^0 NPs and waveguides reported herein requires full laser power. Despite this, it was investigated the effect of focusing the fs-laser deeper into the glass (+ 100 μm) during the micromachining, but keeping the other experimental conditions. The resulting waveguide is illustrated on Fig 7.3, where elliptical cross-section and propagation of the fundamental mode are observed. Major and minor axes of ellipse are ~ 7.5 and 2 μm , respectively. The longitudinal section (top view image) is not shown because it not observable using standard optical microscope. We also investigated the effect of scan speed in the deeper waveguides. By increasing the velocity from 10 - 100 $\mu\text{m}/\text{s}$ no variation was observed on waveguide size, but there was an increase on the propagation

loss, while insertion loss kept the same, as summarized in Table 7.1 for all studied waveguides.

Fig. 7.3: Cross-section and propagation of fundamental mode for a waveguide produced 300 μm deep into BSi-Cu glass using the oscillator laser ($v=10 \mu\text{m/s}$, $E_p=74 \text{ nJ}$, $\text{NA} = 0.65$), which results in the precipitation of Cu^0 NPs.

Source: By the author.

Table 7.1: Coupling and propagation losses at 632.8 nm for different scan speeds and depths of micromachining, using the oscillator laser into BSi-Cu glass.

Scan speed	Waveguide depth	Mode	Coupling loss (dB)	Propagation Loss (dB/mm)
10 $\mu\text{m/s}$	200 μm	LP_{21}	2.30 ± 0.01	3.5 ± 0.1
10 $\mu\text{m/s}$	300 μm	LP_{01}	11.7 ± 0.7	1.3 ± 0.1
50 $\mu\text{m/s}$			10.9 ± 0.8	2.40 ± 0.04
100 $\mu\text{m/s}$			11.8 ± 0.3	2.4 ± 0.1

The reason for that the waveguide in Fig 7.2 is not elliptical, as usually obtained in the transversal micromachining, can be associated with the high threshold of optical breakdown of borosilicate glass. It is known that modifications in glass appear above a certain irradiation threshold, which depends on the laser intensity³⁶. Based on the cross-section of waveguide, we believe to be working close to threshold of optical breakdown. Thus, only the central part of the laser beam induces nonlinear processes, leading to modifications caused by a small fraction of focal volume, figured out by confocal parameter ($b = 2\pi w_0^2/\lambda$)³⁶. On the other hand, the elliptical cross-section observed when the laser was focused deeper into the glass is related to spherical aberration^{36; 122}. The microscope objectives used for fs-laser micromachining are designed for observations on sample surface, in a way to correct spherical aberration for the beam propagation in the air. When the focus is set within the sample this aberration comes to be significant, resulting in elongated waveguides. A. Ferrer et al. reported a

variation of $\sim 20\%$ on aspect ratio of waveguides when the depth was nearly doubled, using fused silica and kHz system for micromachining¹²².

The size and refractive index change of the elliptical waveguide favored the guide of fundamental mode at 632.8 nm. Thus, the propagation losses of the deeper waveguides are smaller when compared to the multimode one, that due to its cylindrical symmetry displayed a better coupling loss. Considering monomode waveguides, the decrease of laser scan speed provided the reduction of propagation loss (2.4 – 1.3 dB/mm), as shown in Tab. 7.1. Such improvement can be related to a better waveguide roughness or a better refractive index contrast caused by the concentration of copper nanoparticles.

7.4 Conclusions

In this chapter we demonstrated the fabrication of 3D waveguides containing copper nanoparticles, using the direct laser writing in a borosilicate glass. Although both lasers, high and low repetition rate, enable the nucleation of nanoparticles, the growth is directly achieved when using high repetition rate due to the increase of local temperature. Thus, waveguides containing copper nanoparticles can be produced using a single laser scan. Elliptical or cylindrical waveguides were obtained, depending on the beam penetration depth. While cylindrical waveguides displayed the propagation of multimode with lower coupling loss (2.30 ± 0.01 dB), the elliptical waveguides showed the propagation of fundamental mode with lower propagation loss, obtained for slower laser scan speed (1.3 ± 0.1 dB/mm).

