Composition dependence of photoinduced second-order nonlinearity of germanosilicate glasses

Jinhai Si

Department of Electronic Science and Technique, School of Electronics & information Engineering, Xi'an Jiaotong University, Xianning-xilu 28, Xi'an, 710049, China
jinhaisi@mail.xjtu.edu.cn

Shingo Kanehira, Kiyotaka Miura, and Kazuyuki Hirao

Department of Material Chemistry, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

Abstract: The dependence of the photoinduced second-order nonlinearity of germanosilicate glasses on the GeO_2-SiO_2 composition was investigated using photoinduced second-harmonic generation (SHG). The photoinduced SHG was encoded by coherent superposition of the 800-nm fundamental and the 400-nm second-harmonic light of a femtosecond laser. Experimental results showed that the photoinduced second-order optical nonlinearity increased with increasing concentrations of GeO_2 in the glasses, and the concentration dependence was mainly due to the dependence of the photoinduced internal dc electric field of the glass on the GeO_2-SiO_2 composition.

OCIS codes: (320.7110) Ultrafast nonlinear optics, (190.4180) Multiphoton processes, (140.7090) Ultrafast lasers, (160.4330) Nonlinear optical materials, (190.4720) Optical nonlinearities of condensed matter

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1. Introduction

Nonlinear optical glasses have been developed as promising candidates for constructing optical signal operation systems because they have the advantages of ease of fabrication of the fiber or film waveguide, high transparency, high chemical and thermal durability, and a high threshold to optical damage [1-6]. Second-harmonic generation (SHG) in glasses is an interesting phenomenon because it usually should be forbidden considering that glass has macroscopic inversion symmetry. When infrared fundamental light was introduced into the glass along with its second-harmonic light, the macroscopic inversion symmetry in the glass could be broken and SHG could be observed in the glass (this process is usually called as optical poling) [7-11]. In the optical poling process, phase matching for SHG can automatically be achieved. The photoinduced second-order optical nonlinear susceptibility $\chi^{(2)}$ in the process can be expressed as $\chi^{(2)} = 3\chi^{(3)}E_{dc}$, where $\chi^{(3)}$ and E_{dc} are, respectively, the third-order optical nonlinear susceptibility of the glasses and the photoinduced internal dc electric field due to photoinduced currents in the glasses [9,10]. The photoinduced currents are usually associated with some photoinduced defects in glasses. So, we expect that the photoinduced $\chi^{(2)}$ of glasses may be increased by varying the composition of the glasses.

In this paper, we investigated the dependence of the photoinduced second-order nonlinearity of germanosilicate glasses on the GeO_2-SiO_2 composition using photoinduced SHG. The photoinduced SHG was encoded by coherent superposition of the 800-nm fundamental and the 400-nm second-harmonic light of a femtosecond laser. Experimental results showed that the photoinduced second-order optical nonlinear susceptibility $\chi^{(2)}$ increased with increasing concentrations of GeO_2 in the glasses. Measurements of third-order harmonic generation (THG) and the photoinduced SHG for the glasses indicated that the composition dependence of the photoinduced $\chi^{(2)}$ was mainly due to the GeO_2-SiO_2 composition dependence of the photoinduced internal dc electric field in the glass.

2. Experiments

The GeO_2-SiO_2 glasses used in our experiments were prepared by Shin-Etsu Chemical Company by a vapor axial deposition method. Figure 1 shows the experimental setup for photoinduced SHG of the germanosilicate using femtosecond laser pulses. A Ti:sapphire regenerative amplifier laser system was used for the photoinduced $\chi^{(2)}$ preparation of the germanosilicate glass, which emitted 150-fs, 800-nm laser pulses at a repetition rate of 1 kHz. The average power of the laser was 900 mW. Seeding beam ω was split from the source beam and passed through a time-delay device and a λ/2 plate to control the path length and the polarization of the beam, respectively. Another beam separated from the source beam was frequency doubled by a KDP crystal, served as another seeding beam, and is denoted seeding beam 2ω here. The two collinear seeding beams were introduced into the 0.5-mm-thick glass sample through a 10-cm focal-length, chromatic quartz lens. We achieved time superposition of pulses between the two seeding beams by adjusting the delay device and observing the optical Kerr effect of CS_2. During the photoinduced $\chi^{(2)}$ preparation, the two seeding beams were introduced simultaneously into the glass sample; during the probe, beam 2ω was blocked by a shutter and only the beam ω remained incident. The SHG signal of beam ω was detected by a photomultiplier tube and observed and averaged by an oscilloscope. A 400-nm bandpass filter was placed in front of the photomultiplier to allow only the SH signal to pass through it. The beam radius ($1/e^2$ of the intensity radius) at the sample and the pulse's maximum-energy were approximately 22 μm and 0.75 μJ for beam ω and 20 μm and 0.02 μJ for beam 2ω, respectively.

