Large and opposite changes of the third-order optical nonlinearities of chalcogenide glasses by femtosecond and continuous-wave laser irradiation

Qiming Zhang, Wei Liu, Liying Liu, and Lei Xu[a)]
The State Key Laboratory for Advanced Photonic Materials and Devices, Department of Optical Science and Engineering, School of Information Science and Engineering, Fudan University, Shanghai 200433, China

Yinsheng Xu and Guorong Chen
Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China

(Received 5 August 2007; accepted 16 October 2007; published online 2 November 2007)

We report that the nonlinear refractive index (n_2) of As_2S_3 glass can be enhanced after irradiation by a femtosecond laser but suppressed after irradiation by a continuous-wave (cw) laser, although both the femtosecond laser and cw laser induce photodarkening in the glass. Photodarkening by the femtosecond laser increases n_2 by as much as 50%, while irradiation by a subbandgap cw laser decreases n_2 by as much as 60% of its original value. The results provide a way to manipulate the third-order optical nonlinearity of this photonic glass. Mechanisms of the optical nonlinearity changes are discussed. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2805636]

All-optical switching relies on the strong third-order optical nonlinearities of photonic materials. Chalcogenide glasses are narrow-bandgap semiconducting glasses. They have broad infrared transmission windows and large, broadband nonresonant third-order optical nonlinearities.[1] Attempts have been made to use chalcogenides for photonic applications. However, even though the nonlinear refractive index (n_2) of chalcogenides is two orders of magnitude higher than that of silica, a fiber length of 48 cm is necessary to demonstrate optical switching.[2] Higher n_2 is required for increasing efficiency and reducing component sizes. A n_2 enhancement of 60% has been observed in an As_2S_3 thin film photodarkened by (cw) light with its wavelength at the bandgap of the material (so-called bandgap light).[3]

According to Miller's rule[4] and the theory of Sheik-Bahae *et al.*,[5] photodarkening can enhance the nonlinear refractive index because photodarkening occurs by a redshift of the absorption edge [a decrease in bandgap (E_g)] and is accompanied by an increase in refractive index (n_0) after irradiation with bandgap or subbandgap light.[6]

Conventional chalcogenide glass photodarkening occurs when laser light is absorbed by the material. Infrared femtosecond radiation to which chalcogenide glasses are transparent can also induce photodarkening through two-photon absorption.[7] Material processing by femtosecond lasers takes advantage of the high peak intensity and local nonlinear absorption that come with ultrashort pulses. However, few reports on changes of optical nonlinearity after femtosecond irradiation can be found.

In this paper, we present experimental results on changes of linear (refractive index and absorption spectra) and nonlinear properties (n_2) of photodarkened As_2S_3 glasses after laser irradiation. The purpose of the work is exploring the possibility of promoting optical applications of chalcogenides by enhancing their nonlinearities. Radiation from femtosecond and subbandgap cw lasers was used to write structures inside As_2S_3 glasses. The results show that the femtosecond radiation increases n_2, while the subbandgap cw radiation decreases n_2.

As_2S_3 plates were prepared by the conventional melt-quench method. An annealed glass rod was cut and polished to a thickness of 760 μm. In the femtosecond laser irradiation experiment, photodarkening was induced by a 130 fs laser at a wavelength of 780 nm and a repetition rate of 78 MHz. The laser was focused to a 5 μm diameter spot inside the glass (sample F) with a microscope objective (4×, numerical aperture=0.1). The light intensity at the focal point varied from 6.5 to 9.8 GW/cm^2, which corresponds to 0.13 to 0.19 nJ/pulse, and the polarization was perpendicular to the scanning direction. A 1×1 mm^2 area was photodarkened by moving the sample in a plane perpendicular to the beam propagation direction with the writing speed varying from 50 to 100 μm/s. The inset of Fig. 1 is a microscopic picture of the region written with the 6.5 GW/cm^2 femtosecond laser at a scanning speed of 50 μm/s. The exposed re-

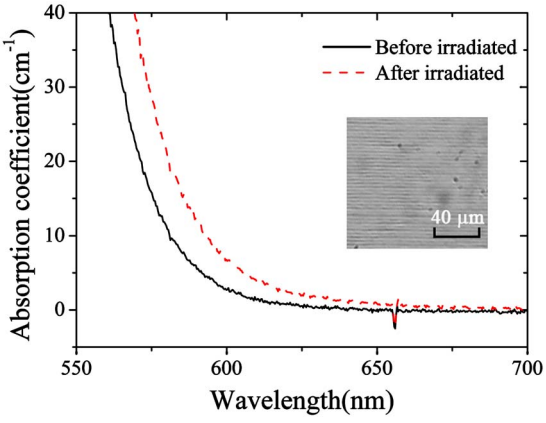

FIG. 1. (Color online) Absorption spectra of the original and femtosecond-laser-irradiated As_2S_3 glasses. Inset: microscope picture of the region irradiated by the femtosecond laser.

