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Saturable absorption of silver nanoparticles in glass for femtosecond laser pulses at 400 nm

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ABSTRACT

The commercially available glass BK7 was chosen to prepare silver-rich layer within the glass by the silver (Ag) ion exchange method in order to enhance its nonlinear optical properties. The glass substrates were doped with Ag at 320 °C by a 50-minute $Ag^+ \leftrightarrow Na^+$ ion exchange in a melt of $NaNO_3$ and KNO_3 containing 14 mol% of $AgNO_3$. Then, one piece of glass BK7 containing Ag ions (as-exchanged sample) was annealed in air for 1 h at 600 °C to prepare the as-annealed sample. The thickness of the layer containing Ag in the as-exchanged glass BK7 was measured to less than 1 μm. It was found that during the post-exchanged annealing most silver diffused deeply into the glass substrate leading to increase the thickness of the layer to 110 μm. However, some amount of Ag nucleated during the annealing, thus creating small nanoparticles (NPs) with an average size of 2 nm. The linear and nonlinear optical properties of the as-exchanged and as-annealed glass BK7 were studied. The as-exchanged sample showed no absorption in the visible spectral region whereas, as-annealed glass BK7 showed a peak absorption at 420 nm which can be attributed to the presence of Ag NPs formed in this glass. The nonlinear optical behavior of the samples was investigated using 800 nm and 400 nm femtosecond pulses. Strong saturable absorption was observed in the as-annealed sample at 400 nm. This feature promises an efficient way for designing all optical switching devices appropriate for the second harmonic of the Ti-sapphire laser. Using nonlinear transmission (NLT) method the saturation intensity for the as-annealed sample was determined 8.5×10^{11} W·cm^{-2}. An intensity dependent switching from saturable absorption (SA) to reverse saturable absorption (RSA) was also observed when the as-annealed sample was irradiated simultaneously by 800 nm and 400 nm femtosecond pulses.

1. Introduction

Metal–glass composites containing nanoparticles (NPs) such as silver (Ag), gold and copper have attracted great interest due to their versatile applications in optical and photonic devices. Interaction between the incoming electric field and the free electrons confined in the metal NPs results in the collective oscillation of the electrons and thus in absorption of light. This phenomenon known as surface plasmon resonance (SPR) [1] is the reason for the narrow band absorption spectrum of transparent solid materials like glasses or polymers doped with metal NPs.

When a bulk glass containing metal NPs is irradiated by intense light with a frequency around the SPR, the saturable absorption (SA) phenomenon may be observed due to the depletion of the ground state population of the oscillating electrons of the conduction band of the metal NPs during the ultrashort laser pulse excitation [2].

SA is observed when the absorption coefficient (Eq. (1)) of a medium under irradiation decreases with irradiating intensity.

$$\alpha(I) = \frac{\alpha_0}{1 + \frac{I}{I_s}} \tag{1}$$

where α_0 is the linear absorption coefficient (i.e. absorption coefficient at low intensity) and I_s the saturation intensity at which the absorption coefficient decreases by a factor of 2 [3].

When a saturable absorber material is irradiated with light, the relation between the output and input intensities is given by Eq. (2)

$$\frac{I_{out}}{I_s} + \ln\left(\frac{I_{out}}{I_s}\right) = \frac{I_{in}}{I_s} + \ln\left(\frac{I_{in}}{I_s}\right) - \alpha_0 L \tag{2}$$

where I_{in} is the input intensity, I_{out} is the output intensity and L is the thickness of the medium.

Since Eq. (2) has no analytical solution it must be solved numerically in order to obtain I_s while I_{out} has been measured as a function of I_{in}. I_{in}

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can be varied by two different means. In the method known as nonlinear transmission (NLT) the medium is placed at the focal point of a focused laser beam and the power of the input laser beam is varied. In another technique known as Z-scan, the input intensity is changed by varying the spot size of the laser beam within the material by scanning the medium along the propagation direction of the focused laser beam. In this technique the input laser power (pulse energy) is kept constant.