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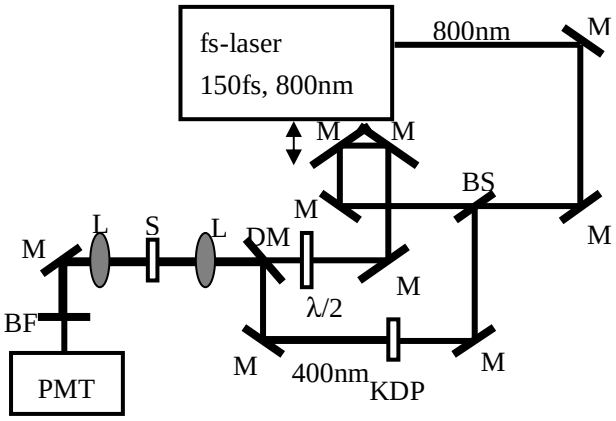

Fig. 1. Schematic of the experimental setup for photoinduced SHG of the germanosilicate using femtosecond laser pulses. M: mirror; BS: beam splitter; DM: diachronic mirror; L: lens; BF: bandpass filter; S: sample; PMT: photomultiplier tube.

3. Results and discussion

First, the growth and decay processes of the photoinduced $\chi^{(2)}$ of a glass sample with 10-GeO_2-90-SiO_2 (mol. %) composition were measured, as shown in Fig. 2(a). For the preparation process the photoinduced $\chi^{(2)}$ reached its saturation value in 10 min; laser intensities in the glass sample for light beams ω and 2ω were set at 81 and 1.2 GW/cm^2, respectively. When seeding beam 2ω was switched off, nonexponential decay was observed. Figure 2(b) shows the temporal correlation dependence of the SHG signals between the two seed beams ω and 2ω. The full width at half maximum was almost equivalent to the pulse width of the two seed beams. These results indicate that the SHG signals resulted from the coherent superposition of the two seed beams.

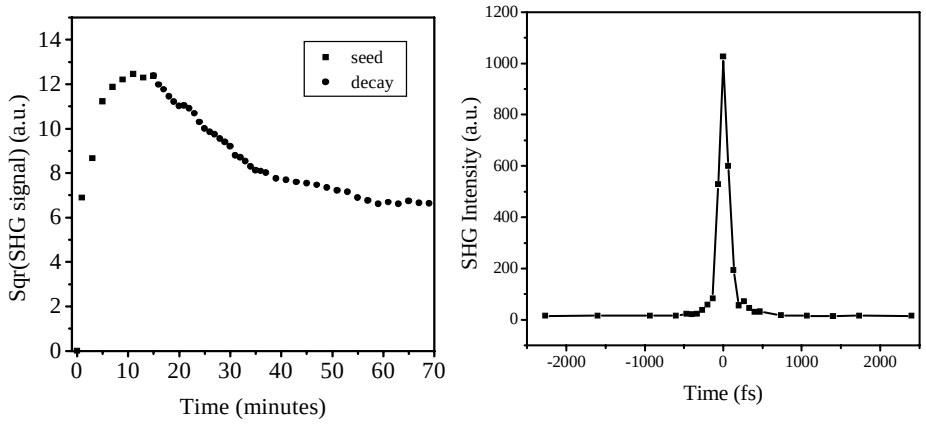

Fig. 2. (a) Growth in time (squares) and decay (circles) of the SHG signal of the germanosilicate glass sample prepared by femtosecond laser pulses at wavelengths of 800 and 400 nm. (b), temporal correlation dependence of the SHG signals of the glass sample between the two seed beams ω and 2ω.

