Optically encoded second-harmonic generation in germanosilicate glass by a femtosecond laser

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Second-harmonic generation in germanosilicate glasses was encoded by coherent superposition of the 810-nm fundamental and the 405-nm second-harmonic light of a femtosecond laser. The difference spectra between the absorption spectra of the glasses before and after preparation were measured. An evident correlation between the induced second-order nonlinearity and the creation of a Ge electron center was observed, suggesting that a band-to-band transition by multiphoton absorption is probably responsible for the photoinduced second-harmonic generation. © 1999 Optical Society of America

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Second-harmonic generation (SHG) in glasses should be forbidden because glass has macroscopic inversion symmetry. However, in 1986 Österberg and Margulis observed SHG in a glass optical fiber after illuminating the fiber with intense infrared light for several hours.[1] A year later, Stolen and Tom showed that, when infrared fundamental light was introduced into a fiber along with its second-harmonic light, the speed of the process increased from 10 h to 5 min.[2] To promote an understanding of this effect, many studies of its mechanism were carried out. Stolen and Tom presented a mode in which they believed that the incident fundamental and its second-harmonic light beams caused a dc electric field to build up in the glass and that this semipermanent dc electric field not only broke the inversion symmetry of the glass but also permitted periodic phase matching of the SHG.[2] Explanations of the microscopic mechanism of this photoinduced dc electric field cite either photoinduced currents[3,4] or structural orientation.[2,5] Dianov *et al.*[3] and Dominic and Feinberg[6] ruled out structural reorientation models by comparing the measured spatial shapes of the dc electric field with the theoretical predictions of photocurrent models. Kyung and Lawandy spatially mapped the photoexcited electron distributions that are responsible for SHG with a charge-selective etching technique.[7,8] Tsai *et al.* demonstrated by electron-spin-resonance spectrometry that SHG in germanosilicate glass is related to the formation of the photoinduced GeE' (germanium E') center.[9] Moreover, the wavelength dependence and the compositional dependence of the photoinduced SHG in lead silicate glass were investigated by Krol *et al.*[10] and Krol and Stepanov[11] and by Nageno *et al.*,[12] respectively. There is now fair agreement that SHG in glass is associated with some photoinduced defects in glasses. However, to date what photochemical reaction is responsible for the photoinduced defects is still not clear.

Most previous studies of photoinduced SHG in glasses were performed with a picosecond Nd:YAG laser, in which 1064-nm fundamental and 532-nm second-harmonic light was used as the preparation beams and the laser pulse intensities in glasses ranged from few to several dozen gigawatts per square centimeter.[12] The SHG photoinduced in germanosilicate glasses by this laser was believed to be related to the oxygen-deficient defect absorption band centered near 5.1 eV,[13] which can be reached with an equivalent energy of four 1064-nm photons.[14,15] We encoded SHG in germanosilicate bulk glass by using femtosecond laser pulses at wavelengths of 810 and 405 nm, whose intensities in the glass ranged from 1 to 600 GW/cm^2. We expected the SHG induced by these laser pulses of high intensity to be different from that induced by Nd:YAG laser pulses. Measurements of the difference spectra between the absorption spectra of the glasses before and after preparation indicated that a band-to-band transition by multiphoton absorption is probably responsible for the photoinduced SHG.

A 10-GeO_2–90-SiO_2 (mol. %) glass rod was prepared by Shin-Etsu Chemical Company as a fiber preform by a vapor axial deposition method. The rod was sliced and polished into 0.5-mm-thick plates. A Ti:sapphire regenerative amplifier laser system was used for the SHG preparation of the germanosilicate glass, which emitted 200-fs, 810-nm laser pulses at a repetition rate of 200 kHz. The average power of the laser was 960 mW. Seeding beam ω was split from the source beam and passed through a time-delay device and a $\lambda/2$ 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 quartz lens. We achieved time superposition of pulses

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between the two seeding beams by adjusting the delay device and observing the optical Kerr effect of CS_2. During the SHG 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 and observed and averaged by an oscilloscope. A 405-nm bandpass filter was placed in front of the photomultiplier to allow only the SHG 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 12 μm and 0.75 μJ for beam ω and 10 μm and 0.02 μJ for beam 2ω, respectively. Absorption spectra were measured at 300 K with a Jasco V-570 spectrometer.

First, the growth and decay processes of the photoinduced SHG of the glass sample were measured, as shown in Fig. 1. For the preparation process the photoinduced SHG 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. The induced second-order nonlinearity $\chi^{(2)}$ was observed to remain constant for ~10 h if the irradiation of the intense beam ω was stopped, indicating that the decay results mainly from the erasure of $\chi^{(2)}$ by beam ω. Figure 2 shows the dependence of the induced $\chi^{(2)}$ on the preparation intensity in the glass sample. All the measurements were made after 2 min of preparation.

To understand what photochemical reaction is responsible for this induced SHG, we measured the difference spectra between the absorption spectra of the glasses after and before preparation for the various intensities shown in Fig. 2. The measurements of the absorption spectra for different preparation intensities were made on different spots of the sample, and the diameter of the spots was set at 2 mm for these measurements. We scanned the SHG preparation for each spot within the spot by translating the stage, mounting the sample in the transverse direction. Figure 3 shows two typical difference spectra, which correspond to preparation intensities of 36 and 322 GW/cm^2. As shown in Fig. 3, some new bands located near 4.7, 5.7, and 6.3 eV were induced after the SHG preparation, which are assigned, respectively, to the absorption of a Ge electron trapped center (GEC) [Ge(1) or Ge(2)] and a GeE' center of 10-GeO_2–90-SiO_2 glasses based on earlier studies.[16] The GEC center is abbreviated Ge(1) or Ge(2), depending on the number of nearest-neighbor Ge ions. The correlation between the induced $\chi^{(2)}$ and the absorption coefficient of the Ge(1) band is shown in Fig. 4. The results clearly show that, with increasing laser intensity, the absorption coefficients of the GEC bands increased along with the induced $\chi^{(2)}$.

