UV-irradiation-induced structural transformation of germanosilicate glass fiber

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During the past few years interest in germanosilicate fiber photosensitivity has grown strongly because of the wide application of refractive-index gratings written in optical fibers by UV irradiation. Despite impressive progress in the fabrication technology of fiber gratings and the development of numerous optical fiber grating-based devices, the microscopic mechanisms of photoinduced refractive-index change are not yet clear.\(^{1,2}\)

UV irradiation of silica and germanosilicate glasses leads to an increase in their densities and refractive indices.\(^{3-5}\) Compaction of silica glass produced by laser irradiation at 248 nm and by hydrostatic pressure could both be the result of modifications of silica glass structure.\(^{6-9}\) In particular it has been shown that hydrostatic pressure results in a considerable change in the Raman spectrum of silica glass, indicating changes in the glass structure.\(^{6-9}\) However, we know of no published results concerning the influence of UV irradiation on the Raman spectra of optical fibers. In this Letter we present for what we believe to be the first time Raman spectra of germanosilicate fibers before and after irradiation with UV light.

Several single-mode fibers (cutoff wavelength \(\lambda_c < 1.1 \, \mu m\)) with germanosilicate cores and pure silica glass cladding were investigated. The core glass contained 20–25-mol. % GeO\(_2\) and \(\sim 2\)-mol. % P\(_2\)O\(_5\). Pieces of each fiber 6 cm long were homogeneously irradiated by side exposure to 248-nm KrF excimer laser pulses. The fluence per pulse was 484 mJ/cm\(^2\), and the total fluence was \(\sim 41\) kJ/cm\(^2\). We also fabricated 4-mm-long Bragg gratings in the same fibers, using a Talbot interferometer with a phase mask. Reflection spectra were recorded during grating fabrication at different total laser fluences with the characterization setup described in Ref. 10. The total fluence used for writing these Bragg gratings is the same as that of homogeneous irradiation.

The Raman-scattering spectra of the fibers were measured by a triple spectrograph (T64000; Jobin–Yvon) with spectral resolution of better than 1 cm\(^{-1}\). Fiber excitation was achieved with the 514.5-nm line of an Ar laser (Stabilite 2017; Spectra-Physics). The laser beam was focused by a microscope (Olympus; BH2-UMA) upon a spot with a diameter of 1–3 \(\mu m\). The scattering signals and the accompanying red luminescence were detected by a silicon CCD matrix (1028 \(\times\) 256 elements) cooled to the temperature of liquid nitrogen. A backward-scattering geometry was used in this experiment.

The reflectivity and the Bragg wavelength as a function of total irradiation fluence \(F_t\) are shown in Fig. 1 for a grating written in a fiber with 25-mol. % GeO\(_2\) in the core. The fluence dependence of the reflectivity and the Bragg wavelength are typical for fibers for which type I and type IIA Bragg gratings were observed. At \(F_t < 5\) kJ/cm\(^2\), the reflection peak position shifts to a higher wavelength and the reflectivity increases with increasing \(F_t\), indicating the development of a type I grating. After reaching a maximum value of \(\sim 5\) kJ/cm\(^2\), the reflectivity decreases. The type I grating completely disappears in the \(F_t\) region 11–20 kJ/cm\(^2\). At higher \(F_t\) values, a type IIA grating develops. As \(F_t\) increases, the reflectivity of the type IIA grating increases, whereas its peak position shifts to a lower wavelength. From Fig. 1 it is obvious that the \(F_t\) values used for homogeneous irradiation correspond to a fluence region in which type IIA gratings occur.

Figure 2 shows the Raman scattering and the luminescence spectra of this fiber as measured before (1)}
and after (2) irradiation. For this fiber the changes in the spectrum were strongest. The Raman spectra obtained by subtraction of the low-frequency edge of the extrapolated red luminescence band from the measured spectra are shown in Fig. 3. A Gaussian function was assumed for the shape of this luminescence band. To compare directly the Raman spectra before and after irradiation, we normalized them to the intensity of the 800-cm\(^{-1}\) Raman band, which is associated with the network structure (Si–O–Si bond).\(^{11,12}\)

Before irradiation, the Raman spectrum is dominated by a main peak with the maximum at \(\sim 435\) cm\(^{-1}\). In accordance with Refs. 11 and 12 this peak is associated with the symmetric stretching modes of bridging oxygen \(\nu_{1}(\text{Si–O–Si})\), \(\nu_{1}(\text{Si–O–Ge})\), and \(\nu_{1}(\text{Ge–O–Ge})\) of sixfold rings of Si\(_4\) and Ge\(_4\) tetrahedra in glass. The weak shoulder of the Raman spectrum near 480 cm\(^{-1}\) is associated with the same modes of fourfold rings. The asymmetry in the main peak is due to the presence of fivefold and sevenfold rings. The shoulder near 580 cm\(^{-1}\) and the peak near 670 cm\(^{-1}\) were assigned in Ref. 13 to other vibrational modes of glass, \(\nu_{5}(\text{Ge–O–Ge})\) and \(\nu_{5}(\text{Ge–O–Si})\). The low-frequency Boson peak\(^{14}\) at 50 cm\(^{-1}\) is due to the quasi-localized vibration modes associated with the middle order of the glass. The very weak peak at 1330 cm\(^{-1}\) is associated with the vibration of the P–O bond.\(^{15}\)

Comparison of the spectra of the fibers before and after irradiation allowed us to notice the following most prominent changes:

1. There was a significant decrease of the total intensity of the measured scattering spectra for all the irradiated fibers that could be explained by the absorption growth in the germanosilicate glass in the visible range after its UV irradiation.\(^{16}\)

2. The maximum shift and the intensity increase of the red luminescence band thus makes analysis of the Raman spectra more difficult.