SA offers the possibility for important applications. It has been exploited extensively to produce short pulses via passive mode-locking technique [4]. It has also recently been shown that it can be used to switch light by light. This could provide a promising means to develop all-optical switching devices [5,6]. This nonlinear optical (i.e. intensity dependent) behavior has been observed for different kinds of metal NPs such as Ag [2,7–12], gold [13–16] and copper [17,18] around their SPR. The SA of gold NPs and to some extent also copper NPs has been examined extensively at 532 nm [14,18] (the second harmonic of Nd:YAG laser) since their SPR lies in this spectral region. Analogously, the Ag NPs can play an important role as gold NPs because their SPR occurs around the second harmonic of the Ti-Sapphire laser; one of the most reliable femtosecond pulse sources. To our knowledge, this paper is the first to report on the SA of Ag NPs embedded in glass using sub-30 fs laser pulses at 400 nm.

Several methods have been already used to produce bulk glass with embedded metal NPs [19–21] and among them ion exchange represents the most convenient and feasible method for NP formation. During the ion exchange process, the glass wafer is submerged into a reaction melt containing the ions, which are to be introduced into the surface of the glass. In our case, Na^+ ions from the glass surface are gradually replaced by Ag^+ ions from the melt. The advantage of the ion exchange method is that the process of doping can be easily controlled, e.g. by composition of the melt and temperature or time of the exchange. The resulting optical properties of the metal–glass composites depend mainly on the parameters of the NPs [22,23].

2. Sample preparation and characterization

2.1. Preparation of samples

Ag NPs were embedded into glass substrates by the ion exchange method. We used a commercially available glass BK7 containing 64.8% SiO_2, 11.5% B_2O_3, 9.3% Na_2O, 3.9% K_2O, 0.4% Al_2O_3, and 10.2% BaO (wt.%) supplied by the Glass Institute Hradec Kralove Ltd., Czech Republic. Both sides of the substrates with thickness of 0.7 mm were polished to optical quality and then thoroughly cleaned in acetone and CrO_3 before and after the ion exchange process. The conditions of the ion exchange process were chosen according to our previous results obtained from a study performed on different silicate glasses [24]. The glass substrates were doped with Ag at 320 °C by a 50-minute $Ag^+ \leftrightarrow Na^+$ ion exchange in molten salt baths of eutectic melt of $NaNO_3$ and KNO_3 containing 14 mol% of $AgNO_3$. Then, one piece of BK7 containing Ag ions (as-exchanged sample) was annealed in air for 1 h at 600 °C in order to prepare the as-annealed sample (according to [25]).

2.2. Characterization of samples

Optical absorption spectra were collected by a dual beam spectrophotometer Cary 50 from 300 to 800 nm. In Fig. 1 it is seen that the as-exchanged sample shows no absorption band around 400 nm (a characteristic wavelength indicating the presence of Ag NPs in the glass). After the annealing of the as-exchanged sample, a substantial increase of optical absorption was observed at 420 nm (Fig. 1) which can be attributed to SPR of Ag NPs formed in the glass [26–30]. The SA is thus expected to be observed for the as-annealed sample at 400 nm (the second harmonic of the Ti-sapphire laser) due to the presence of Ag NPs.

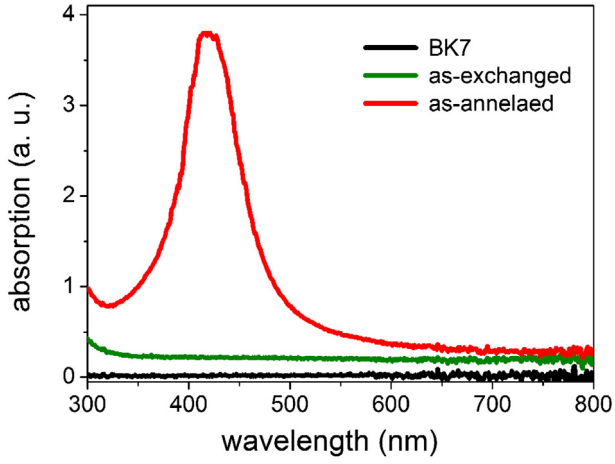

Fig. 1. Absorption spectra of the as-exchanged and as-annealed for glass BK7.

