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Abstract: We have determined two-photon absorption and nonlinear refraction spectra of the 50BO\textsubscript{1.5} - (50-x)PbF\textsubscript{2} - xPbO glasses (with x = 25, 35, 50 cationic %) at the range of the 470 and 1550 nm. The replacement of fluor atoms by oxygen leads to an increase in the third-order susceptibility, due to the formation of non-bridging oxygens (NBO). The nonlinear index of refraction is one order of magnitude higher than the one for fused silica, and it increases almost twice for the sample with x = 50. This sample has also shown promising features for all-optical switching as well as for optical limiting.

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References and links

1. Introduction

The large interest in nonlinear optical materials has been motivated by their potential use in the fabrication of all-optical photonic devices. Distinct types of materials, from polymers to inorganic semiconductors, have been investigated as promising candidates to accomplish such task. Therefore, studies in this area are focused on the development and optimization of materials with the proper combination of the required features. Among several interesting candidates for photonic applications, glasses are receiving special attention because of their chemical and mechanical stability and wide compositional range that can be explored to tune the desired property for a specific application. Furthermore, glasses may present fast response times and high nonlinearities, features of foremost importance for photonic devices [1].

Glasses containing highly polarizable atoms present good nonlinear optical properties on account of their easily deformable electron clouds [2]. Heavy-metal oxide glasses have shown to be promising materials for all-optical devices due to the largest hyperpolarizabilities of their heavy-metals [2,3]. Particularly, the presence of lead oxide have been investigated in tellurite, germinate, silicate and borate glass [4–7]. Waveguide structures were produced inside PbO-B₂O₃-Ga₂O₃-GeO₂ glass [7]. Lead silicate glasses were used on the fabrication of highly nonlinear and low loss fibers [5]. Studies on binary systems TeO₂-PbO and B₂O₃-PbO have shown an enhancement of the third-order nonlinearities with the increased of lead content due to Pb⁺² ions [4,6]. In order to evaluate the capability of a given material for optical devices, a broadband spectral analysis of its nonlinearities, absorptive and refractive, is required. It is known, for instance, that glasses presenting high nonlinear index of refraction also exhibit strong two-photon absorption, which is deleterious for all-optical switching applications. However, the majority of the studies reported on the nonlinear characterization of glasses were carried out only in a few wavelengths or in a limited wavelength range, independently of the glassy system [3]. The knowledge of both properties, the nonlinear refraction and absorption, could help selecting, for example, the optimum operational wavelength for an optical device using a certain sample.

In this paper, we report a study on the two-photon absorption and nonlinear refraction spectra (470 and 1550 nm) of the 50BO₁₅-(50-x)PbF₂-xPbO glasses, with x = 25, 35, 50 cationic %. Lead-base borate glasses exhibit high transparency in the visible and near infrared, low melting temperature and second harmonic generation [8,9], thus being promising materials for optical applications. We have investigated not only the nonlinear optical properties of the Pb oxifluoroborate glasses as a function of the wavelength, but also how they are affected by the replacement of fluor atoms by oxygen, while the content of Pb (heavy metal) is kept constant. Such substitution can promote the formation of B–O bonds [10], whose free electron can positively affect the optical nonlinearity of borate glasses [3].

The nonlinear index of refraction and the two-photon absorption coefficient, represented, respectively, by γ (m²/W) and β (m/W), were determined by Z-scan measurements using pulses of 120 fs, which have been a useful tool to characterize several nonlinear optical materials [2,11,12]. The values we obtained for γ are one order of magnitude higher than the ones determined for fused silica. Moreover, considering the two-photon absorption coefficient, the glass with x = 50 revealed potential for all-optical switching devices in the wavelength range of 650-800 nm (figure of merit 2βλ/γ < 1). We have also studied the optical...
limiting properties of the lead oxifluoroborate glasses, which demonstrated interesting features that can be explored in ultrashort pulse optical limiters.