[a)]Author whom correspondence should be addressed. Electronic mail: leixu@fudan.ac.cn

TABLE I. Summary of changes in optical properties after femtosecond laser irradiation.

Scanning speed (μm/s)	100	100	75	50	100
Laser Intensity (GW/cm^2)	9.8	7.8	6.5	6.5	6.5
Δn_0[a]	<0.001	<0.001	<0.001	0.001	<0.001
ΔE_g (eV)[a]	−0.041	−0.024	−0.022	−0.043	−0.016
n_2[a] (10^{-14} cm^2/W)	3.2±0.3	2.9±0.3	2.7±0.3	3.6±0.4	2.6±0.3
$(\Delta n_2/n_2)$[a] (%)	33	21	13	50	8.3
$(\Delta n_2/n_2)$[b] (%)	<1	<1	<1	1	<1
$(\Delta n_2/n_2)$[c] (%)	17	8.9	8.6	17	5.3

[a]n_2, Δn_0, ΔE_g, and $\Delta n_2/n_2$ are experimentally measured.
[b]Calculated by Miller's rule.
[c]Calculated by the theory of Sheik-Bahae's *et al.*

gion is made up of parallel lines. In comparison, photodarkening was also induced in another sample (sample C) by an Ar^+-laser-pumped cw dye laser centered at 579 nm. The absorption coefficient of As_2S_3 at 579 nm is 12 cm^{-1}, so about 40% of the laser light is absorbed by the 760 μm thick glass. The laser spot size on the glass is 1.77 mm^2, and its intensity is 3.6 W/cm^2. Photodarkening was induced by exposure times from 20 to 150 min.

The bandgap energy (E_g) of As_2S_3 before photodarkening is 2.4 eV, which corresponds to a bandgap wavelength (λ_g) of 517 nm. Radiation from both the femtosecond and subbandgap cw lasers induced photodarkening (an increase of λ_g) in As_2S_3 glasses. For example, Fig. 1 shows the absorption spectra before and after femtosecond laser irradiations at 6.5 GW/cm^2 with a writing speed of 50 μm/s. The changes in bandgap energy (ΔE_g) were calculated by $\Delta E_g = -1240\Delta\lambda/\lambda_g^2$, in which $\Delta\lambda$ is the change in λ_g.

In sample C, in addition to photodarkening, a volume expansion of a few microns on the front surface was observed as well. The change in thickness was measured by a surface profilometer (Zygo Co.). A similar effect has been reported before.[8] On the other hand, sample F did not display any change in surface morphology.

The conventional optical Kerr effect was used to measure n_2. 28 ps laser pulses at 1064 nm with a repetition rate of 10 Hz from a mode-locked Nd doped yttrium aluminum garnet laser were used as the pump and probe beam.[9] Time-resolved optical Kerr effect signals of the photodarkened and unphotodarkened areas showed the same profile and time response. Before photodarkening, n_2 was 2.4 $\times 10^{-14}$ cm^2/W. The measured values of n_2 after irradiation by the femtosecond laser at different intensities and writing speeds are listed in Table I. For all conditions of irradiation, n_2 of the photodarkened area increases. At the same writing speed, n_2 increases monotonically with the writing energy, while at a fixed writing intensity, n_2 decreases monotonically with the writing speed. The largest enhancement is 50%. Table II summarizes the changes in n_2 when the glass was irradiated by the 579 nm cw laser for different durations and shows that n_2 decreases after irradiation. Longer irradiation time results in a larger reduction of n_2. The enhancement of n_2 induced by the femtosecond laser is stable for more than 9 months. On the other hand, the reduction of n_2 induced by the cw laser recovered almost completely after 4 months.