Chalcogenide Glasses

8. Single-step synthesis of silver sulfide nanocrystals in arsenic trisulfide[†]

Silver sulfide nanocrystals and chalcogenide glasses (ChGs) are two distinct classes of semiconductor materials that have been exploited for new infrared technologies. Each one exhibits particular optoelectronic phenomena, which could be encompassed in a hybrid material. However, the integration of uniformly distributed crystalline phases within an amorphous matrix is not always an easy task. In this chapter, we report a single step method to produce Ag₂S nanocrystals (NCs) in arsenic trisulfide (As₂S₃) solution. The preparation is carried out at room temperature, using As₂S₃, AgCl and propylamine resulting in highly crystalline Ag₂S nanoparticles in solution. These solutions are spin-coated on glass and silicon substrates to produce As₂S₃/Ag₂S metamaterials for optoelectronics.

8.1 Introduction

Despite all the qualities associated to oxide glasses, as addressed in Part I of this thesis, they are not transparent at medium-infrared, which prevents their application in such spectral region. Chalcogenide glasses (ChGs) are semiconductor materials with interesting optical properties at the infrared region. ChGs have high refractive index ($n \approx 2-3$) and high transmittance over to $\sim 11 \mu\text{m}$ for sulfides, $\sim 15 \mu\text{m}$ for selenides and beyond $\sim 20 \mu\text{m}$ for tellurides ^{4; 124}. Moreover, they present a variety of photosensitive phenomena, including photocrystallization, photodarkening, and photodiffusion, which have motivated numerous researches for decades ^{5; 124}. Since the first observation of metal photodoping in ChGs, many studies have been performed on the diffusion mechanism of silver in amorphous arsenic trisulfide (As₂S₃) ^{125; 126; 127}. Basically, by shining light on As₂S₃, in which a thin metallic layer of silver is deposited, Ag ions can

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readily dissolve, resulting in a homogeneous doped layer. The mechanism has been explained through the initial formation of Ag–S bond at the silver and ChG interface, followed by the generation of electron-hole pairs and by the mobility of holes toward the silver layer, while Ag^+ move in the opposite direction ¹²⁶. Although studies on Ag photodoping in ChGs have achieved considerable advances, the production and investigation of silver-based nanoparticles in these glasses have not received enough consideration.

Recently, the formation of metallic silver nanoparticles in chalcogenide solution using laser ablation of a silver target ¹²⁸ has been studied. Nonetheless, in contrast to metallic nanoparticles that have a plasmon band in the visible or UV portion of the spectrum, semiconductor NPs exhibit localized surface plasmon resonances in the infrared region ^{129; 130}, making them promising for infrared metamaterials. Equally to ChGs, silver sulfide is also a semiconductor with interesting optical properties at the infrared region. It is commonly used as a solid-state electrolyte, presenting both ionic and electronic conduction, and direct bandgap at $E_g \sim 1$ eV ^{131; 132}. On account of the quantum confinement effect when synthesized at the nanometer scale, indirect transitions have been observed in the range of 0.9 – 1.8 eV and direct transitions are blue shifted, to the range 2.7 – 4.0 eV ¹³³. Based on these transitions, new applications have been proposed for silver sulfide, such as, NIR emitters for in vivo imaging ^{134; 135}, sensitizers for solar cells ¹³⁶, and substrates for surface-enhanced Raman scattering (SERS) ¹³⁷. Therefore, semiconductor NCs and quantum dots are of great interest for their use in several applications from optoelectronics to biological systems^{138; 139}.