According to [31], the average radius R of the embedded Ag NPs in glass BK7 can be calculated using the following formula:

$$R = \frac{V_f \lambda_p^2}{2\pi C \Delta\lambda} \tag{3}$$

where V_f is the Fermi velocity of the electrons in bulk metal (for silver the value of V_f is 1.39×10^8 cm·s^{-1}), $\Delta\lambda$ is the full width at half maximum of the absorption band, λ_p is the characteristic wavelength at which SPR occurs and C is the speed of light in free space. From Eq. (3) the average radius of the embedded Ag NPs was calculated to be 2 nm.

The distribution of silver in both as-annealed and as-exchanged samples was determined by Electron Microprobe Analysis. The analysis was done by the CAMECA SX-100 equipped with four crystal spectrometers, detector of backscattered electrons and detector of secondary electrons. In Fig. 2a it is seen that the as-exchanged sample contained 3.5% silver at the surface. The concentration of silver decreased towards the depth of the sample and reached zero in approx. 1 μm below the surface. After annealing the concentration of silver decreased to 0.2% and the layer containing silver became much thicker (110 μm) than resulting from the ion exchange process (Fig. 2b).

We assumed that during the annealing most silver diffused deeply into the glass substrate and that this process happens very fast (comparing with other ion exchanges, e.g. $K^+ \leftrightarrow Na^+$). Since glass BK7 contains alkali ions, it seems probable that Ag migrated through the glass by the ion exchange mechanism also during the annealing. However, some amount of Ag nucleates, creating thus very small NPs with an average size of 2 nm because the time of the annealing process is not long enough to allow all Ag to diffuse.

Information on the presence of defects in the glass structure [32,33] as well as the energy transfer of silver between levels $4d^{10} \rightarrow 4d^9\ 5s^1$ [34–37] can be obtained from photoluminescence (PL) spectra. PL spectra of our samples were measured in the range of 200–900 nm by spectrophotometer Hitachi F 4500. The samples were measured under excitation wavelengths from 200 nm to 900 nm. Fig. 3 shows the PL spectra for excitation wavelength of 260 nm at which the highest PL emission was observed.

The PL spectrum in Fig. 3 indicates that luminescence of the glass BK7 decreased in two steps: immediately after the ion exchange and then again after the annealing.

It is supposed that the decrease of the luminescence could indicate the re-ordering of the glass structure during the ion exchange and also during the annealing. Both procedures, ion exchange and annealing, were done at such temperatures (320 °C and 600 °C, respectively) where the major changes of the glass network can be expected to

