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

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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

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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].

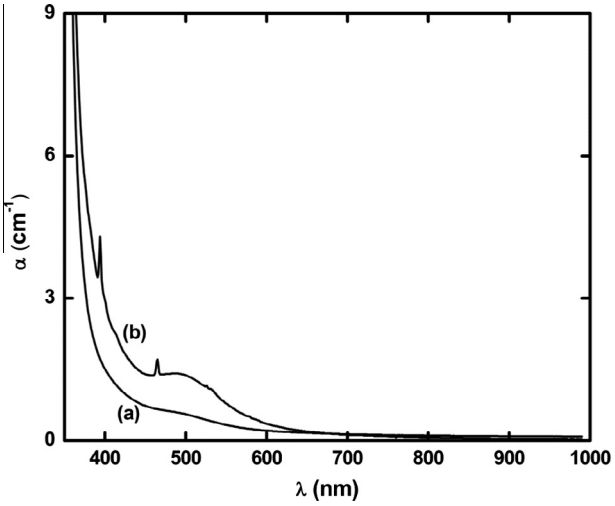

Fig. 1. Linear absorption spectrum of (a) GB and (b) GB–Au samples.

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

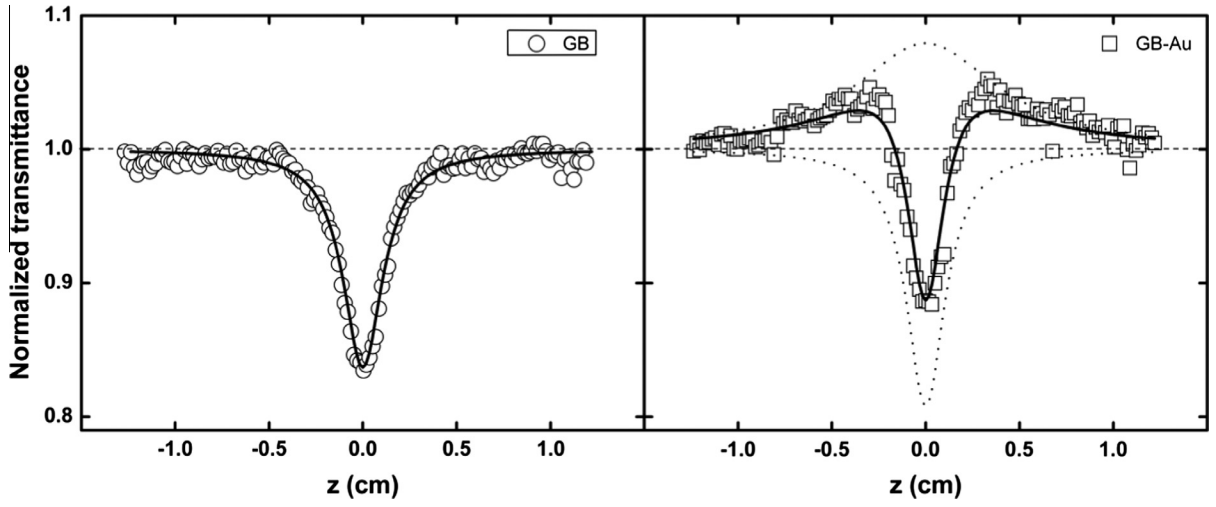

Fig. 2. Open aperture Z-scan signature at 500 nm for GB and GB–Au. Open symbols represent the experimental results, while solid lines are the fitting curves. In the GB–Au, the dotted lines correspond to the individual theoretical curves for SA (normalized transmittance higher than one) and 2PA (normalized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

Table 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 GB	β_{sat} (cm/GW) ± 0.01 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

2PA and SA magnitudes from the experimental result presented in Fig. 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. 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. 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. 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 refraction [17]. 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 and 1.8×10^{-19} m^2/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 [6,7,18], 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 [19]. An explanation for this result can be 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 [20]. In this sense, the magnitude of the nonlinear refractive index shown in Fig. 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 [2,13]. 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 [19], 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 [4]. 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 [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 [4,21,22].