To the best of our knowledge, the synthesis of silver sulfide nanoparticles in ChGS has not been demonstrated yet. In this sense, we report in this chapter a one-step in-situ synthesis of uniformly dispersed Ag_2S nanoparticles in As_2S_3 . The raw materials (As_2S_3 and AgCl) are diluted in an amine solvent and solid-state As_2S_3 :NCs films are prepared by spin-coating the solution on glass or silicon substrates. Such approach enables fabricating samples with arbitrary shapes using soft lithographic processes ⁶, which is an advantage over other conventional methods like vacuum coating or pulse laser deposition.

8.2 Materials and methods

Solution-processing of ChGs in amine solvents has been long established, and the dissolution mechanism involves an electrophilic substitution reaction, where As atoms are attacked by the lone pair electron associated with the amine group ^{6; 140; 141}. The chemical synthesis employed in this study consists of the dissolution of arsenic trisulfide (alfa aesar 99.999%) in n-propylamine (C_3H_9N Sigma-Aldric >99%), with a concentration of 133g/L. The dissolution was performed at room temperature, and usually takes 24h to be completed for a solute-solvent ratio of 1 g/7.5 ml. In order to produce Ag_2S NPs in-situ, silver chloride (Alfa Aesar 99.997%) was dissolved in n-propylamine (80g/L), and then, both solutions, arsenic sulfide and silver chloride, were mixed together in a ratio of 1ml of As_2S_3 to 0.25ml of $AgCl$. The reaction readily occurs, resulting in the formation of silver sulfide NPs in suspension. Due to the absence of stabilizing agents, the reaction also produces a dark precipitate. Figure 8.1 summarizes the chemical synthesis and shows pictures of each solution used during the experimental procedure. It is important to point out that no heating or expensive instruments were employed for the synthesis of NCs in chalcogenide solution, featuring a facile, fast and low cost method.

Fig. 8.1: Chemical synthesis used for the preparation of Ag_2S nanoparticles in As_2S_3 solution. From left to right: pictures of As_2S_3 (133 g/L), $AgCl$ (80g/L) and $As_2S_3+Ag_2S$ NPs solutions, in which propylamine (C_3H_9N) is the solvent.

Source: By the author.

The absorption spectra of the solutions were recorded with a Cary-5000 spectrometer and the nanocrystals were investigated with a Philips CM200 transmission electron microscope (TEM), operating at 200kV, also employed for electron diffraction measurements. Sample preparation for TEM analyses consisted of drop coating a diluted solution (60x with propylamine) over copper grids with a carbon film support. Size

distribution was investigated by dynamic light scattering (DLS) measurements using the upper portion of $\text{As}_2\text{S}_3/\text{AgCl}$ solution. The reaction residue was investigated with a Bruker-D8 x-ray diffractometer, from $30\text{--}60^\circ$ (2θ), with steps of 0.02° , using $\text{Cu K}\alpha_1$ radiation. In order to avoid contamination with oxygen, the whole synthesis and solution processing were carried out inside a dry-box with H_2O and O_2 levels below 1 ppm.

Thin films of As_2S_3 and $\text{As}_2\text{S}_3\text{:Ag}_2\text{S}$ NCs were also prepared in a dry-box from their respective solutions by spin-coating. The upper portion of $\text{As}_2\text{S}_3/\text{AgCl}$ solution was spun at 2000 rpm for 10 - 20s, on glass or silicon substrates. For solvent removal, the thin films were vacuum baked at 60°C for 1h and then post-baked at 110°C for 7h. After such annealing, no amine group from the solvent is expected to remain in the film structure^{140; 141; 142}, while pore formation is avoided, once the onset temperature for pore formation has been reported at $\sim 120^\circ\text{C}$ ¹⁴³. Raman spectra were acquired with a LabRAM – Horiba equipment, using a $50\times$ objective lens, 20s of integration time and excitation at 532 nm from Ar laser. Film thickness was estimated by ellipsometry (M-2000 Woollam) and AFM (Easy scan - NanoSurf) measurements to be approximately 500 nm.