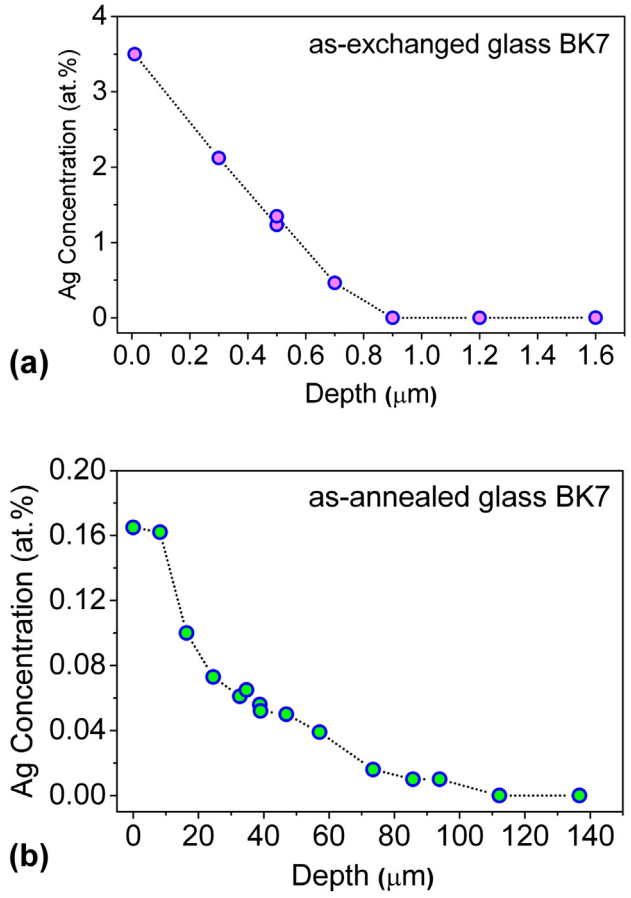

Fig. 2. Concentration depth profile of Ag in the (a) as-exchanged and (b) as-annealed glass BK7.

occur. Moreover, the annealing temperature was higher than the transformation temperature T_g of the glass (T_g of glass BK7 is approx. 560 °C) and it means that the formation of a new glass network is very probable. However, it is well known that borosilicate glasses are very stable against crystallization. It is assumed that crystallization of the glass did not occur because the kinetics of nucleation and growth is slow. In order to see the sign of crystallization the glasses should be annealed for longer time [38].

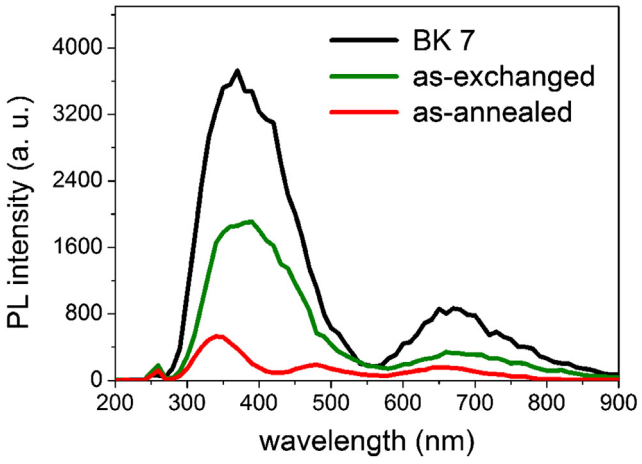

Fig. 3. Photoluminescence spectra of the as-prepared, as-exchanged and as-annealed glass BK7.

It should be also noted that luminescence band between 200 and 400 nm of the as-annealed sample can be attributed to silver ions Ag^+, while that one around 450 nm can be attributed to the dimmers Ag^+–Ag^+. Small aggregates (such as Ag-pairs, trimers) can be understood as intermediate species before the precipitation of metallic NPs. Their presence suggests that post-exchange annealing led to increase the size of the molecule of nucleus Ag^0 into silver NPs Ag_n as follows: $Ag^0 \rightarrow Ag_2^+ \rightarrow Ag_3^+/Ag_3^{2+} \rightarrow \cdots \rightarrow Ag_n$ [39]. The observed PL behavior can be related to a progressive Ag aggregation as it was observed in [35,40]. Therefore, it is supposed that a certain amount of silver was transformed into NPs, certain amount stayed in form of nucleus and intermediate species and the rest of silver was in state Ag^+. It is expected that with longer time of annealing, the amount of silver in oxidation state Ag^+ will decrease as a result of creation of Ag NPs.

