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doi: 10.1063/1.1361284

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(Received 6 July 2000; accepted for publication 13 February 2001)

We report on a photosensitivity in soda-alumino-phosphate glass doped with silver ions Ag^+ upon exposure to near-ultraviolet femtosecond laser pulses. The photosensitivity, i.e., formation of color centers such as Ag^0 and Ag^{2+} in the glass is found to be associated with intensity-dependent nonlinear optical process induced by extremely high irradiance up to $\sim TW/cm^2$ of the femtosecond pulses. We demonstrate a bright orange fluorescence from the induced color centers inside the glass, that should be applicable to a functional optical device. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1361284]

Recently, photosensitivities in optical materials induced via irradiation with ultrashort laser pulses have been of great interest, because of their potential applications to functional optical devices.[1–4] For instance, utilizing the photosensitivity associated with intense ultrashort laser pulse at near infrared (IR) wavelength, Glezer and co-workers demonstrated a three-dimensional optical storage inside transparent materials,[1] while Miura and co-workers succeeded in a fabrication of optical waveguide in various glasses.[2] Further, photosensitivities associated with the femtosecond IR pulses were found to be advantageous for introducing a variety of chemical/physical modifications into optical materials.[3,4] Though the exact mechanisms responsible for the IR photosensitivity are still under investigation, the phenomena must be related closely to nonlinear optical process, such as multiphoton absorption/ionization, being due to extremely high field intensity of the ultrashort laser pulse.

Here, we report on a photosensitivity in phosphate glass doped with silver ions Ag^+ induced by irradiation with intense ''near-UV'' femtosecond laser pulses. Irradiation with the near-UV pulses results in formation of silver-associated color centers, of which the population density increases proportionally with averaged power of incident laser beam. We demonstrate that the irradiated portion inside the glass exhibits a visible fluorescence upon excitation with a conventional UV source: the phenomenon should be applicable to a functional optical device.

A sample glass of the nominal composition 17.2 Na_2O: 12.1 Al_2O_3: 70.5 P_2O_5: 0.2 Ag_2O (in mol %) was prepared from reagent grade Na_2CO_3, $NaNO_3$, $Al(PO_3)_3$, and $AgNO_3$. A mixture of raw materials with that desired composition was melted in an alumina crucible under ordinary atmosphere for 4 h, and subsequently poured onto a stainless plate. The glass thus obtained was cut and polished into a plate of 3 mm thick. A glass, free from Ag, was also prepared for comparison. Photosensitivity of the glass sample was examined with a commercial femtosecond laser source equipped with 1 kHz repetition rate Ti:sapphire regenerative-amplified laser system (CPA2001, Clark-MXR). The frequency of the fundamental pulse was doubled in a 5 mm thick beta barium borate crystal and we obtained ~350 fs-duration pulses with averaged power P_{ave} of ~70 mW(70 μJ/pulse) at the 388 nm wavelength. The near-UV beam was focused with a lens of 200 mm focal length. The glass sample was placed behind the focal plane at where the beam diameter was about 0.2 mm.

As shown subsequently, photosensitivity of the glass sample appeared as a coloration of the glass upon irradiation with the intense near-UV femtosecond laser pulses. In order to examine the nature of coloration, we attempted to measure the optical transmission spectrum of the irradiated glass. Then, the glass was irradiated with the near-UV laser beam at $P_{ave}=40$ mW with preserving the beam diameter of 0.2 mm. During irradiation, the glass was scanned over 3.0×3.0 mm area within a plane perpendicular to the incident beam. The sample thus irradiated was subjected to the transmittance measurement with a conventional spectrophotometer (UV2400, Shimadzu).

The intensity-dependent nature of the photosensitivity was examined simply by measuring the change in transmittance at 388 nm before and after irradiation with the intense near-UV femtosecond laser pulses. In practice, the sample was kept in a fixed position, i.e., beam diameter of 0.2 mm, for the both transmittance measurement and irradiation process. In the transmittance measurement, incident power P_{ave} was suppressed at a low level, e.g., $P_{ave}=0.45$ mW. The high power irradiation was carried out at $P_{ave}=4.0\sim45.0$ mW for 10~20 s. The transmittance was found to decrease after the high power irradiation, though, prolonged irradiation exceeding 20 s did not cause further decrease in the transmittance.

Figure 1 shows optical transmission spectra for the glass sample of 3 mm thick before (dashed line) and after (solid line) the near-UV irradiation. As seen in Fig. 1, transmittance of as-prepared (unirradiated) glass was more than 90% at the wavelength longer than 350 nm. A rapid decrease in the transmittance observed at the wavelength shorter than 340 nm was considered to be due to fundamental absorption in the glass. It should be noted that the transmittance at 388

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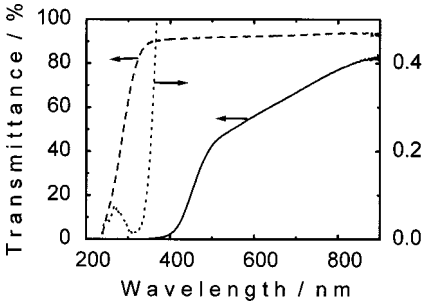