8.3 Results and discussion

Figure 8.2 shows the absorption spectra of As_2S_3 and AgCl dissolved in propylamine individually, and the mixture of both solutions, named $\text{As}_2\text{S}_3\text{:AgCl}$. As_2S_3 solution has a sharp absorption edge at 510 nm, resulting in the typical yellowish color of As_2S_3 compounds, while silver chloride solution is transparent throughout the entire visible spectrum. Absorption bands at 915, 1044 and 1200 nm are due to the organic solvent. The resulting solution from the mixture ($\text{As}_2\text{S}_3\text{:AgCl}$) presents a wide absorption band covering the region 600 - 1000 nm and an absorption edge at 555 nm, conferring a brownish color to the solution. Such features are indicative of the chemical reaction which occurred between the species in solution. The specific wavelength of this absorption suggests the formation of Ag_2S in solution as indirect transitions have been reported in this spectral range¹³³. However in order to check for the formation of nanocrystals, TEM images are obtained from the diluted solution, as shown in Fig. 8.3a along with electron diffraction measurement. As it can be seen, the chemical reaction produces spherical nanoparticles, uniformly dispersed, with an estimated diameter of 8

nm (obtained using DLS measurements). The diffraction pattern confirms the formation of monoclinic silver sulfide (α -Ag₂S), in agreement to ICDD card #00-014-0072, also represented in Fig. 8.3a. A representative high-resolution image (HRTEM) is depicted in Fig. 8.3b, in which the interplanar distances corresponding to (120), ($\bar{1}$ 03) and (031) planes of Ag₂S NPs are seen.

Fig. 8.2: Absorption spectra of As₂S₃ and AgCl dissolved in propylamine, and the resulting solution after mixing As₂S₃/AgCl in a ratio of 1/0.25 ml.

Source: By the author.

Fig. 8.3: a) TEM image of the NCs disperse in As₂S₃:AgCl solution and its electron diffraction pattern in which seven crystallographic planes corresponding to monoclinic Ag₂S were identified. b) HRTEM of a single particle, with diameter of 12 nm, where the interplanar distances match to (120), ($\bar{1}$ 03) and (031) planes of Ag₂S.

Source: By the author.

Interesting, we have noted that those particles are sensible to the electron beam, presenting atomic transport during TEM measurements. Figure 8.4 illustrates sequential images taken from a video that shows the association of a NPs sizing about 4 nm with one of 15 nm. By focusing the electron beam, there is atomic mobility from the big to the small one, until its complete transformation in only one NP. A similar behavior was reported by Motte and Urban ¹⁴⁴, who concluded that the darker and initially smaller particles are Ag⁰ clusters bound at Ag₂S nanoparticle interface. The authors claimed that silver clusters are produced during the synthesis of Ag₂S nanocrystals, and not by electron beam exposure, as observed by Terabe et al. ¹⁴⁵.

Formation and growth was explained based on an electrochemical process of mobile Ag ions in Ag₂S crystal, which is ionic/electronic mixed conductor. The electrons reduce the mobile Ag ions to neutral Ag⁰ atoms that precipitate on the surface of Ag₂S ¹⁴⁵. The latter authors also noted that behavior is reversible ($Ag_{(Ag_2S)}^+ + e^- = Ag_{cluster}$), and took advantage of this fact to build an atomic switching ¹⁴⁶. We could not evaluate the differences in the lattice constant for each individual particle reported herein, but surely the electron diffraction corresponds to monoclinic Ag₂S and may overlap diffraction of Ag⁰ atoms. Thus, the possibility of production of metallic silver during the synthesis or under electron beam exposure should not be ruled out, and it can be exploited in further investigations.

Fig. 8.4: Illustration of the video that shows the transformation of Ag₂S to Ag NPs (initially smaller and darker particle).

Source: By the author.

