Optical absorption and luminescence of germanium oxygen-deficient centers in densified germanosilicate glass

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Spectroscopic properties of germanium oxygen-deficient centers were studied in vapor axial deposition and modified chemical-vapor deposition germanosilicate glass after hydrostatic densification by as much as 19%. Gaussian decomposition showed a broadening and a significant shift of the initial absorption bands at 5.11 and 5.42 eV. A threefold decrease of the 3.15-eV luminescence band was revealed, whereas the 4.25-eV luminescence band was only slightly sensitive to densification. This shows that these two bands belong to different luminescence centers. A drastic growth of a new metastable absorption band near 7.3 eV was observed. The pressure-induced changes disappeared as a result of thermal annealing. These changes are discussed with respect to in-fiber grating phenomena. © 1997 Optical Society of America

Much attention is being paid to the study of the mechanisms of the photorefractive effect in germanosilicate glass, which is revealed in the process of UV writing of refractive-index gratings in optical fibers. The research is focused on photosensitive germanium oxygen-deficient centers (GODC's), which are commonly considered to be responsible for the refractive-index change in germanosilicate glass. Among the suggested mechanisms for this phenomenon, one is related to stress relief in optical fibers caused by glass network rearrangement around UV-destroyed wrong bands (GODC's). Another model invokes densification of germanosilicate glass under UV exposure. Densification of pure silica under UV irradiation was also reported; however, this effect was not shown to be related to point defects of the glass.

In our opinion, even though transformation of point defects is not the direct cause of the UV-induced densification, it can trigger the densification. In turn, the remaining defects should change their spectroscopic properties owing to network rearrangement. To remove the combined effects of UV irradiation on defect transformations and on glass densification, we examined the influence of mechanical pressure treatment of germanosilicate glass on the spectroscopic properties of GODC’s. This Letter presents the results of such an investigation.

Samples of germanosilicate glass prepared by the modified chemical-vapor deposition (MCVD) and the vapor axial deposition (VAD) methods (GeO2 concentrations 10 and 7 mol. %, respectively) were thin plates (0.24 mm × 2 mm × 2 mm) cut from fiber performs. The samples were hydrostatically pressurized at 9 GPa and a temperature of 300 °C during 15 min. We chose these values to achieve a significant densification while avoiding crystallization of the samples (note that at room temperature densification of only ~1% was obtained). We determined the densification by measuring the size and weight of the samples. To investigate relaxation of the residual densification and that of induced absorption spectra, we annealed the samples to 1000 °C. Temperature was increased by a step of 100 °C, the annealing time at each temperature being 15 min. UV absorption spectra, luminescence spectra under excitation by N2- and KrF-laser radiation (photon energies 3.68 and 5.0 eV, respectively), and luminescence excitation spectra were measured. In measuring the luminescence excitation spectra, we normalized the luminescence intensity to the incident radiation by using a luminophor with a known quantum yield and separated the luminescence bands with filters. Electron spin resonance spectra of initial and densified samples were also registered. All the measurements were carried out at room temperature.

As a result of high-hydrostatic-pressure treatment residual isotropic densification of 16 ± 2% (MCVD) and 19 ± 2% (VAD) was achieved. These values correspond to the data for pure silica glass. The results presented below are mainly focused on VAD samples. The MCVD samples did not demonstrate any peculiarities related to the specific glass-synthesis method.

Absorption spectra of initial and densified glass and their decomposition into three Gaussian components in initial glass corresponding to different types of GODC (1, 2, and 3) are shown in Fig. 1. A certain scattering loss in the densified glass (~3 dB/mm) seen in the long-wavelength range was taken into account. The mean-square deviation was 0.1 dB/mm (as much as 0.5 dB/mm in certain spectra). The band’s parameters before and after densification are shown in Table 1. As only a tail of the short-wavelength band could be measured, especially in the case of densified sample, the accuracy of determination of its parameters was somewhat lower than that of the other bands.

Figure 1 and Table 1 show substantial changes in the spectra and their components, which reflect the changes in defect concentration (areas) and modifica-
tion of both the defects’ structure and the surrounding glass network (band displacement and broadening). All the bands undergo different changes: The first band experiences the fewest changes, the second one is strongly shifted and increases in amplitude, and the third one does not change its position and width within the accuracy of decomposition, but its amplitude grows by a factor of 15.

The absorption spectra obtained qualitatively resemble those induced by UV irradiation in germanosilicate glass. Paramagnetic germanium centers Ge(2) and GeE′ are known to appear in the case of UV irradiation and to have absorption bands at 5.8 and 6.2 eV, respectively. In densified glass a large absorption is also induced in the range of 5.5–6.5 eV. However, electron spin resonance measurements showed the absence of any paramagnetic defects created during the densification of glass within the experimental error of ~10^{-19} cm^3. Only GeE′ centers with a concentration of ~5 x 10^{15} cm^{-3} were observed in both initial and densified samples. Thus, contrary to UV irradiation, pressure treatment of glass does not produce free charge carriers and radicals with unpaired spins. This result again confirms the validity of the absorption-spectra decomposition into three Gaussian components.

