Photosensitivity of Ge-doped phosphate glass to 244 nm irradiation

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UV photosensitivity of Ge-doped phosphate glasses is examined by writing photoinduced gratings in bulk glass samples. Radiation-induced index changes up to $\sim 3.5\times 10^{-5}$ were obtained by diffraction efficiency measurements of UV written gratings. In contrast to phosphate glasses without intentional doping, no significant photodarkening at visible wavelength was observed in Ge-doped phosphate glasses after UV exposure. The measured index changes demonstrate the potential of Ge-doped phosphate glasses for the fabrication of a fiber Bragg grating, a key component for phosphate-glass-based photonic devices. © *2006 American Institute of Physics*.
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Phosphate glasses are promising materials for photonics because of their high solubility of rare earth ions without quenching.[1] This enables appropriately doped phosphate glasses to provide higher optical gain compared to other glasses. Recently, highly Er/Yb-doped phosphate glasses were utilized to produce up to ~2.3 W of single frequency outputs with cm-long fiber lengths.[2–4] In these devices fiber Bragg gratings (FBGs) written in silica fibers are being used for selecting wavelength and narrowing bandwidth emission.[3,4]

The combination of different glasses within one device constitutes a significant challenge, in particular since the thermal properties of phosphate and silica glasses are quite different—typical fiber drawing temperatures for phosphate and silica fibers are ~800 and ~2000 °C, respectively. Considering this difference, the fabrication of splices between phosphate and silica fibers exhibiting low optical loss and reasonable mechanical strength requires special techniques. It also makes it virtually impossible to reduce the splicing loss by thermal diffusion of dopants.[3,5] In addition there is a large difference in the coefficients of linear thermal expansion (CLTEs) for phosphate and silica glasses that are typically $\sim 100\times 10^{-7}/°C$ and $\sim 5\times 10^{-7}/°C$, respectively. This induces thermal stress at splicing joints that can also modify the index distribution of spliced fibers and lower the mechanical strength of the splices.

The possibility to induce photosensitivity in silica glass through Ge-doping was first observed using visible Ar^+ ion laser radiations.[6] Later it was confirmed that the photosensitivity is due to the Ge–O vacancy defects at ~240 nm.[7] Although other routes to photosensitive silica glasses have been found, Ge-doped silica glasses are the most common photosensitized glass materials for making FBGs. UV-induced defects in phosphate glasses have also been studied by researchers.[8,9] They have examined UV photosensitivity of phosphate glasses doped with As, Sb, Sn, Pb, and so on. However, UV photosensitivity of Ge-doped phosphate glasses has not been reported. Recently, the photosensitivity to 248 nm excimer laser radiation of a commercial Er-doped phosphate glass suitable for ion exchange and its potential application in photonics were reported.[10] Index changes of up to $\sim 2.0\times 10^{-3}$ were measured in silver ion-exchanged samples; however, the index changes can only reach a few microns below the glass surface making this technique unsuitable for writing FBGs into the core of phosphate glass fibers. Other researchers demonstrated 193 nm excimer laser written gratings in a commercial nondoped phosphate glass and its application to a waveguide laser.[11]

In this letter we examine the photosensitivity of Ge-doped phosphate glasses to 244 nm cw light from a frequency doubled Ar^+ ion laser. The glass samples were made by conventional melt and quench in air using high purity chemicals. The host glass is a modified phosphate glass with 55.6 wt % P_2O_5. Ge-doped samples; Ge10, Ge30, and Ge40 are doped with 10, 30, and 40 wt % GeO_2 and contain 50, 38.9, and 33.3 wt % P_2O_5, respectively. Writing gratings into these glasses through a phase mask and analyzing the grating diffraction, we studied the UV-induced index changes created in these phosphate glasses. The largest index change of up to $\sim 3.5\times 10^{-5}$ is found in Ge30 indicating that this glass is suitable for the fabrication of UV written FBGs.

Indices of refraction (n) shown in Table I, were measured using a prism coupler and thermal properties of the samples were obtained by thermomechanical analysis. The glass samples were cut and polished into 0.5–1 mm thick slabs. Periodic index modulations were induced in each sample using the phase mask method. The phase mask has a relief pattern period of 1048 nm that forms an interference pattern with 524 nm period and was designed to suppress the zeroth order diffraction at the writing wavelength. The writing laser was a frequency doubled Ar^+ ion laser at 244 nm and the power density at the phase mask was $\sim 4\ W/cm^2$.

TABLE I. GeO_2 concentration, index of refraction (n), glass transformation temperature (T_g), and coefficient of linear thermal expansion (CLTE) of phosphate glasses used in the experiments. The index of refraction increases as GeO_2 concentration increases.