FIG. 1. Transmission spectra of the glass sample before (dashed curve) and after (solid curve) irradiation with near-UV laser beam. Dotted curve represents the rescaled spectrum for the irradiated glass.

nm was 91% and there was no appreciable absorption at the wavelength region of interest. Irradiation caused a drastic change in the transmission spectrum of the glass, as shown by solid curve in Fig. 1. The significant decrease in transmittance at visible wavelength region resulted in yellowish brown color of the glass. The dotted curve in Fig. 1 represents the rescaled spectrum for the irradiated glass, which shows the extremely low transmittance less than 400 nm apparently. In the spectrum, there was an explicit absorption band centered at 320 nm. Including the band at 320 nm, the whole spectrum for the irradiated glass was quite similar to that previously observed in x-ray irradiated metaphosphate glass doped with Ag^+.[5,6] The characteristic transmission spectrum had been explained as the consequence of radiation-induced formation of color centers associated with Ag^+, i.e., trapped electron center, Ag^0 and the trapped hole center, Ag^{2+} in the glass.[5,6] These color centers gave rise to characteristic absorption bands centered at UV region, 250–400 nm.[5,6] It had been well known that the both Ag^0 and Ag^{2+} possessed bright orange fluorescence against excitation with UV light.[6,7] Figure 2 shows the fluorescence/excitation spectrum of the sample glass irradiated with the near-UV femtosecond laser pulses. Curve a represents the excitation spectrum obtained with fluorescence at 600 nm, while curve b represents the fluorescence spectrum obtained with excitation at 320 nm. Curves c and d represent the spectra which had been observed in γ-irradiated phosphate glass doped with Ag^+.[7] Schulman had concluded that the radiation-induced Ag^0 center in the glass was responsible to the characteristic fluorescence.[7] Further, we have confirmed the presence of Ag^{2+} centers[6] in the laser-irradiated glass by a preliminary electron spin resonance measurement.

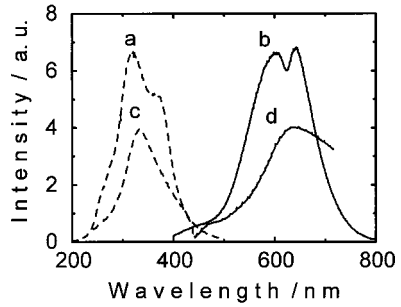

FIG. 2. Excitation (a) and fluorescence (b) spectra for the irradiated glass. Curves c and d are those reproduced from Ref. 7.

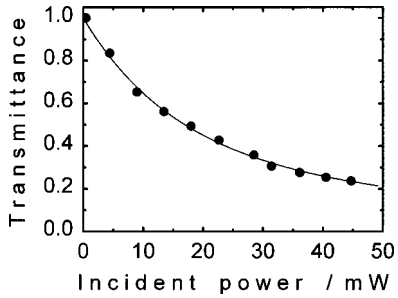

FIG. 3. Transmittance at 388 nm after near-UV irradiation as a function of averaged power of the incident beam.

We confirmed that silver, in the as-prepared-(unirradiated) glass, was in the monovalent state, Ag^+, by observing the characteristic blue fluorescence[7] in the glass under UV excitation. Then, we concluded that the Ag^+ played a key role for the observed photosensitivity via irradiation with intense near-UV femtosecond laser pulse, i.e., formation of color centers, Ag^0 and Ag^{2+} in the present glass sample.

Figure 3 shows the transmittance at 388 nm wavelength after irradiation with intense near-UV femtosecond laser pulses, as a function of the P_{ave} of incident laser beam. In Fig. 3, the transmittance T_{388} is normalized to the initial transmittance of ~0.91, i.e., the transmittance before irradiation. As seen in Fig. 3, T_{388} was found to be less than 1.0 after the irradiation at P_{ave}=4–45 mW, being responsible for formation of the Ag-associated color centers via near-UV irradiation (cf. Fig. 1). Further, T_{388} decreased with increasing P_{ave}, being T_{388}=0.24 at P_{ave}=45 mW. The solid curve in Fig. 3 is drawn under an assumption in which the absorption coefficient at 388 nm increases proportionally with P_{ave}. A tolerable agreement between the data and the fitted curve might support the adequacy of the above assumption, that was, the population density of color centers increased proportionally with the incident laser power.

Formation of Ag-associated centers by ionizing radiation (γ- and/or x-ray) had been explained as a consequence of capturing ''radio-activated'' electron and/or hole onto Ag^+ within the glass.[5–7] Then, for the present result, it should be reasonable to consider that Ag-associated centers are formed by capturing ''photoexcited'' electron or hole onto Ag^+ via near-UV irradiation. In order to specify the ''photoexcitation process,'' we carried out a similar experiment by using ''nanosecond pulse'' of 355 nm wavelength at a similar ''energy'' level, 70 μJ/pulse with the beam diameter of 0.2 mm: There were no observable changes in the transmission spectrum of the glass sample before and after irradiation with the nanosecond pulses. Thus, we concluded that photoexcitation process responsible for the resultant photosensitivity was not due to one-photon absorption (excitation) but to intensity-dependent nonlinear optical processes associated with the extremely high irradiance in the order of ~TW/cm^2 for the near-UV ''femtosecond'' laser pulse.