2. Experimental

The preparation process of the glasses and some of their physical properties are described in [13]. Polished flat samples with 1 mm of thickness were used for the Z-scan measurements with femtosecond laser pulses. A Ti:sapphire chirped pulse amplified system (150-fs, 775 nm and 1 kHz) was used as the excitation source for an optical parametric amplifier, which provides 120-fs pulses from 460 up to 2000 nm. To ensure a Gaussian profile for the laser beam used in the experiments, spatial filtering is performed before the Z-scan setup. The output signal was monitored by a silicon or germanium photodetector, depending on the wavelength region, coupled to a lock-in amplifier that integrates 1000 shots for each point of the Z-scan trace. The laser pulse energies and beam waist size used in this experiment range from 5 to 200 nJ and 14 to 27 µm, respectively, according to the excitation wavelength. Details about the Z-scan technique, developed by Sheik-Bahae et al. can be found in [14]. For comparison purposes, we have also measured the nonlinear index of refraction, \( n_2 \), for fused silica at the visible and infrared regions, and found values of approximately \( 1.9 \times 10^{-20} \) m\(^2\)/W, which are in accordance to results from the literature [15]. In our Z-scan measurement, the estimated error was ± 10% for open aperture and ± 30% for closed aperture configuration. A Cary 17 spectrophotometer was used to measure the linear absorption spectra of the samples.

Optical limiting measurements were performed at 650 nm, using the optical parametric amplifier, previously described as the excitation source. The excitation light intensity was controlled using two polarizers. To obtain a reference signal for the input intensity, the incident laser light was separated by a beam splitter located after the second polarizer. Then, the laser beam is focused at the sample position with a \( f = 15 \) cm lens (\( w_0 = 13 \) µm). Fused silica was used as a reference material for the optical limiting experiments.

3. Results and discussions

The linear (left axis) and nonlinear (right axis) absorption spectra of the 50BO\(_{1.5}\) - (50-x)PbF\(_2\) - xPbO glasses, with x = 25, 35, 50 cationic %, are shown in Fig. 1. One can notice that the linear absorption shifts to red when PbF\(_2\) is replaced by PbO. For oxide glasses, it has been shown that an increase in non-bridging oxygens (NBO) leads to a red shift in the sample absorption spectra [3,16]. These NBOs are oxygen atoms bonded to only one network cation and negatively charged, which is important for nonlinear optical materials. Changes in the NBO content can be checked through Raman spectroscopy. Pan et al. reported that the addition of PbX\(_2\) (X = F, Cl, Br or I) in (65-x)PbO-xPbX\(_2\)-35B\(_2\)O\(_3\) glasses leads to a reduction of the B–O vibration, and to the disappearance of the Raman peak at 570 cm\(^{-1}\), which has been attributed to metaborate groups [10]. Each metaborate unit has three NBOs. Therefore, the red shift observed in the linear absorption spectra (Fig. 1) is attributed to the increase of the NBO in the glass matrix. By extrapolating the linear region of the absorption, we determined the band gap energy, \( E_g \), that decreases from 3.63 to 3.37 and 3.14 eV for the samples with x = 25, 35 and 50% of PbO respectively. It is important to mention that such procedure overestimate the band-gap energy.

Two-photon absorption (2PA) was observed from 470 up to 760, 780 and 790 nm, according to the addition of lead oxide (left axis in Fig. 1). In Fig. 1, the inset shows a typical open aperture Z-scan signature for the lead oxifluoroborate glass with x = 50 of PbO. The 2PA spectra present a monotonous increase as the excitation energy approaches the bandgap energy. Such process, known as resonant enhancement of the nonlinearity, occurs when the laser frequency approaches the linear absorption of the material [2]. For the samples with x = 25, 35 and 50, we noticed that the 2PA coefficients tend to a constant value, equivalent to 0.03, 0.04 and 0.05 cm/GW, for wavelengths greater than 580, 610 and 650 nm respectively.
This behavior indicates that the 2PA in the samples studied herein has a small dependence with the compositional change, at regions far from one photon resonance. The differences in the 2PA values, among the distinct samples, at the enhancement region follow the changes in the linear absorption spectra caused by the substitution of PbF$_2$ by PbO.

![Fig. 1. Linear (line) and nonlinear (line + symbols) absorption spectra of 50BO$_{1.5}$ - (50-x)PbF$_2$ - xPbO glasses (x = 25, 35 and 50 cationic %), whose labels are defined in the figure. The inset shows the open aperture Z-scan signature for the x = 50 sample at 700 nm.](image1)

The spectrum of the nonlinear index of refraction ($\gamma$) for the sample x = 50 is shown in Fig. 2. A representative closed aperture Z-scan signature is presented in the inset of this figure. As it can be seen, $\gamma$ is practically constant in the range of the wavelengths analyzed, with a value of approximately $4.7 \times 10^{-19}$ m$^2$/W. Similar behaviors were obtained for samples with x = 25 and 35, with average values for $\gamma$ of $2.6 \times 10^{-19}$ m$^2$/W and $3.1 \times 10^{-19}$ m$^2$/W respectively. Compared to the value obtained for fused silica, the $\gamma$ values for the lead oxifluoroborate glasses with x = 25, 35 and 50 of PbO, are 14, 16 and 25 times higher respectively.