3. Results and discussions

A Ti-sapphire amplifier was used as a source of ultrashort laser pulses of 25 fs duration with a central wavelength of 800 nm and a repetition rate of 1 kHz. The nonlinear absorption of the as-exchanged and as-annealed samples was studied at 800 nm using Z-scan method. First, the threshold intensity, at which the as-prepared glass substrates show nonlinear absorption, was determined and then the as-exchanged and as-annealed samples were examined. Although the as-annealed glass BK7 was expected to show two-photon absorption (2PA) at 800 nm corresponding to linear absorption around 400 nm, no detectable Z-scan signal was observed within the range of applied intensities (below the as-prepared glass intensity threshold). This could be due to the low concentration of the Ag NPs. In order to observe 2PA and detect a Z-scan signal the irradiation intensity should be increased but it will be very complicated to separate the contribution of 2PA of the Ag NPs and three-photon absorption (3PA) of the glass substrate (glass BK7 has a band gap of 4 eV thus, absorption of three photons at 800 nm provides enough energy to bridge the gap). The as-exchanged sample also showed no nonlinear absorption below the as-prepared glass intensity threshold that is not unexpected since no linear absorption was observed around 400 nm in this sample.

The SA effect of the as-exchanged and as-annealed samples was investigated using femtosecond pulses at 400 nm produced via second harmonic generation of the original laser pulses at 800 nm by a Barium borate crystal (BBO). The crystal was followed by a band-pass blue filter to block the 800 nm pulses in order to avoid nondegenerate process resulting from simultaneous excitation at 400 nm and 800 nm and measure pure degenerate process at 400 nm.

In NLT method the blue laser beam with 5 mm diameter was focused within the sample using a 300 mm focal length lens leading to a beam waist radius of 21.4 μm and a Rayleigh length of 2.6 mm considering a beam quality factor of 1.4. The Rayleigh length is much greater (24 times) than the thickness of Ag NPs layer (0.11 mm) and also greater (3.5 times) than the thickness of the glass substrate providing a uniform intensity distribution over the whole length of the sample. The sample was kept at the focus while the input pulse energy was changed and the output pulse energy was measured as a function of the input pulse energy. The result of NLT experiment for as-annealed sample is shown in Fig. 4a. As seen, the slop of the curve indicates that the transmittance (quotient of the output to the input pulse energy) increases versus pulse energy. This reveals the occurrence of the SA phenomenon. The as-exchanged sample looked transparent at 400 nm thus no SA was observed in this sample.

In Fig. 4a the circle points show the measured data and the solid curve represents the best fit to the data using Eq. (2) from which the linear absorption coefficient was extracted to be 143 mm^{-1}. The saturation pulse energy was determined to 330 nJ corresponding to a saturation intensity of 8.5×10^{11} $W \cdot cm^{-2}$. The information for saturation intensity of Ag NPs using femtosecond pulses at 400 nm is very rare in the literature (most works have been done using ns pulses) thus, it is