n_2 can be calculated by using Miller's rule and the theory of Shiek-Bahae *et al.* Two linear optical parameters are required for the calculation: the change in the energy gap (ΔE_g) and the change in the linear refractive index (Δn_0). ΔE_g can be deduced directly from the absorption spectra. Two experimental setups were used to measure Δn_0. In the case of cw laser irradiation, the total sample area under the laser spot was exposed. A total internal reflection angle method using prism coupling[10] was used to measure Δn_0 at 632.8 nm. The minimum measurable Δn_0 was 0.001. The largest value ($\Delta n_0 = -0.01$) was measured in a spot that was written by 3.6 W/cm^2 light for 150 min. In contrast, since the femtosecond light was focused inside the sample, the area with the maximum change in the refractive index is beneath the surface. Therefore, Δn_0 was measured by a microinterference method. Light from a He–Ne laser (632.8 nm) is split into two beams; one beam passes through the sample and interferes with the other (reference) beam, which propagates through a length of free space, and generates straight interference fringes. The parallel interference fringes shift when the beam passes through an area that has different refractive indices. Figure 2 shows the interference pattern from light passed through an area written by a 6.5 GW/cm^2 femtosecond laser with a writing speed of 50 μm/s. The distortion shows an increase of $\Delta n_0 = 0.001$. Δn_0 with other femtosecond laser processing conditions is smaller and thus no clear interference fringe shifts could be resolved. The n_0 of As_2S_3 before photodarkening is 2.476 at 1.064 nm. Using the measured Δn_0 and ΔE_g, Δn_2 can be calculated. All calculated Δn_2 are summarized in Tables I and II for various femtoseconds and cw laser irradiation conditions, respectively.

It is clear from Table I that, although both Miller's rule and the theory of Sheik-Bahae *et al.* predict an increase of n_2

TABLE II. Summary of changes in optical properties after cw subbandgap laser irradiation.

Exposure time (min)	20	40	80	150
Δn_0[a]	−0.003	−0.003	−0.004	−0.01
Surface bump depth ΔD (μm)[a]	0.5	1	2	2
ΔE_g (eV)[a]	−0.0046	−0.007	−0.012	−0.021
n_2[a] (10^{-14} cm^2/W)	2.1±0.2	1.7±0.2	1.6±0.2	1.0±0.1
$(\Delta n_2/n_2)$[a] (%)	−13	−29	−33	−60
$(\Delta n_2/n_2)$[b] (%)	−1	−1	−2	−4
$(\Delta n_2/n_2)$[c] (%)	1.8	2.6	4.5	8.3

[a]Experimentally measured data.
[b]Calculated by Miller's rule.
[c]Calculated by the theory of Sheik-Bahae *et al.*

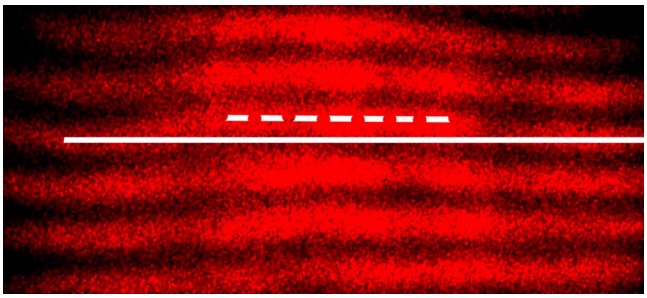

FIG. 2. (Color online) Interference pattern of the glass. Clear fringe shifts can be seen in the central, photodarkened area. Displacement between solid line and dash line represents interference fringe shift.

if the material has larger n_0 and λ_g, the measured n_2 enhancement is significantly larger than the value predicted from the theories. On the other hand, in the case of cw laser irradiation (Table II), the sample still shows photodarkening, but n_0 and n_2 decrease after irradiation. Therefore, when the theory of Sheik-Bahae *et al.* is applied, a positive Δn_2 is expected because $\Delta E_g < 0$, while a negative Δn_2 is obtained from Miller's rule because $\Delta n_0 < 0$. Similar to the results for femtosecond irradiation, the calculated value of Δn_2 is much smaller then that from experiment.

The reason that the values of Δn_2 derived from the two theories are smaller than the experimental results can be explained by the oversimplifications of the models. The theory of Shiek-Bahae *et al.* is based on the electronic structure of direct-gap crystalline semiconductors. Miller's rule is basically an empirical rule for existing glasses. Neither theory is suitable for describing the change of n_2 in semiconducting chalcogenide glasses, especially when the glass has local metastable structural variations (local polarizability and density changes).

One origin of the decrease of n_2 in cw irradiation may be the photoexpansion observed in our experiment. Photoexpansion is a volume expansion process accompanying photodarkening.[8] According to the classical anharmonic oscillator model,[11] The third-order nonlinear optical susceptibility is proportional to atomic density (N) and the second hyperpolarizability (γ). Photoexpansion results in a density decrease, which leads to a decrease in n_2. However, photoexpansion alone cannot explain such a large decay in n_2 as observed here because a decrease of 60% in n_2 would require an increase of 150% in volume, which is much larger than the value observed in our experiment (about 0.3%). Therefore, a decrease in γ is expected as well. In the femtosecond irradiation experiment, no volume change was observed. The main origin of the enhancement in n_2 should be the increase of γ. The mean value of γ for each atom of As_2S_3 is 2.0×10^{-36} esu. Since γ is proportional to $\chi^{(3)}$, γ should be 3.0×10^{-36} esu in an exposed region where the enhancement in n_2 is 50%. In an exposed region where the reduction in n_2 is 60%, γ should be 0.8×10^{-36} esu. By comparing with the γ of other materials,[12–14] the expected variation in γ after exposure is in a reasonable range.