The stability of As_2S_3 solution containing Ag_2S nanocrystals was evaluated over time through its absorption spectrum. The variation of the absorption edge ($\Delta\lambda_{\text{cutoff}}$) is displayed on Fig. 8.5, where negative values indicate changes towards smaller wavelengths over the time. A blue shift of 45 nm in the absorption edge was observed during the first 3h after preparation. For longer periods no significant change was detected, and the solution kept stable for at least 20 days. The blue shift is related to the precipitation process, in which large particles precipitate leaving smaller particles in suspension and a corresponding increase in the apparent bandgap energy due to the quantum size effect ¹³³.

Fig. 8.5: Variation of the absorption edge ($\Delta\lambda_{\text{cutoff}}$) over the time of $\text{As}_2\text{S}_3\text{:AgCl}$ solution.

Source: By the author.

As a result of the chemical reaction, besides the formation of Ag_2S NCs in suspension, a dark precipitate was also observed in the bottom of the reaction vial. XRD and EDS measurements of this precipitate revealed an amorphous phase containing Ag (~ 4 at.%), As (~ 38 at.%) and S (~ 58 at.%). This result suggests that the precipitate is predominantly amorphous As_2S_3 , because the As:S ratio (0.66) is equivalent to the stoichiometric compound. In order to avoid As_2S_3 precipitation and investigate the nature of the silver portion in the precipitate, the chemical synthesis was performed using a hundred-fold diluted solution of As_2S_3 . The XRD pattern of the resulting precipitate is displayed in Fig. 8.6, in which unreacted precursor AgCl and monoclinic Ag_2S were identified. This confirms the formation and precipitation of silver sulfide crystals.

Fig. 8.6: XRD pattern of the precipitate formed by mixing the solutions of As_2S_3 hundredfold diluted and AgCl (regular concentration) in propylamine. Monoclinic Ag_2S and cubic AgCl were identified using ICDD.

Source: By the author.

The formation of Ag_2S NCs can be explained based on the sulfidation of silver ions in solution. It is known that the dissolution process of As_2S_3 results in arsenic sulfide clusters terminated by excess sulfide dangling bonds⁶. Thus, sulfur anions spontaneously react with silver ions that originated from AgCl dissociation, producing nanocrystals of silver sulfide through the reaction $2\text{Ag}^+ + \text{S}^{2-} \rightarrow \text{Ag}_2\text{S}$ ($\Delta H = -2199.5$ kJ/mol)¹⁴⁷. The sulfidation of Ag^0 nanoparticles using H_2S exposure is a known method to obtain Ag_2S NCs in several systems^{148; 149}. However, the presence of sulfur atoms in the chalcogenide solution enables the formation of Ag_2S NCs without any gas exposure, enabling a single-step synthesis. It is important to note that no additional source of energy (as temperature or irradiation) is necessary to promote the chemical reaction, configuring a simple and fast way to prepare *in situ* Ag_2S NCs. In addition, this approach can be exploited for the production of other semiconductor sulfide NCs in ChGs to create novel materials for Mid-IR photonics^{150; 151}.

To investigate the structure and physical-chemistry properties of solid-state samples, thin films are prepared from $\text{As}_2\text{S}_3\text{:AgCl}$ solution (containing Ag_2S NCs), and also from the As_2S_3 solution, for comparison purposes. EDS measurements showed that the films are composed of 63 at.% of S and 37 at.% of As. Thus the As:S ratio is 0.59, indicating an arsenic deficiency when compared to initial As_2S_3 compound (0.67). Such deficiency has been reported for spin-coated chalcogenide glass, and it is related to the As_2S_3 dissolution, which leads to the formation of As_2S_x clusters terminated with excess

of negatively charged S ions ^{140; 152}. This feature is preserved in the solid phase, resulting in thin films with excess of sulfur atoms. The composition of $\text{As}_2\text{S}_3/\text{Ag}_2\text{S}$ NCs films is 3.2 at.% of Ag, 60.7 at.% of S and 36.1 at.% of As. Considering all Ag atoms form Ag_2S NCs, the doping amount is half of silver content (1.6 at.% of Ag_2S NCs) and the remaining S atoms (59.1 at.%) along with As provide a matrix with As:S ratio of 0.61.

