Photoinduced changes in the Raman spectra of germanosilicate optical fibres

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Abstract. An investigation was made of changes in the Raman spectra of germanosilicate optical fibres as a result of UV irradiation. The photoinduced changes in the spectra were of the same nature for all types of irradiation used. These changes increased with increase in the radiation dose and in the GeO_2 concentration in the fibre core and were evidence of a structural modification of glass.

1. Introduction

Photoinduced modification of the refractive index of germanosilicate glasses plays an important role in the development of a new class of integrated-optical and optical-fibre instruments and devices (see, for example, Ref. [1]). Investigations of microscopic mechanisms of this effect are needed in optimisation of the technology of refractive structures. The changes in the refractive index of germanosilicate optical fibres caused by irradiation are the result of several mutually related processes activated by the photoexcitation of germanium oxygen-deficient (GOD) centres in a singlet [1] or triplet [2] absorption band.

One of the proposed mechanisms of this effect is the transformation of GOD centres giving rise to other defects [GeE', Ge(1), Ge(2), DID] in the glass as a result of UV irradiation [3]. For example, it was shown in Ref. [4] that such a transformation of defect centres in the germanosilicate glass network, with a corresponding change in the UV absorption spectra, can alter — in accordance with the Kramers – Kronig relationship — the refractive index by up to 2×10^{-4}. However, the experimentally observed photoinduced change in the refractive index can reach 2×10^{-3} [5]. Such a large change is most likely associated with the experimentally observed increase in the density of glass as a result of the action of high-intensity UV radiation from pulsed lasers or of low-intensity UV radiation from cw lasers [5]. The microscopic mechanism of the photoinduced densification of the core of a germanosilicate glass fibre is currently under discussion. Nevertheless, it is obvious that the macroscopic densification of glass should be the result

of a change in its structure. Therefore, an investigation of this change is important for the understanding of the nature of the high photosensitivity of germanosilicate glasses.

One of the methods for investigating the microstructure of glasses is the Raman scattering of light, which makes it possible to use the positions and intensities of the bands in the Raman spectra to study the vibrational spectra associated directly with the glass structure. In Ref. [6] it was shown for the first time that exposure of a germanosilicate optical fibre to powerful pulsed excimer laser radiation of the 248 nm wavelength alters considerably the Raman spectra. According to Ref. [6], these changes are evidence of a considerable photoinduced modification of the microstructure of the glass shown by a reduction in the number of multimember (six members or more) rings consisting of SiO_4 tetrahedra and an increase in the number of rings with few members in the glass structure. Since only one radiation dose (41 kJ cm^{-2}) was used [6] and, moreover, the molecular concentrations of GeO_2 and P_2O_5 in the optical fibre cores were 25% and ~2%, respectively, it seemed to be rather interesting to investigate the influence of UV irradiation on the Raman spectra of optical fibres with a pure germanosilicate core with various GeO_2 concentrations and the effects of different radiation doses.

Our aim was to study the UV-induced changes in the Raman spectra of germanosilicate optical fibres as a function of the concentration of germanium dioxide in the fibre core, and also of the UV dose and of the kind of irradiation.

2. Experiments

The Raman spectra of fibres were recorded, as in Ref. [6], by a T64000 spectrograph (made by Jobin Yvon) with a 1 cm^{-1} resolution. The excitation was provided by a green line ($\lambda = 514.5$ nm) of a Stabilite 2018 Spectra-Physics argon laser, used in combination with an Olympus BH2-UMA microscope, which made it possible to concentrate the laser beam in a spot 1 – 100 µm in diameter. The Raman spectra and the concurrent luminescence were recorded with a silicon CCD array (1024×256 elements) cooled to liquid nitrogen temperature. Measurements were made of the intensity of the backscattered radiation emerging from the same end of a fibre into which the exciting radiation was injected. The power of the Ar$^+$ laser radiation entering the investigated waveguides was 30 – 40 mW and determination of the spectra required a few minutes to half an hour.

Optical fibres with a germanosilicate core and a cladding made of pure fused silica, free of any additional dopants, were made by the modified chemical vapour deposition method. The parameters of the investigated fibres are listed

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Table 1. Parameters of the investigated optical fibres.

Fibre	Molecular concentration of GeO_2 in the core (%)	Core diameter/μm	Absorption coefficient at $\lambda = 240-250$ nm, measured in a preform/cm^{-1}
A	10	~ 40	$150-500$
B	18	~ 5	$200-800$
C	25	~ 8	1000
D	18	~ 1	$200-800$

in Table 1. The length of the irradiated fibres was increased, compared with the length in Ref. [6], from 6 to 20 cm, which improved the signal/noise ratio in determination of the Raman spectra and increased the sensitivity of the method.