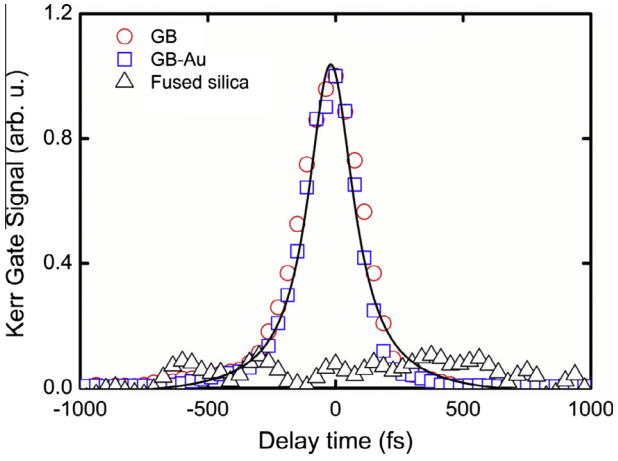

Fig. 4. Kerr gate signal of the GB and GB–Au samples excited at 780 nm. The result of fused silica is shown in order to check the signal on the nonlinear glasses. Open symbols are the experimental data while the solid line represents the Gaussian fit.

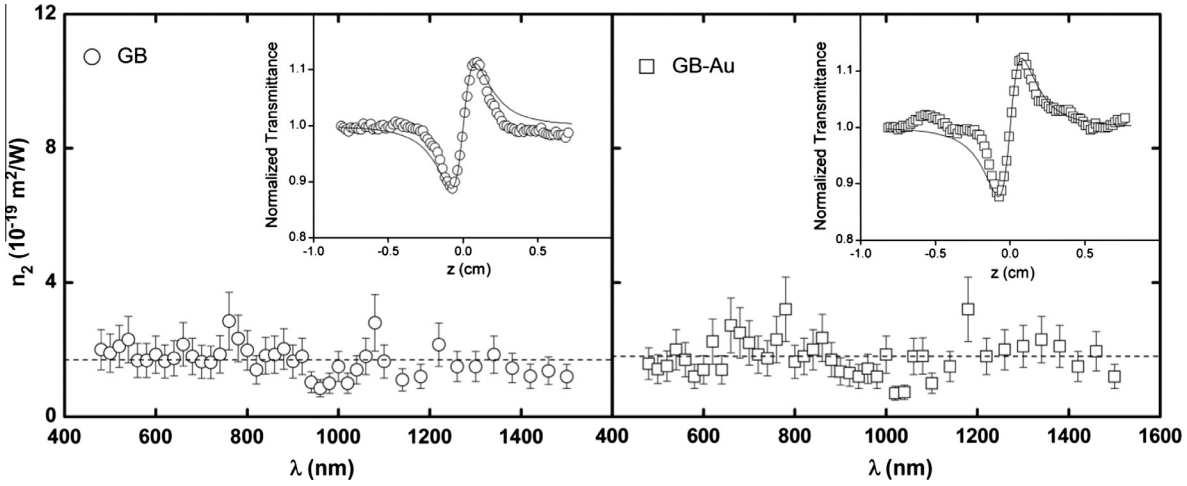

Fig. 3. Spectra of nonlinear refractive index (n_2) of GB and GB–Au glasses. The insets show the closed Z-scan signature for each sample at 780 nm, which are representatives for the whole spectrum.

In the same way, the presence of gold nanoparticles do not affect the Kerr gate signal, as shown in Fig. 4 for excitation at 780 nm. The fused silica signal was added in Fig. 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 birefringence [23], in the present case directly related to n_2. As one can notice the 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 indicates an ultra-fast electronic process (less than 220 fs).

4. Conclusions

We have investigated the third-order nonlinear optical properties and the response times of GeO_2–Bi_2O_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 1.8×10^{-19} m^2/W and it is one order of magnitude larger than that of fused silica. When compared to the PGO glass, the GeO_2–Bi_2O_3 sample has a n_2 1.5 times higher. Therefore, the use of Bi_2O_3 is a better alternative when compared to PGO 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 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.

Acknowledgments

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