![Fig. 2. Values of the nonlinear refractive index as a function of wavelength for the 50BO$_{1.5}$ - (50-x)PbF$_2$ - xPbO glass with x = 50 cationic %. For this sample at 700 nm, a closed aperture Z-scan signature is illustrated in the inset.](image2)
An analysis on the variation of the third-order properties, as a function of the band gap energy, is presented in Fig. 3. Both, the nonlinear refractive index and the 2PA coefficient, increase with the decrease of the $E_g$. This result is a consequence of the increase in the NBO content. Because NBO are less stable and weakly bound to the boron or lead atoms, its valence electrons are easily deformable by the laser electromagnetic field, resulting in larger nonlinearities [3]. In Fig. 3, one can observe a higher variation of $\gamma$ than of $\beta$ with the band gap energy. Such results imply that, probably, the nonlinear index of refraction is more sensible to the NBOs than the two photon absorption coefficient.

![Graph showing variation of $\gamma$ and $\beta$ with $E_g$.](image)

Distinct criteria have been proposed to analyze materials for specific applications [17]. For all-optical switching, the figure of merit $F = 2\beta\lambda/\gamma$ has been used to select nonlinear optical materials; if the condition $F < 1$ is satisfied, the material could be used for all-optical switching devices [18].

In Fig. 4, we have shown the dependence on $F$ as a function of the wavelength for the lead oxifluoroborate glass with $x = 50$, since this sample is the one that presents the higher optical nonlinearity among the ones studied herein. Figure 4 shows that $F$ is close to 1 for wavelengths between 650 and 800 nm, which makes this sample an interesting candidate for photonic devices, specifically optical switches, at this region of wavelengths.

![Graph showing figure of merit $F$ vs. wavelength.](image)
Another possible device application for this type of glass system is in optical limiters. Figure 5 shows optical limiting curves (closed symbols) for the three samples studied as a function of the incident laser intensity (input intensity). One can observe that all samples present an optical limiting behavior when compared with fused silica (open circles). However, the sample with $x = 50$ presents a lower intensity threshold for optical limiting action in comparison to the other ones. Such behavior can be explained by the gradual replacement of PbF$_2$ by PbO in the matrix, which increases the optical attenuation and it is associated to the higher 2PA coefficient exhibited by the sample with $x = 50$. The increase of PbO leads to a decrease in the optical limiting threshold; for the samples with $x = 25$, 35 and 50, the limiting process starts to occur for intensities of 90, 72 and 40 GW/cm$^2$, respectively.

In Fig. 5, the solid lines represent the modeling of the optical limiting curves considering only the 2PA mechanism [19], where the 2PA coefficient was the one obtained from the Z-scan measurements. We can notice that the 2PA process solely does not describe the optical limiting behavior. The dashed lines in Fig. 5 represent the modeling carried out considering both processes, 2PA and three-photon absorption (3PA) [19,20]. The values of the 3PA coefficient were estimated to be around $1.2 \times 10^{-4}$ cm$^3$/GW$^2$. Although such mechanism has been shown to be adequate to fit results for silicon waveguides [21], it does not properly describe the optical limiting behavior presented here. We believe that the differences between the experimental data and the modeling indicate that other mechanisms, rather than 2PA and 2PA + 3PA, are contributing to the limiting processes. Therefore, the lead oxifluoroborate glasses investigated in this work could be used in the development of optical limiting devices for ultrashort laser pulses.

4. Conclusion

In summary, we have investigated the third-order optical nonlinearities of lead oxifluoroborate glasses (50BO$_{1.5}$ - (50-x)PbF$_2$ - xPbO, $x = 25, 35$ and 50% mol) at visible and infrared wavelength. In addition, changes of the optical nonlinearities were investigated as a function of the oxygen content for a fixed lead (heavy metal) concentration. Our results revealed that non-bridge oxygens have an important role in the nonlinear optical properties of heavy metal oxide glasses; the presence of this oxygen improves both, the nonlinear index of refraction and the 2PA coefficient. The nonlinear index of refraction was determined to be 14, 16 and 25 times higher than fused silica, respectively for the glasses with $x = 25$, 35 and 50. The samples have also shown interesting optical limiting features at 650 nm. Moreover, the figure of merit analyses for the sample with $x = 50$ reveals this sample as being a potential material for the development of all-optical switching at the wavelength range of 650–800 nm.

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