In the process of annealing the absorption induced by the high-pressure compression gradually decreases and, at temperatures of 900–1000 °C, practically returns to the initial state (Fig. 2). On the basis of spectra decomposition the values A_{3}\sigma_{3} and (A_{1}\sigma_{1} + A_{2}\sigma_{2}) were determined. These values are a measure of the corresponding defect concentrations. The temperature dependencies showed the maximum annealing rate in the temperature range 350–450°C. After annealing at 1000 °C, the sizes of the samples, and consequently their densities, return to the initial values.

The luminescence spectra of the initial and the densified glass feature UV (4.25-eV) and blue (3.15-eV) bands. These spectra, excited by 3.68- and 5.0-eV photons, are shown in Fig. 3. It should be noted that the lifetime of the blue luminescence excited at 3.68 eV decreased slightly after densification, from 107 to 90 μs. The main result of these measurements is that the blue luminescence band in densified glass decreased fourfold in the case of both excitations, whereas the UV luminescence band decreased by only a factor of 1.5.

To illustrate better the influence of densification on the luminescence bands’ shape, we present the blue luminescence spectra excited at 3.68 eV in MCVD and VAD glasses normalized in pairs in the inset of Fig. 3. Displacement of the peak (0.02–0.03 eV) to higher energies and especially band broadening (FWHM increased from 0.39 to 0.49 eV) can be clearly seen.

The luminescence excitation spectra shown in Fig. 4 confirm the difference in the nature of the influence of glass densification on the UV and the blue luminescence bands. The efficiency of excitation of the former band changes only slightly: A shape alteration and broadening are observed. However, the excitation spectrum of the latter band changes strongly. The efficiency of excitation in the band near 5.1 eV decreases threefold, with a certain broadening and a shift to higher energy. These relations between the bands are more correct than those given above, because they correspond to the integral of the luminescence bands and not to the spectral density of luminescence only.

It is commonly accepted that the UV luminescence band is due to singlet-to-singlet (S_1 → S_0) transition, and the blue luminescence band, to triplet-to-singlet (T_1 → S_0) transition inside the same defect. However, the difference in the behavior of these bands under glass densification seems to be too large to be explained in terms of this interpretation. On the one hand, no substantial nonradiative relaxation for the T_1 state arises in the densified glass, because the lifetime of the blue luminescence changes only slightly. On the other hand, the decrease of the blue luminescence is not accompanied by an increase of the UV luminescence.

<table>
<thead>
<tr>
<th>Band Number i</th>
<th>Maximum Position</th>
<th>FWHM</th>
<th>Amplitude</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E_i (eV)</td>
<td>Initial</td>
<td>Densified</td>
<td>Initial</td>
</tr>
<tr>
<td>1</td>
<td>5.11</td>
<td>5.29</td>
<td>0.43</td>
<td>0.67</td>
</tr>
<tr>
<td>2</td>
<td>5.42</td>
<td>5.79</td>
<td>0.41</td>
<td>0.65</td>
</tr>
<tr>
<td>3</td>
<td>7.35</td>
<td>7.27</td>
<td>1.32</td>
<td>1.25</td>
</tr>
</tbody>
</table>
Therefore the rate of the intercombinational conversion $S_1 \rightarrow T_1$ assumed in the above model is not affected considerably by glass densification. From this it follows that blue and UV luminescence bands belong to different defects.

The decrease of blue luminescence is usually observed at UV writing of the refractive-index gratings. The decrease was associated only with the photobleaching of GODC. Our results show that glass densification owing to UV exposure can result in an additional decrease in blue luminescence.

Figure 4 also shows that the short-wavelength band at $E > 6.5$ eV disappears in the densified sample. There can be two reasons for this. First, initial GODC-3, which determines the initial absorption and is connected with the defect that gives the blue luminescence, can be destroyed in the process of glass densification. Second, partial absorption of GODC-3 decreases because of a competition with the strong pressure-induced absorption. In any case the initial and the induced absorption in the short-wavelength range are caused by different defects. The different nature of these defects is additionally confirmed by their thermostabilities.

In conclusion, we have demonstrated the following:

1. Isotropic densification of germanosilicate glass by 16–19% results in a significant shift and a broadening of the absorption bands of initial GODC’s. These changes indicate rearrangement of the glass network.
2. A new defect with an absorption band near 7.3 eV is formed. Thermoinduced decay of the absorption band occurs at $\sim 400$ °C.
3. Germanium paramagnetic centers are not formed in densified glass.
4. Densification of germanosilicate glass has a minor influence on the UV luminescence intensity (the 4.25-eV band) but lowers by threefold the blue luminescence (the 3.15-eV band). All the data prove that these bands belong to different defects.
5. The known blue luminescence decay during writing of in-fiber gratings is a result of a combined action of GODC’s photobleaching and glass densification.

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References