The investigated fibres were subjected to three types of UV irradiation (Table 2). Since at the 244 and 248 nm wavelengths the absorption in the germanosilicate glass of the fibre cores was $500-1000$ cm^{-1} (Table 1), the fibres were irradiated through their side surfaces from which the polymer coating was first removed. The relatively large diameter of the core of the investigated fibres (Table 1) gave rise to a gradient of the UV radiation intensity. Therefore, the reported changes in the Raman spectra were averaged over the core cross section.

The cw UV radiation from the Ar^+ laser (emitting simultaneously three lines with $\lambda = 333$, 351, and 364 nm), corresponding to the weaker (by approximately three orders of magnitude) triplet absorption band of the GOD centres with its maximum at 330 nm, was injected into the fibre core through the end face. Since the attenuation of the radiation in the fibres was different at all three wavelengths, it was not possible to determine the exact dose and the effective length of the irradiated region. Nevertheless, a qualitative analysis of the changes in the Raman spectra could be made also for this type of irradiation.

The dependences of the photoinduced changes on the UV dose were determined for a fibre (sample D) which was 4 cm long and was irradiated systematically with the cw second harmonic of the argon laser ($\lambda = 244$ nm) which had the intensity given in Table 2.

3. Results and discussion

An analysis of the Raman spectra of the investigated fibres before their irradiation showed that an increase in the GeO_2 concentration induced changes in the spectra similar to those observed for bulk samples of germanosilicate glasses [7]. In particular, an increase in the germanium concentration in the core increased the intensity of the 670 cm^{-1} band, which was absent from the spectra of pure SiO_2 and GeO_2, and was attributed to vibrations of the oxygen atoms bound to the

atoms of Si and Ge (Si–O–Ge bonds). A band near 580 cm^{-1}, associated with the Ge–O–Ge bonds, also appeared. According to Ref. [8], the intensity of this band did not vary in the range of the molecular concentrations of GeO_2 from 1%–2% to at least 20%.

Before discussing the photoinduced changes in the Raman spectra we should mention that UV irradiation of germanosilicate fibres with our sources generated defects with a wide and complex red luminescence band which had its maximum at 630–650 nm and was excited by visible radiation [9]. This luminescence was excited also by radiation with $\lambda = 514.5$ nm and was superimposed on the investigated Raman spectrum, which greatly complicated its analysis particularly at frequencies above 1000 cm^{-1}. The intensity of this luminescence increased with the GeO_2 concentration in the core and with the UV dose. As before [6], the influence of luminescence on the Raman spectra of the irradiation fibres was taken into account by computer subtraction from the experimental spectrum of the luminescence band consisting of one or two Gaussian subbands with parameters found by the method of approximation of each spectrum separately. This band was present also in the spectra of the fibres before irradiation, but its intensity was considerably less and the influence on the Raman spectra was slight, compared with that observed after irradiation.

For all the fibres and all types of UV irradiation, the changes in the recorded Raman spectra were in qualitative agreement with those reported earlier [6] and they depended considerably on the nature of the UV irradiation and on the composition of the glass. The changes were as follows:

(1) There was a considerable reduction in the total intensity of the recorded Raman and luminescence spectra of all the irradiated fibres. This was the consequence of a reduction in the effective length of the zone of interaction of the exciting radiation with the fibre core because of a reduction of the core transmission associated, according to Ref. [10], with an increase in the visible absorption by germanosilicate glasses after the UV irradiation.

(2) The maximum of the red luminescence band shifted and its intensity increased, so that after the UV irradiation this intensity could exceed considerably that of the Raman line.

(3) The direct changes in the Raman spectra of the fibres were as follows : the most important was a considerable enhancement of the band near 580 cm^{-1}; a shift of the maximum of the main Raman band (430 cm^{-1}) in the direction of higher frequencies and an overall deformation of this band with reduction in the intensity of its low-frequency wing and an increase in the intensity of the high-frequency wing, indicating a reduction in the concentration of multifold rings composed of SiO_4 tetrahedra and an increase in the concentration of fewfold rings; a small reduction in the intensity of the 670 cm^{-1} band; an increase in the intensity of a low-frequency 'boson' peak, its broadening, and a shift of its

Table 2. Parameters of UV irradiations.

Radiation source	Wavelength/nm	Radiation dose/kJ	Radiation intensity/kW cm^{-2}	Radiation energy density/J cm^{-2}	Pulse repetition rate/Hz	Radiation power/W	Duration of irradiation/min
Second harmonic of Ar^+ laser	244	~ 7.5	~ 17	–	–	–	–
KrF excimer laser	248	~ 1	–	~ 0.3	10	–	–
Ar^+ laser	333–364	–	–	–	–	0.6	15

maximum by about 10 cm^{-1} in the direction of higher frequencies.