It seemed difficult to specify a nonlinear optical process being dominant for the generation of photoexcited electron and hole within the glass. Multiphoton absorption (MPA) might be a possible process for the photoexcitation. However, it was impossible to measure the MPA in the glass at 388 nm wavelength, since the subsequent formation of color

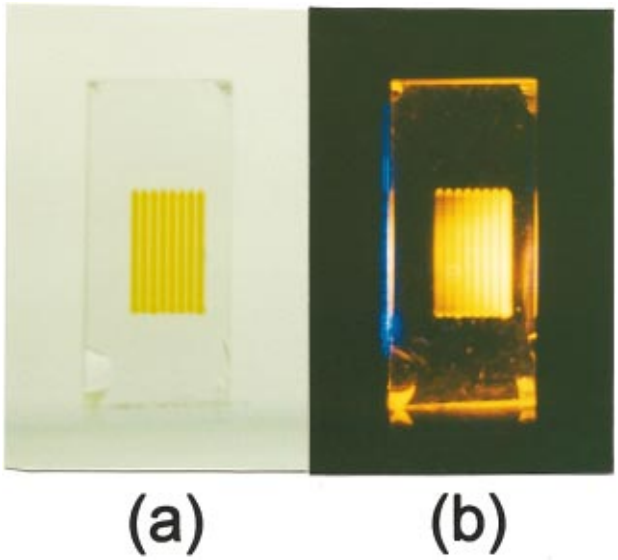

FIG. 4. (Color) Photograph of the sample glass after near-UV irradiation. (a) Coloration observed from laser-incident surface. (b) Fluorescence observed by excitation with an Hg lamp. Note that excitation was from the orthogonal side of the irradiated surface, (a).

center prevented to detect the spontaneous response of MPA. Here, we only give two tentative explanations for the intensity-dependent nature of the photosensitivity, with due regard to the ''linear'' relationship between the increase in absorption coefficient and the incident beam power (Fig. 3). An initial explanation is based on a supercontinuum generation, i.e., spectral broadening of incident laser pulse. Recently, Efimov and co-workers reported formation of color center in multicomponent silicate glass with intense IR femtosecond laser pulse.[8] They explained the mechanism of formation of color centers as a consequence of linear absorption of the short wavelength (in UV region) component of the supercontinuum within the glass. Then, so far as the degree of spectral broadening was proportional to beam intensity, the population density of color center (or absorption coefficient) should be proportional to the incident beam power. The second explanation is based on two competitive photochemical reactions during near-UV irradiation. In this process, the color centers are assumed to be formed via capturing ''two-photon'' excited electron and/or holes. During the process, part of color centers are subsequently destructed by releasing the trapped charge carriers via ''one-photon'' absorption process associated with the color centers themselves. At the equilibrium between the above two competitive photochemical reactions, the population density of color center should be proportional to the incident power. This mechanism has been applied successfully to explain the intensity-dependent photosensitivity, e.g., formation and destruction of color centers in lead silicate glass[9] and phosphate glass containing colloidal silver particles,[10] respectively. Except for the above explanations, there are many possible mechanisms responsible to the intensity-dependent photosensitivity that we have observed. Further investigations are ongoing now to clarify the exact nature.

Figure 4 shows an example of glass of $6\times6\times14$ mm in size, irradiated with near-UV femtosecond laser pulse at an appropriate beam power and a beam size. During irradiation, the glass sample was scanned along a direction perpendicular to the beam. Figure 4(a) shows the incident surface of the glass in which induced coloration can be observed clearly as eight colored lines with an excellent reproducibility. The coloration was found to be uniform sufficiently as deep as 6 mm along the beam propagating direction within the glass. Figure 4(b) demonstrates characteristic fluorescence from the irradiated portion in the glass under excitation with a conventional mercury lamp: The excitation was carried out not from the near-UV irradiated surface but from the orthogonal side of the glass slab [right-hand side in Fig. 4(b)]. As seen in Fig. 4(b), bright orange fluorescent light is emitted exactly from the colored portion ''inside'' the glass. These observations imply the possible applications of the photosensitivity in the glass for a wide variety of functional devices, such as three-dimensional optical data storage[1] and/or photonic band gap devices.[11]

In summary, we have reported on an intensity-dependent photosensitivity in soda-alumino-phosphate glass doped with Ag^+. The photosensitivity, i.e., formation of Ag-associated color centers (Ag^0 and Ag^{2+}), should be characteristic to the glass upon irradiation with extremely high intensity near-UV femtosecond laser pulses. The fluorescence from the induced color centers inside the glass should be applicable in the field of optical devices.

The authors acknowledge supplement of glass sample from Okamoto Glass, Co. Ltd. This work was, in part, supported by the 2000 Research Grant from Tokuyama Science Foundation, and by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture (Grant No. 12650674).

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