Raman spectra of As_2S_3 and As_2S_3 :NCs films are displayed in Fig. 8.7. The broad bands indicate the amorphous structure of the films, and are mainly associated with As_2S_3 and As_4S_4 structural units, according to the vibrational energy presented in Table 6.1 ^{153; 154; 155}. As shown in Fig. 8.7, the presence Ag_2S NCs causes minor alterations to the As_2S_3 structure, indicated by a decreasing shoulder at 297 cm^{-1} and the vanishing band at 414 cm^{-1} , while peaks at 225 and 330 cm^{-1} get stronger. Thus, based on the assignments presented in table 6.1, we believe that the addition of Ag_2S NPs causes a transformation of As_2S_3 into As_4S_4 basic units, in agreement with the increase in As content in As_2S_3 :NPs films, seen in the EDS data. The As:S ratio is 0.59 for the undoped film, increasing to 0.61 for the films containing Ag_2S NCs. In fact, Iovu et al. described the dissociation $2\text{As}_2\text{S}_3 \rightarrow \text{As}_4\text{S}_4 + \text{S}_2$ due to rare earth and Mn doping of arsenic sulfide ¹⁵³. The preparation of arsenic sulfide films containing nanoparticles of silver sulfide reported herein presents a promising metamaterial for infrared technologies, in which photoactive phenomena associated with semiconductor nanocrystals can be exploited to improve the overall material performance ^{156; 157}.

Fig. 8.7: Raman shift of As_2S_3 and As_2S_3 :NCs thin films, in which the amorphous structure was lightly affected by the presence of Ag_2S NCs.

Source: By the author.

Table 8.1: Raman signatures of As_2S_3 and As_2S_3 :NPs thin films.

Peak position (cm^{-1})	Raman signature	Ref.
180	As_4S_4 units	153;
225	As_4S_4 units, As clusters	154
297	Asymmetric stretching modes of $\text{AsS}_{2/3}$ pyramids (As_2S_3 units)	153;
330	Symmetric stretching vibrational mode of $\text{AsS}_{2/3}$ pyramids (As_2S_3 units)	153;
356	As_4S_4 units	154
414	As_4S_5	155
480	S-S stretching vibration in S_8 rings	153

8.4 Conclusions

We have used a wet chemistry approach to produce silver sulfide nanoparticles in chalcogenide solution. The chemical synthesis consists of independently dissolving As_2S_3 and AgCl in propylamine, and mixing both solutions using the ratio $\text{As}_2\text{S}_3/\text{AgCl} = 1:0.25\text{ml}$. Such method results in the spontaneous formation of Ag_2S nanocrystals, where the sulfur ions are provided by the As_2S_3 in solution. The monoclinic structure of Ag_2S NCs is confirmed through TEM and XRD analyses. By spin-coating the resulting solution, we are able to produce ~ 500 nm thick arsenic sulfide films, doped with 1.6 (at.%) Ag_2S . The glass network of these films differs from that of an undoped film due to a decrease of As_2S_3 units in favor of As clusters and As_4S_4 units.

9. Conclusions and perspectives

The main goal of this PhD research was to exploit femtosecond laser pulses for the nonlinear optical characterization of nanoparticle doped glasses, as well as, to produce 3D waveguides containing nanoparticles. Below, the results are summarized according to its fundamental and applied aspects.

Concerning the third-order optical properties, we analyzed $\text{GeO}_2\text{-Bi}_2\text{O}_3$ and $\text{Pb}_2\text{P}_2\text{O}_7\text{-WO}_3$ glasses containing gold and copper nanoparticles, respectively. In general, the nonlinear refractive index (n_2) is about $2 \times 10^{-19} \text{ m}^2/\text{W}$ for visible and infrared regions. Slight higher n_2 values were obtained close to the plasmon band region, which may be associated to the higher third-order susceptibility or concentration of copper nanoparticles, when compared to the gold ones. Regarding the nonlinear absorption, at the plasmon band wavelengths, both glassy systems displayed effects of saturable absorption, while two-photon absorption or reverse saturable absorption were verified at the other regions of the spectrum, depending on the glass matrix.