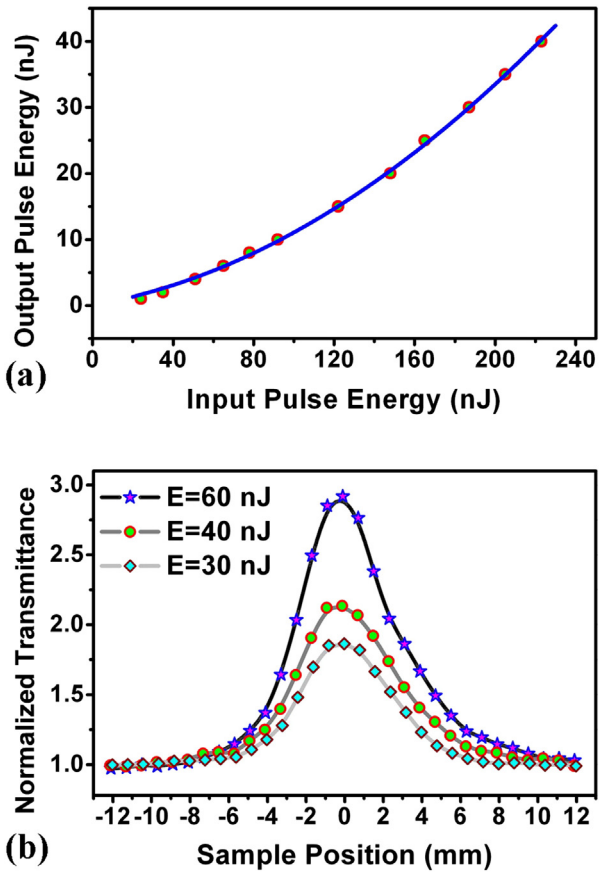

Fig. 4. (a) Output pulse energy versus input pulse energy for as-annealed glass BK7. Circle points show the experimental data and the solid curve is the best fit to the data using Eq. (2). (b) Z-scan results for as-annealed glass BK7 with different pulse energies. The points are the measured data and the solid lines were just displayed to guide the eye.

not possible to make a real comparison between our results and the reported results. However, just as a rough comparison, some literature data are reviewed here. The saturation intensity for Ag NPs prepared by chemical reduction of silver nitrate in aqueous solution has been reported 2×10^8 W·cm^{-2} using 7 ns pulses at 532 nm [7], 7×10^7 W·cm^{-2} using 5 ns pulses at 532 nm [41] and 9×10^{13} W·cm^{-2} using 100 fs pulses at 800 nm [41]. The difference between our results and the reported results is due to three reasons. 1) The nonlinearities of most materials using ns pulses are about three–four orders of magnitude larger than those using fs pulses at the same wavelength. 2) The reported data have been obtained at off resonance wavelength (530 nm and 800 nm) whereas our study has been performed close to resonance wavelength (400 nm). 3) These differences could be also due to the different concentrations, sizes or shapes of Ag NPs. Compared with the reported data for Ag NPs, the saturation intensity for our sample (as-annealed glass BK7) measured with sub-30 fs pulses at 400 nm seems to be very low revealing a strong nonlinearity. Therefore, it can be concluded that the as-annealed sample containing Ag NPs showed strong SA at the second harmonic of the Ti- sapphire laser (400 nm) which proves a promising requirement to be exploited for designing all optical switching devices. The investigation on such an application is an ongoing research.

Z-scan technique was also used to study the SA behavior of the prepared samples using femtosecond pulses at 400 nm. The same NLT setup was used for the Z-scan setup providing a large Rayleigh length of 2.6 mm which is much greater than the thickness of the Ag NPs layer. This fulfilled the thin sample criterion which is required for Z-scan experiment. In Z-scan method the input pulse energy is kept constant while the sample is scanned along the propagation direction of the laser beam through the focus. The beam size and thus the intensity within the sample change as the sample moves towards and then away from the focus. The Z-scan result, showing the measured transmittance versus the sample position, would be a symmetric peak (valley) indicating the SA behavior (multi-photon absorption).

The Z-scans of the as-annealed sample for three different input pulse energies are demonstrated in Fig. 4b. As seen in Fig. 4b, the transmittance is low when the sample is far away from the focal point where the beam size is larger and thus the intensity is not enough to saturate the absorption. As the sample is moved towards the focus the beam size becomes smaller thus, the sample is irradiated with higher intensity leading to the saturation of absorption which is observed as an increase in the transmittance. This happens due to the depletion of the ground state population of the oscillating electrons of the conduction band of the Ag NPs during the ultrashort laser pulse excitation. The as-exchanged sample was also examined by Z-scan technique using femtosecond laser pulses at 400 nm. At lower pulse energies its transmittance was a straight line indicating no nonlinearity. At higher intensity it showed a valley-shape transmittance; a sign of 2PA at 400 nm in the glass substrate. No SA was observed for the as-exchanged sample.

An interesting behavior was observed for as-annealed sample when the band-pass blue filter was removed thus, the sample was irradiated simultaneously by both 800 nm and 400 nm pulses (Fig. 5). A transmittance increase at lower intensities followed by a rapid decrease at higher intensities (in the vicinity of the focus) indicates that the as-annealed sample exhibits an intensity-dependent switching from SA to reverse saturable absorption (RSA). A very similar behavior has been reported in [42,43] and in [28,44] and attributed to the presence of gold and Ag NPs in the substrate.