The opposite change in γ by femtosecond and cw laser processing implies that different defects were generated. That is because femtosecond laser light is absorbed via two-photon absorption between the valence and conduction bands (corresponding to a wavelength of 390 nm), and the wavelength of the cw laser (579 nm) is at the Urbach edge, which means that the absorption occurs between the valence and conduction band tail states.[15] Thus, different kinds of defects are created. These defects are related to the photodarkening. Although the microscopic origin of photodarkening is not fully understood yet, some models have been suggested.[16,17] Several kinds of defects may be responsible for the change of γ. Since $\gamma \propto \alpha^2$,[18] (α is the linear polarizability) if the femtosecond laser generates defects that have larger α, n_2 will go up. These defects include self-trapped excitons, which are conjugate pairs of As_4^+ and S_1^- defects[16] (the subscripts describe the coordination and the superscripts correspond to the charge). On the contrary, the cw laser generates defects that decrease α such as the homopolar As–As and S–S bonds that are converted from the heteropolar As–S bonds.[17] Therefore, the signs of the changes in n_2 may be different after irradiation by femtosecond laser and cw laser.

In conclusion, we have demonstrated that when As_2S_3 glass is photodarkened by irradiation with radiation from femtosecond and subbandgap cw lasers, n_2 of the glass changes in opposite directions. Photodarkening by a femtosecond laser leads to an increase of the nonlinear refractive index, while irradiation with a cw subbandgap laser suppresses n_2. Hence, it is possible to manipulate the third-order optical nonlinearity of chalcogenide glasses by irradiating the material with different lasers.

This work was supported in part by National Natural Science Foundation of China (Grant Nos. 60638010, 10574032, 50532030, 60478005, and 60478005) and Science and Technology Commission of Shanghai (06JC14010).

[1] J. Zarzycki, *Glasses and Amorphous Materials* (Wiley, New York, 2001), Chap. 7, p. 330.
[2] M. Asobe, T. Kanamori, and K. Kubodera, IEEE Photonics Technol. Lett. **4**, 362 (1992).
[3] J. M. Laniel, N. Ho, R. Vallee, and A. Villeneuve, J. Opt. Soc. Am. B **22**, 437 (2005).
[4] R. C. Miller, Appl. Phys. Lett. **5**, 17 (1964).
[5] M. Sheik-Bahae, D. C. Hutchings, D. J. Hagan, and E. W. Van Stryland, IEEE J. Quantum Electron. **27**, 1296 (1991).
[6] G. Pfeiffer, M. A. Paesler, and S. C. Agarwal, J. Non-Cryst. Solids **130**, 111 (1991).
[7] O. M. Efimov, L. B. Glebov, K. A. Richardson, E. W. Van Stryland, T. Cardinal, S. H. Park, M. Couzi, and J. L. Bruneel, Opt. Mater. (Amsterdam, Neth.) **17**, 379 (2001).
[8] H. Hamanaka, K. Tanaka, A. Matsuda, and S. Iizima, Solid State Commun. **19**, 499 (1976).
[9] X. Liu, P. Yang, L. Ji, L. Liu, and L. Xu, Opt. Express **14** 11709 (2006).
[10] P. K. Tien, R. Ulrich, and R. J. Martin, Appl. Phys. Lett. **14**, 291 (1969).
[11] R. W. Boyd, *Nonlinear Optics* (Academic, New York, 1992), Chap. 1, p. 28.
[12] J. L. Bredas, C. Adant, P. Tackx, A. Persoons, and B. M. Pierce, Chem. Rev. (Washington, D.C.) **94**, 243 (1994).
[13] L. Zhao, L. Mu, G. Yang, Z. Su, C. Qin, and C. Shao, Chin. J. Chem. **25**, 465 (2007).
[14] S. Wang, W. Huang, H. Yang, Q. Gong, Z. Shi, X. Zhou, D. Qiang, and Z. Gu, Chem. Phys. Lett. **320**, 411 (2000).
[15] J. Tauc, *The Optical Properties of Solids* (North-Holland, Amsterdam, 1970), Chap. 5, p. 277.
[16] R. A. Street, Solid State Commun. **24**, 363 (1977).
[17] M. Frumar, A. Firth, and A. E. Owen, Philos. Mag. B **50**, 463 (1984).
[18] C. C. Wang, Phys. Rev. B **2**, 2045–2048 (1970).