At the standpoint of applied science, we demonstrated the ability to produce 3D waveguides composed by silver or copper nanoparticles, using a single-step laser processing. The phenomenon behind the generation of both copper and silver nanoparticles in glass by ultrashort laser pulses was investigated. It consisting of a nucleation stage, accomplished by nonlinear interactions followed by the photoreduction of Ag^+ and Cu^{2+} ions. The aggregation of the resulting metallic atoms is achieved through a heating process, provided by heat accumulation effect associated with high repetition rate of lasers or by an additional annealing, when using low repetition rate. One obtained roughly cylindrical or elliptical cross-sections, sizing from 2 to 30 μm , which were able to support mono- or multimode guiding at 632.8 nm. Propagation losses at this wavelength lied between 0.5 – 3.5 dB/mm, depending on the sample and experimental conditions applied for fs-laser micromachining.

Considering the fundamental aspect of this study, we proposed to answer: Do nanoparticles significantly show the resonant enhancement effect for nonlinear optical response by improving the nonlinear refractive index of glassy materials?

Although there are several reports on the enhancement effect associated with the plasmon resonance of metallic nanoparticles observed in many optical properties (mainly linear optical properties), no significant effect was observed on the nonlinear refractive index of heavy metal oxide glasses doped with gold or copper nanoparticles investigated herein. It is worth mentioning that we have investigated the optical nonlinearities at femtosecond regime, using ordinary concentrations of nanoparticles. The observation of enhancement effects may be strictly related to the concentration level of those particles in the matrix. Thus, new issues could be proposed regarding the dependence of resonant enhancement effect on n_2 with the concentration of nanoparticles. Less widely studied is the nonlinear response of semiconductor nanoparticles in glass; investigations about the evidence (or not) of enhancement effect on n_2 and the comparison with metallic nanoparticles would be interesting for understanding the effect of nanostructures on the optical nonlinearities.

In this sense, the synthesis and nonlinear optical characterization of glass containing nanoparticles is still a great opportunity for extending knowledge in the field of experimental science. Preliminary results on nonlinear optical properties of chalcogenide glass with semiconductor nanoparticles have shown to be interesting, configuring our ongoing and future investigations, which also include laser direct writing techniques aiming at photonic devices.

10. References

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Appendix A - Publications in Journal Papers

Part of this thesis was published in the following papers:

- 1) **J. M. P. Almeida**, C. Lu, C. R. Mendonca, C. Arnold, "Single-step synthesis of silver sulfide nanocrystals in arsenic trisulfide", *Optical Materials Express*, vol. 5, Jul 2015.
- 2) **J. M. P. Almeida**, P. H. D. Ferreira, D. Manzani, M. Napoli, S. J. L. Ribeiro, and C. R. Mendonca, "Metallic nanoparticles grown in the core of femtosecond laser micromachined waveguides," *Journal of Applied Physics*, vol. 115, May 21 2014.
- 3) **J. M. P. Almeida**, D. S. da Silva, L. R. P. Kassab, S. C. Zilio, C. R. Mendonca, and L. De Boni, "Ultrafast third-order optical nonlinearities of heavy metal oxide glasses containing gold nanoparticles," *Optical Materials*, vol. 36, pp. 829-832, Feb 2014.
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- 5) **J. M. P. Almeida**, G. F. B. Almeida, L. De Boni, C. R. Mendonça, "Nonlinear optical properties and femtosecond laser micromachining of special glasses". *Journal of the Brazilian Chemical Society*, v.00 Set 2015.

Complementary publications related to the PhD research:

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