However, we assume that the observed SA and RSA arise from different origins and processes. The SA behavior of the as-annealed sample occurs due to the depletion of the ground state population of the oscillating electrons of the conduction band of the Ag NPs as the result of absorption of 400 nm pulses which leads to SPR effect. This behavior dominates when the sample is far away from the focal point where the light intensity at 400 nm is enough to saturate the absorption but the light intensity at 800 nm is not sufficient so that the multi-photon absorption in the glass substrate can compensate the effect of SA. The RSA of the sample that dominates at higher intensities in the vicinity of the focus is ascribed to degenerate 3PA absorption at 800 nm and/or non-degenerate 2PA at 800 nm and 400 nm by the glass substrate (the band gap of BK7 is 4 eV thus, absorption of three photons at 800 nm or two photons at 800 nm and 400 nm can lead to bridge the gap).

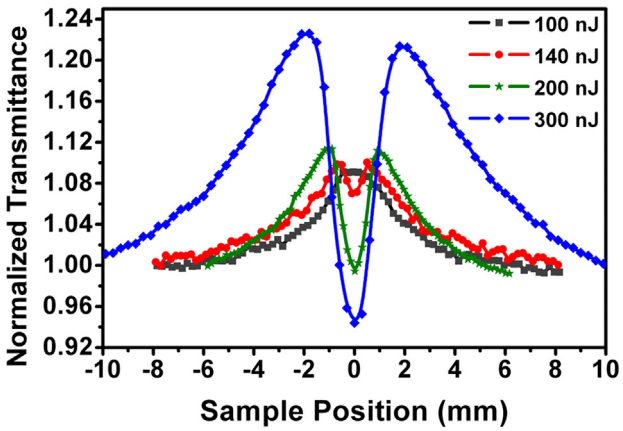

Fig. 5. Z-scans of the as-annealed glass BK7 when it was irradiated simultaneously by 800 nm and 400 nm. The pulse energies represent the summation of both 800 nm and 400 nm pulse energy.

4. Conclusions

In this publication the ion exchange method and subsequent post-exchange annealing were used to embed Ag NPs within the glass BK7. The linear and nonlinear optical properties of the prepared samples were studied. The presence of Ag NPs with an average size of 2 nm was confirmed in the as-annealed glass BK7 by the optical absorption spectrometry. It was found that during the annealing most silver diffused from the surface of the glass deeply into the glass substrate. However, some amount of silver nucleated during the annealing, thus resulting in the formation of very small NPs. The results showed that the probable mechanism of silver migration during the annealing was the ion exchange process accompanied by re-ordering of the glass structure due to the high temperature of the annealing process. The as-exchanged glass BK7 showed no evidence to confirm the presence of Ag NPs within the glass. For the first time to our knowledge, the nonlinear optical behavior of the as-annealed glass BK7 with embedded Ag NPs was studied using sub-30 fs laser pulses at 400 nm by the NLT and Z-scan techniques. From the SA behavior measured by the NLT method, a saturation intensity of 8.5×10^{11} W·cm^{-2} was obtained for the as-annealed glass BK7. The strong SA observed in the as-annealed glass BK7 at 400 nm promises an efficient means for designing all optical switching devices appropriate for the second harmonic of the Ti-sapphire laser operating at 800 nm. An intensity dependent switching from SA to RSA was also observed when the as-annealed glass BK7 was irradiated simultaneously by 800 nm and 400 nm femtosecond pulses. This could be attributed to two different processes. The SA observed at lower intensity can be ascribed to the depletion of the ground state population of the oscillating electrons of the conduction band of the Ag NPs whereas, the RSA, which was observed at higher intensity, can be ascribed to multi-photon absorption of the glass substrate.

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