	Host	Ge10	Ge30	Ge40
GeO_2 concentration (wt %)	0	10	30	40
n (at 633 nm)	1.564	1.565	1.615	1.620
T_g (°C)	547	630	634	608
CLTE ($\times 10^{-7}/°C$) (30–300 °C)	108	65	74	75

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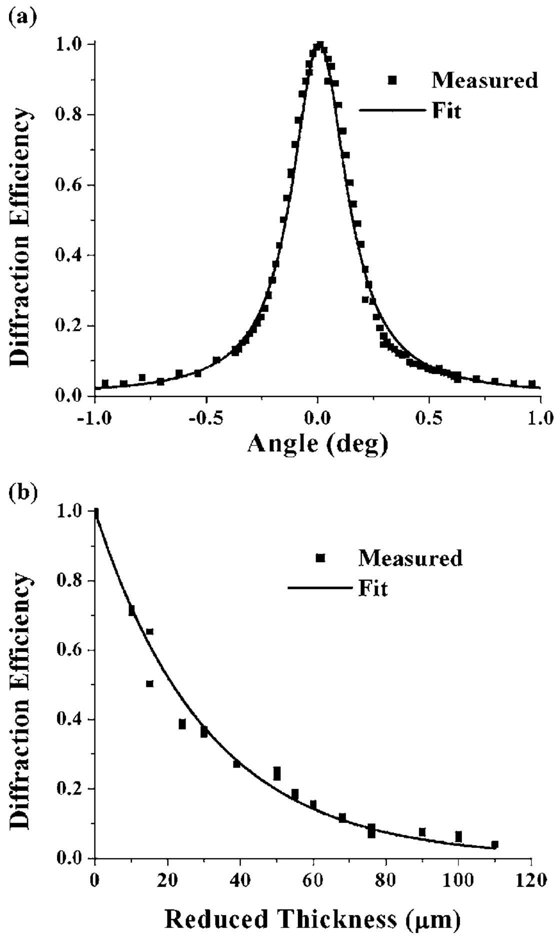

FIG. 1. (a). Angular dependence of the diffraction efficiency of Ge30 after UV exposure of ~1500 J/cm^2. The diffraction efficiency is normalized to the peak value. The angle is measured relative to the Bragg angle of maximum diffraction. (b) Diffraction efficiency in Ge30 after UV grating writing at ~1500 J/cm^2 as a function of thickness reduction. The diffraction efficiency is normalized to the value before reducing the thickness.

Varying the exposure time each sample was irradiated at various fluences up to ~4000 J/cm^2.

Figure 1(a) shows the measured angular dependence of the normalized diffraction efficiency for Ge30 at ~1500 J/cm^2 together with a theoretical fitting curve.[12] The diffraction efficiency of the induced index modulation was measured with a He–Ne laser at 633 nm. The theoretical equation for the diffraction efficiency is derived with the assumption of a sinusoidal index modulation along the direction parallel to the surface of the medium (x) and an exponentially decaying of the index modulation along the direction perpendicular to the surface (z). The index distribution $n(x,z)$ is expressed by

$$n(x,z) = n_0 + \delta n \sin(Kx)\exp(-\alpha_g z), \quad 0 \leq z \leq L, \tag{1}$$

where n_o is the dc term of the refractive index, δn is the amplitude of the index modulation, K is the magnitude of the grating vector, α_g is the attenuation coefficient of the modulation, and L is the thickness of the medium. The best fit indicates that the depth of grating in Ge30 is ~60 μm. Using the same analysis, the depths of the gratings in the host glass, Ge10, and Ge40 are obtained to be ~66, ~72, and ~72 μm, respectively. According to these results, the effective grating depths are very similar for the different glasses under consideration although the 244 nm penetration depths prior to UV exposure were rather different; ~550, ~400, ~200, and ~300 μm for host, Ge10, Ge30, and Ge40, respectively. This observation can be attributed to absorption changes during UV illumination. To confirm the grating depth, the UV exposed surface of Ge30 at ~1500 J/cm^2 was carefully polished and its diffraction efficiency was measured as a function of the reduced thickness. Each time ~5 μm of material were removed from the surface and the diffraction efficiency was remeasured. Figure 1(b) shows the distribution of the normalized diffraction efficiency as a function of the thickness reduction. As the model predicts the efficiency drops exponentially as the thickness reduction increases. Theoretically the diffraction efficiency is proportional to the square of the index modulation for smaller diffraction efficiencies.[12] Assuming an exponential decay of the index modulation, a $1/e$ depth of the grating of ~62 μm is obtained by least squares fitting of the experimental data [see solid line in Fig. 1(b)]. This grating depth is in good agreement with the value obtained by fitting the angular dependence of the diffraction discussed above.

