Optical Materials 36 (2014) 829–832

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Ultrafast third-order optical nonlinearities of heavy metal oxide glasses containing gold nanoparticles

Juliana M.P. Almeida [a], Diego S. da Silva [b,c], Luciana R.P. Kassab [b], Sergio C. Zilio [a], Cleber R. Mendonça [a], Leonardo De Boni [a,*]

[a] Instituto de Física de São Carlos, Universidade de São Paulo, CP 369, 13560-970 São Carlos, SP, Brazil
[b] Faculdade de Tecnologia de São Paulo, CEETEPS, 01124060 São Paulo, SP, Brazil
[c] Departamento de Engenharia de Sistemas Eletrônicos, Escola Politécnica da USP, 05508-900 São Paulo, SP, Brazil

ARTICLE INFO

Article history:
Received 9 September 2013
Received in revised form 25 October 2013
Accepted 4 December 2013
Available online 29 December 2013

Keywords:
Nonlinear optics
Nonlinear refractive index
Ultrafast response
Glasses
Z-scan
Optical Kerr gate

ABSTRACT

This work reports on the third-order nonlinear properties and the response time of GeO_2–Bi_2O_3 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–GeO_2) 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.

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 devices [1]. 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) [1–3]. Nonetheless, it has been reported that bismuth oxide leads to 1.5 times larger χ^3 than lead oxide, both in borate matrix [4]. Although Pb^{2+} and Bi^{3+} have the same electronic structure [(Xe) $4f^{14}$ $5d^{10}$ $6s^2$ $6p^0$] and optical transition mechanism ($^1S_0 \rightarrow {}^3P_1$), the higher susceptibility associated to the bismuth glass is due to its smaller optical band gap [4]. 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 [5].

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 [6–9]. Enhancement of rare-earth ions emission on glasses containing metallic nanoparticles have been demonstrated [8,10,11]; a growth of ~1000% in the photoluminescence intensity of Eu^{3+} doped GeO_2–Bi_2O_3 glass containing gold nanoparticles was reported in Ref. [8], 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 GeO_2–Bi_2O_3 glass. Because a strong enhancement of the photoluminescence was observed in the GeO_2–Bi_2O_3 glass doped with Eu^{+3} [8], 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 femtosencond Z-scan technique. In addition, the response times of the nonlinearity have been evaluated at 780 nm by the optical Kerr gate technique.

2. Experimental

The 58.4 GeO_2–41.6 Bi_2O_3 (wt%) glass matrix and the $3Au_2O_3$–$0.5Eu_2O_3$ (wt%) doped sample (GB and GB–Au respectively), were prepared by the melt-quenching method as described

* Corresponding author. Tel./fax: +55 16 3373 8085.
E-mail address: deboni@ifsc.usp.br (L. De Boni).

0925-3467/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.optmat.2013.12.012

in Ref. [8]. The Au nanoparticles were obtained by adequate annealing of the GB–Au sample at 420 °C for 3 h. Spherical shaped nanoparticles, with size distribution around 5 nm, were observed in the transmission electron microscopy (TEM) images. The third-order nonlinearities from 480 to 1500 nm, and its response time, obtained at 780 nm, were measured using an optical parametric amplifier (OPA) with 120-fs pulses in both samples. The OPA is pumped by Ti:sapphire chirped pulse amplified system (150-fs, 775 nm and 1 kHz) and has the same repetition rate as the laser. The nonlinear refractive index (n_2) and the nonlinear absorption coefficient (β) spectra were obtained using open and closed aperture Z-scan techniques [12], while for the response times, optical Kerr gate (OKG) measurements were employed. The average pulse energy ranged from 20 to 180 nJ, depending on the wavelength. Fused silica has been used as standard calibration, and its nonlinear refractive index was approximately 1.9×10^{-20} m^2/W at visible and infrared regions which are in accordance to results from the literature [13]. Details about our Z-scan and OKG experimental setups were recently described in the references [2,14].