3. Direct changes of the Raman spectra in the fibers included the following: The most prominent feature was significant growth of the Raman band near 580 cm\(^{-1}\). There was also a shift of the main Raman-band maximum (435 cm\(^{-1}\)) to the higher-frequency range and a general deformation of this band at which the intensity of its low-frequency side decreased and the intensity of its high-frequency side increased. The intensity, broadening, and maximum shift of the low-frequency “bozon” peak\(^{14}\) increased by \(\sim 10\) cm\(^{-1}\) into the high-frequency range. There was also a small decrease in the intensity of the Raman band near 670 cm\(^{-1}\), and the Raman band near 1330 cm\(^{-1}\) disappeared. Table 1 summarizes the observed features of the Raman spectrum and their changes.

During the Raman measurements the exciting Ar-laser beam transmitted by the fiber can affect the fiber transmission and the intensity of the luminescence.

### Table 1. Raman Bands and Their UV-Irradiation-Induced Changes

<table>
<thead>
<tr>
<th>Raman Peak</th>
<th>Designation</th>
<th>Initial Raman Spectra Wavelength Number (cm(^{-1}))</th>
<th>Irradiated Raman Spectra Reference</th>
<th>Relative Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Boson peak</td>
<td>50</td>
<td>14</td>
<td>Increased</td>
</tr>
<tr>
<td>II</td>
<td>Sixfold ring</td>
<td>435</td>
<td>11, 12</td>
<td>Decreased</td>
</tr>
<tr>
<td>III</td>
<td>Fourfold ring</td>
<td>490</td>
<td>11, 12</td>
<td>Increased</td>
</tr>
<tr>
<td>IV</td>
<td>Threefold GeO ring</td>
<td>580</td>
<td>(^{a})</td>
<td>Increased</td>
</tr>
<tr>
<td>V</td>
<td>Ge–O–Si</td>
<td>670</td>
<td>13, 15</td>
<td>Decreased</td>
</tr>
<tr>
<td>VI</td>
<td>Si–O–Si</td>
<td>800</td>
<td>11, 12</td>
<td>Normalized</td>
</tr>
<tr>
<td>VII</td>
<td>P–O bond</td>
<td>1330</td>
<td>15</td>
<td>Disappeared</td>
</tr>
</tbody>
</table>

\(^{a}\)Analogous to Ref. 12 for SiO\(_2\).
ence and the Raman bands. However, our measurements showed that the power of the exciting radiation was twice that used in the spectra measurements during 1–4 h of transmission through the fiber, causing insignificant changes in the measured spectra, if any, and then only toward returning to their initial state.

The significant changes in the fiber Raman spectra after UV irradiation indicate changes in the density of the oscillation vibrational states of germanosilicate glass. The objective of the analysis of the Raman and the luminescence spectra is to clarify their correlation with the UV-irradiation-induced refractive-index change in germanosilicate glass. We use assumptions based on the existing interpretation of several bands in the Raman spectra of silica and GeO$_2$–SiO$_2$ glass.

The observed changes in the main Raman band near 435 cm$^{-1}$ can be associated mostly with the decrease of order of the tetrahedron rings in the glass. UV irradiation may induce breaking of large (sixfold or near 480–490 cm$^{-1}$ frequency) and the formation of fourfold, threefold, or twofold (>480–cm$^{-1}$ frequency) rings.

If we suppose that the Raman band at ~580 cm$^{-1}$ is related to the presence of Ge–O–Ge bonds in the threefold rings and the Raman band with the maximum near 480–490 cm$^{-1}$ is due to the presence of fourfold rings in the germanosilicate glass (in analogy to the Raman bands at 606 and 495 cm$^{-1}$ in silica glass), then the main changes in the Raman spectra can be explained by the UV-irradiation-induced transformation of glass structure.

The increase in the number of low-fold rings in germanosilicate glass after UV irradiation can occur as a result of the destruction of the GeO$_2$ deficiency centers and the conversion of the broken bonds formed during UV irradiation into oxygen atoms with the formation of Ge–O–Ge and possibly Si–O–Ge(Si) bonds. A possible scheme for such a glass-structure transformation in which three coordinated oxygen atoms and low-fold rings are formed was suggested and numerically calculated for silica glass in Ref. 17. It is possible that other defects formed or destroyed in glass during UV irradiation also participate in this process.

An increase in the concentration of low-fold rings in the glass structure should result in an increase in its density and refractive index, as was observed for UV-irradiated germanosilicate glasses. A correlation between refractive-index change and stress change in the fiber core during Bragg grating formation by UV irradiation was also reported.

The intensity increase, the broadening, and the peak shift to higher frequency of the bozon band could be the result of spreading in size of the regions with increased refractive index in the glass. These regions can be the rings themselves as well as the regions with a high concentration of Ge–O–Ge bonds in the glass.

The disappearance of the weak Raman band at the frequency near 1330 cm$^{-1}$ indicates breaking of the double bond P=O, which leads to a change in the local glass structure in the vicinity of the phosphorus atom. The peak shift and the intensity increase of the red luminescence band after UV irradiation can be explained by the existence and creation of different forms of nonbridging oxygen-hole centers in glass or the creation of drawing-induced centers.

Note that significant differences between the Raman spectra reported previously for germanosilicate glasses and fibers and those measured after UV irradiation clearly indicate a change in the glass structure. This structural change could not be realized in the ordinary process of glass production or preform fabrication or during drawing of germanosilicate core fibers. The stability of this structure at room temperature is confirmed by weak changes of the Raman spectra during at least one year after they were first observed.

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References