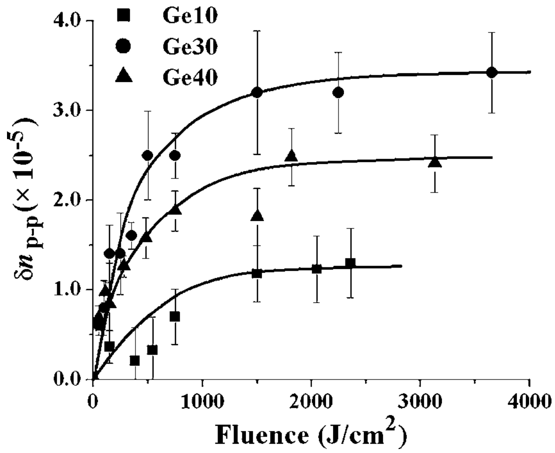

FIG. 2. Index modulation (δn_{p-p}) of Ge-doped phosphate glass as a function of fluence. δn_{p-p} is the peak to peak index modulation. Each data point represents several measurements of the diffraction from different UV written gratings. Lines are drawn to guide the eye, and the error bars show the standard deviation.

Figure 2 shows the evolution of the UV-induced refractive index changes of the three Ge-doped phosphate glasses as a function of writing laser fluence obtained by diffraction efficiency measurements at different exposures. The lines in Fig. 2 are drawn to guide the eye. All Ge-doped samples exhibit a similar saturation behavior. Initially the index modulation increased steeply, and after ~1500 J/cm^2, the index modulation did not increase any further. The maximum index modulation of $\delta n_{p-p} \equiv 2\delta n = \sim 3.5 \times 10^{-5}$ is observed in Ge30. While the increase in index modulation from Ge10 to Ge30 is expected, the smaller modulation at higher Ge-doping in sample Ge40 appears counterintuitive. We tentatively attribute this observation to a saturation of the network by GeO_2 molecules, causing phase separation and possible formation of nanocrystals. Assuming a UV-induced index modulation of $\sim 3 \times 10^{-5}$ at ~1550 nm, we can estimate a reflectivity of ~40% for a 25 mm long FBG with a reflection bandwidth that is narrow enough to achieve single frequency operation of a few cm-long fiber laser.[4]

Transmission spectra of the host glass and Ge30 were measured before and after UV exposure of ~1500 J/cm^2. Figure 3 shows the observed absorption changes over a wide

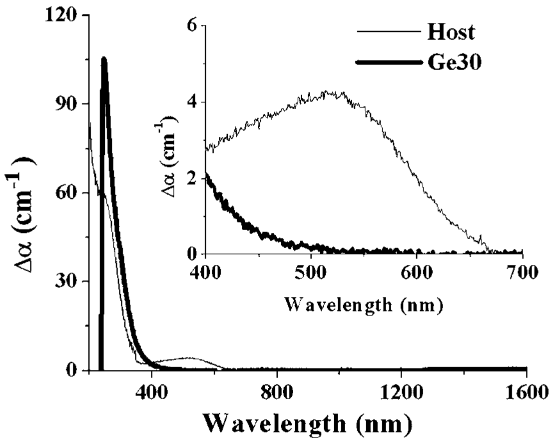

FIG. 3. Absorption change spectra ($\Delta\alpha$) for Ge30 and the host glass after UV exposure of ~1500 J/cm^2. $\Delta\alpha$ was calculated from transmission spectra measured before and after the exposure. Due to high absorption data below ~240 nm are noisy. The inset shows a selected wavelength range in the visible to emphasize photodarkening processes in the host glass.

wavelength range from UV to IR wavelengths. Here we assumed that the depth of the absorption change is the same as the grating depth obtained in the diffraction efficiency measurements. In the transmission measurements each sample was exposed to the beam of the frequency doubled Ar^+ ion laser without the phase mask. The output beam from the laser was expanded to achieve a more uniform exposure. Samples were exposed through a circular amplitude mask selecting the center part of the expanded beam with a power density of ~150 mW/cm^2. As seen in Fig. 3, photodarkening at visible wavelengths was observed only in the host glass at wavelengths up to 700 nm while the Ge30 glass shows absorption changes only at wavelengths below ~500 nm. The absorption change in the host glass between 400 and 600 nm might be related to reported phosphorous oxygen hole centers.[8,9] It is expected that in the Ge-doped glasses the hole center is formed at the Ge site instead of the *P* site. $\Delta\alpha$ at wavelengths below ~240 nm is not measurable in our Ge30 sample because the absorption is too high to obtain any transmission changes. For the host glass the measurements are limited to wavelengths above 220 nm. Comparing the Ge30 result with a typical UV-induced absorption change in Ge-doped silica glasses, Ge30 does not exhibit reduced absorption around ~240 nm that has been observed in silica glass.[13] Using the observed absorption change in Ge30 from 240 to 500 nm the Kramers-Kronig transformation[14] gives the same order of magnitude in index change as observed from the diffraction efficiency experiments. To study the nature of defects in Ge-doped phosphate glasses in more detail further investigations are required.

In conclusion, the UV-induced index modulation of a phosphate glass doped with 30 wt % GeO_2 reached $\sim 3.5 \times 10^{-5}$. This index change is enough to make narrow band FBGs. Our development of Ge-doped phosphate glasses opens the door for the fabrication of fiber lasers that exclusively use phosphate glasses and can be expected to exhibit better performance and reliability than current hybrid phosphate-silicate fiber lasers.

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