These defect centers are produced by a band-to-band excitation as follows[16]: Under irradiation of a laser with high photon energy or high peak power, the lone pair electron on the bridging oxygen (BO), which occupies the uppermost level ($2p$ orbit of O) of the valence band, is excited to the conduction band by band-to-band excitation and then trapped on the fourfold-coordinated Ge ions (GeO_4), yielding a GEC^- center. Furthermore, the GEC center can be converted into GeE' and NBO^- (where NBO^- is nonbridging oxygen arrived at by trapping of an electron). In contrast, the BO is converted into a self-trapped hole center, termed STH^+, after releasing an electron. The photochemical reaction can be given by

$$GeO_4 + BO \xrightarrow{h\nu} GEC\ (GeO_4 + e^-) + STH\,, \qquad (1)$$

$$GEC \longrightarrow GeE' + NBO\,. \qquad (2)$$

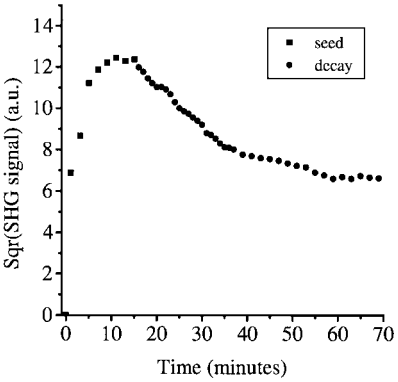

Fig. 1. Growth in time (squares) and decay of the SHG signal of the germanosilicate glass sample prepared by femtosecond laser pulses at wavelengths of 810 and 405 nm.

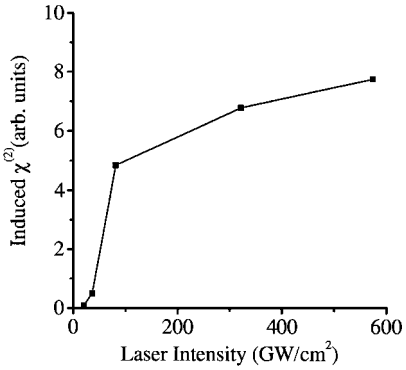

Fig. 2. Plot of the photoinduced $\chi^{(2)}$ at several intensities of preparation beam ω.

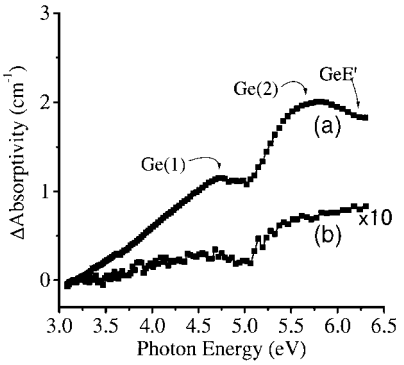

Fig. 3. Difference spectra between the spectra after and before preparation. (a), (b) Difference spectra for preparation intensities of 36 and 322 GW/cm^2, respectively.

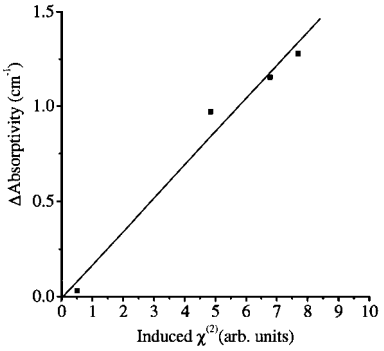

Fig. 4. Correlation between the induced $\chi^{(2)}$ and the absorption coefficient of the Ge(1) band.

As described above, our experimental data suggest that SHG of germanosilicate glass induced by a femtosecond laser with high power is related to the band-to-band transition by means of multiphoton absorption. Therefore we propose the following mechanism for formation of the photoinduced dc field in germanosilicate glass: Under the combined action of the fields at ω and 2ω the lone pair electrons on BO are excited to the conduction band through a multiphoton absorption process, transferred in the conduction band, and then trapped on the fourfold-coordinated Ge ions (GeO_4). This directional electron transfer associated with the creation of the STH^+ with a positive charge and the GEC^- with a negative charge results in a periodic frozen-in dc field that is satisfied for phase matching of SHG. In this model, the GeE' center, which has no nominal charge, is produced only as an incidental defect, as described in photochemical reaction relation (2). In addition, the concentration of the intrinsic structure unit GeO_4 is much higher than that of the intrinsic oxygen-deficient defect,[16,17] because these are, respectively, the intrinsic structure unit and the intrinsic defect of germanosilicate glass. Therefore we expect that the dc field in germanosilicate glass induced through band-to-band excitation will provide a stronger dc field.

In summary, we encoded SHG in germanosilicate bulk glass by femtosecond laser pulses at wavelengths of 810 and 405 nm. The evident dependence of the induced second-order nonlinearity on the creation of GEC's suggests that a band-to-band transition by multiphoton absorption is probably responsible for photoinduced SHG.

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