In optical poling, the phase matching for SHG can be automatically achieved, so SHG signals are determined by thickness of the glass samples (not by the coherence length of the

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glass). Although the refractive index of the glass increases with the increase of Ge content, the influence of the refractive index change of the various samples to the $\chi^{(2)}$ values is negligible. Therefore the relative $\chi^{(2)}$ values of the glasses can be deduced directly from the ratio of the observed SHG signals. Figure 3 shows the dependence of the photoinduced $\chi^{(2)}$ of germanosilicate glasses on the GeO_2-SiO_2 composition. From Fig. 3, one can see that the photoinduced $\chi^{(2)}$ increased with increasing concentrations of GeO_2 of the glasses. When the concentration of GeO_2 in the glasses was increased from 3% to 10%, the photoinduced $\chi^{(2)}$ was enhanced about a little over 6 times. All the measurements were made after 10 min of the optical poling preparation. We guess that the enhancements of the photoinduced $\chi^{(2)}$ should arise either from the composition dependence of $\chi^{(3)}$ of the glass or from the composition dependence of the photoinduced internal dc electric field of the glass considering $\chi^{(2)} = 3\chi^{(3)}E_{dc}$.

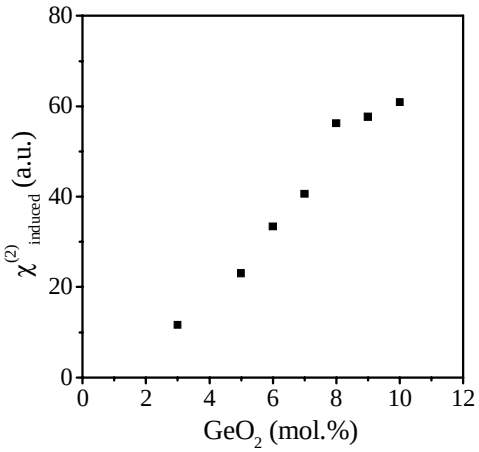

Fig. 3. Dependence of the photoinduced $\chi^{(2)}$ of germanosilicate glasses on the GeO_2-SiO_2 composition. All the measurements were made after 10 min of the optical poling preparation.

To investigate the composition dependence of the third-order optical nonlinear susceptibility $\chi^{(3)}$ of the glasses, we performed THG measurements using the Ti:sapphire regenerative amplifier laser at 800-nm pump wavelength. A similar experimental configuration to the holographic experiments was used for the THG measurements, where two pump beams were introduced into the sample at an angle of 9°. The diameter of the two beams on the sample was 0.1 mm. A time-delay device was used to adjust the timing of pulse collisions. Both the two pump beams generated THG in their propagation directions of $\boldsymbol{K_{1p}}$ and $\boldsymbol{K_{2p}}$. When the two pump beams were at a coherent superposition by adjusting the delay device, two THG signal beams generated in the directions of $2\boldsymbol{K_{1p}}$-$\boldsymbol{K_{2p}}$ and $2\boldsymbol{K_{2p}}$-$\boldsymbol{K_{1p}}$ respectively, which resulted from $\chi^{(3)}(3\omega;\omega,\omega,\omega)E_{1p}^2(\omega)E_{2p}^*(\omega)$ and $\chi^{(3)}(3\omega;\omega,\omega,\omega)E_{2p}^2(\omega)E_{1p}^*(\omega)$, respectively. $\chi^{(3)}(3\omega;\omega,\omega,\omega)$ is the third-order optical nonlinear susceptibility of glasses, and $E_{1p}(\omega)$ and $E_{2p}(\omega)$ are the electric fields of the two pump beams, respectively. We measured the $\chi^{(3)}$ of germanosilicate glasses by detecting the THG signals in the direction of $2\boldsymbol{K_{1p}}$-$\boldsymbol{K_{2p}}$. Figure 4(a) shows the laser power dependence of the THG of the germanosilicate glass with 10-GeO_2-90-SiO_2 (mol. %) composition. The THG intensity shows cubic pump-power dependence as expected, indicating the signals arise from THG of the germanosilicate sample. The dependence of the $\chi^{(3)}$ of germanosilicate glasses on the GeO_2-SiO_2 composition was also measured. The results are shown in Fig. 4(b), where the $\chi^{(3)}_{silica}$ is the third-order optical nonlinear susceptibility of a silica glass. The laser power was

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set at 100 mW. Experimental results showed that the $\chi^{(3)}$ of the germanosilicate glasses has no evident composition dependence.