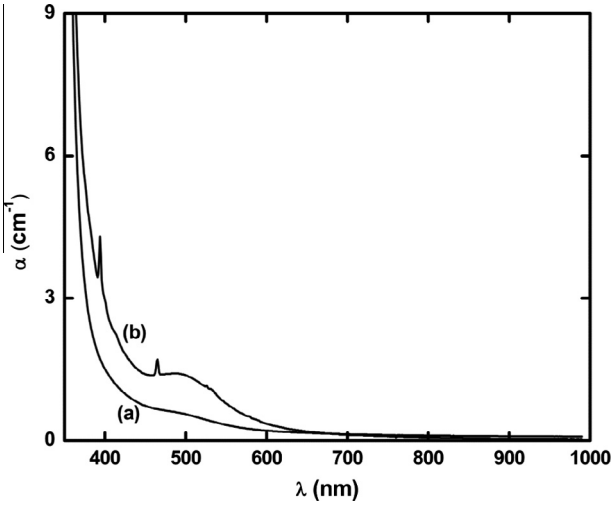

Fig. 1. Linear absorption spectrum of (a) GB and (b) GB–Au samples.

3. Results

The linear absorption spectra of GB (a) and GB–Au (b) samples, displayed in Fig. 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 Eu^{3+} $4f$–$4f$ electronic transitions originated from the ground state ($^7F_0$) [8]. 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 3 h. Such nanoparticles have spherical shape with diameter around 5 nm, according to TEM images as reported in Ref. [8].

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. 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 to 580 nm. According to the Z-scan signature displayed in Fig. 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 ($Eg = 3.2$ 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. 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) [15]. 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 considerable the transmittance at the focal position ($z = 0$) [16]. To obtain the

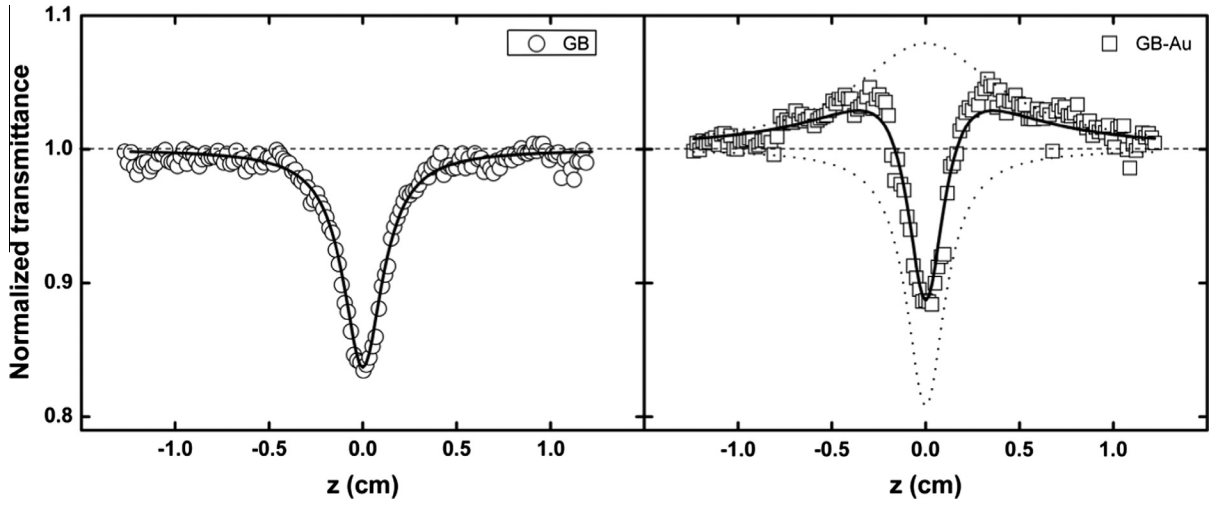

Fig. 2. Open aperture Z-scan signature at 500 nm for GB and GB–Au. Open symbols represent the experimental results, while solid lines are the fitting curves. In the GB–Au, the dotted lines correspond to the individual theoretical curves for SA (normalized transmittance higher than one) and 2PA (normalized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