Several studies of glass composition have showed that glass that has a high refractive index exhibits large $\chi^{(3)}$ [3]. In other words, in some cases $\chi^{(3)}$ of glasses strongly depends on glass composition when the frequency of the interacting light approaches the frequency of one-, two-, or three-photon resonance because their optical bandgap E_g depends on glass composition. However, no evident composition dependence was observed in our experiments, and the reason can be probably explained as follows:

An enhancement in $\chi^{(3)}$ occurs when the frequency of the interacting light approaches the frequency of one-, two-, or three-photon resonance. If three-photon resonance is dominant in THG as in the case of an optical bandgap E_g higher than three-photon energy, the most significant term that is due to three-photon resonance can be obtained as follows:

$$\chi^{(3)} = \frac{A}{(E_g - 4.62)(E_g - 3.09)(E_g - 1.54)}(esu);$$

$$Eg > 4.62,$$

where A is a phenomenological constant, and 1.54, 3.09, and 4.62 eV are one-, two-, and three-photon energies of an 800-nm laser beam, respectively. The optical bandgap E_g of germanosilicate glasses decreases with the increase of the concentrations of GeO_2, and E_g of glasses for 10-GeO_2-90-SiO_2 composition was measured to 7.1 eV [12]. In our experiments, optical bandgap E_g ($\geq$ 7.1 eV) of glasses was very higher than three-photon energy 4.62 eV, therefore $\chi^{(3)}$ of the glasses didn't show an optical bandgap dependence for different composition glasses.

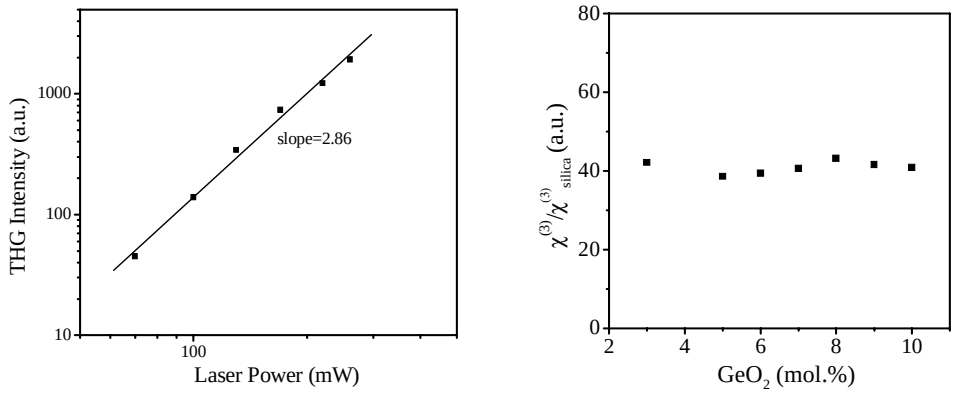

Fig. 4. (a) pump power dependence of the THG signal of the germanosilicate glass with 10-GeO_2-90-SiO_2 (mol. %) composition. The THG intensity shows cubic pump-power dependence. (b), measurements for $\chi^{(3)}$ of germanosilicate glasses for different GeO_2-SiO_2 composition. The laser power was 100 mW.

According to the experimental results described above, we conclude that the photoinduced second-order optical nonlinear susceptibility $\chi^{(2)}$ of germanosilicate glasses can be enhanced by increasing concentrations of GeO_2 of the glasses and this composition dependence of the photoinduced $\chi^{(2)}$ is mainly due to the dependence of the photoinduced internal dc electric field E_{dc} of the glass on the GeO_2-SiO_2 composition. These experimental results also indicate that the formation of the photoinduced internal dc electric field E_{dc} of the glass was probably associated with some defects, which resulted from Ge doped in glasses.

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4. Conclusion

We investigated the dependence of the photoinduced second-order nonlinearity of germanosilicate glasses on the GeO_2-SiO_2 composition using photoinduced SHG. Experimental results show that the photoinduced $\chi^{(2)}$ of the glass increased with increasing concentrations of GeO_2 of the glasses. The composition dependence of the photoinduced $\chi^{(2)}$ is mainly due to the dependence of the photoinduced internal dc electric field of the glass on the GeO_2-SiO_2 composition.

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