Unfortunately, because of difficulties encountered in taking into account the influence on the Raman spectra of the fibres of such factors as the nonuniformity of irradiation, the spectral and spatial dependences of the absorption induced near 514.5 nm in the fibres, the changes in the refractive index profile of the fibres as a result of irradiation, etc., it was not yet possible to determine the functional dependence of the changes in the Raman band intensities on the concentration of germanium, on the UV wavelength, and on the UV intensity (dose). These changes clearly increased with increase in the germanium dioxide concentration (Fig. 1) in the fibre core. This was evidence of the participation of the GOD centres, the concentration of which also increased with the concentration of GeO$_2$ [11], in the process of photoinduced modification of the glass structure. The photoinduced changes in the refractive index of germanosilicate fibres also increased with the GeO$_2$ concentration in the core [4]. The role of phosphorus is evidently not dominant in the photostructural transformations of germanosilicate glasses under the action of UV radiation, because our fibres (in contrast to those used earlier [6]) did not contain P$_2$O$_5$.
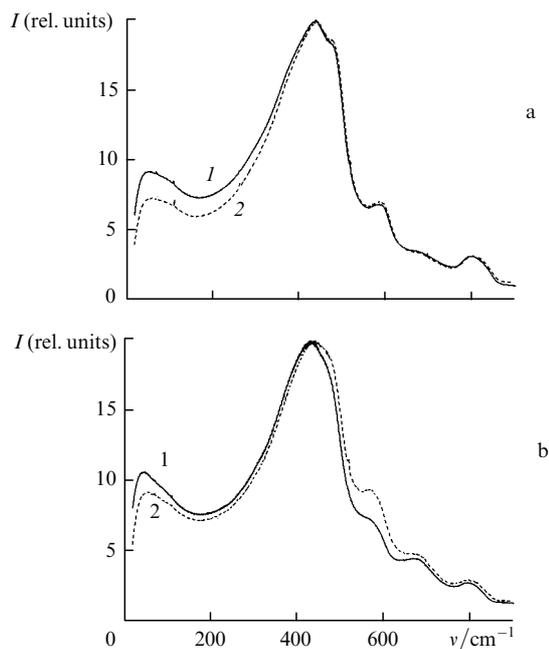

Figure 1. Raman spectra of fibres A (a) and B (b) before (1) and after (2) UV irradiation at the 244 nm wavelength with a dose of 7.5 kJ cm^{-2}.

Fig. 2 gives the Raman spectra of a fibre (C) obtained after irradiation with different UV wavelengths (the radiation doses are given in Table 2). Since irradiation of fibres induced visible-range absorption, dependent on the UV wavelength, the intensities in the Raman spectra differed even when the intensity of the exciting radiation (514.5 nm) injected into the fibres was the same. Therefore, for the purpose of comparative analysis, the dependences in Fig. 2 were normalised to the maximum of the main band near 430 cm^{-1}. All types of the UV irradiation (particularly the irradiation at 244 nm, when the dose was the highest) increased the
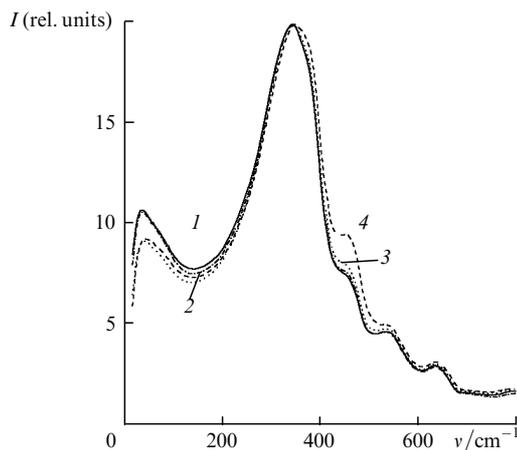

Figure 2. Raman spectra of a fibre C before (1) and after irradiation at the wavelengths $\lambda = 330$ nm (2), 248 nm (3), and 244 nm (4). The parameters of the radiation sources are listed in Table 2.

intensity of the band with its maximum at 570 cm^{-1} and shifted slightly the main band with its maximum at 430 cm^{-1} towards higher frequencies.

In contrast to Ref. [6], where it was reported that the relative intensity of the 'boson' peak increased as a result of irradiation at the 248 nm wavelength with a dose of 41 kJ cm^{-2}, in the present investigation we found that this intensity decreased at lower doses of the $\lambda = 244$ and 248 nm radiation. The difference was evidently associated with predominance of the absorption rise in the wavelength range 500 – 550 nm induced by UV radiation.

Fig. 3 gives the spectral dependence of the absorption induced by irradiation with $\lambda = 244$ nm and 7.5 kJ cm^{-2}. Near the 514.5 nm wavelength (in the region of the 'boson' peak) this absorption reached 0.1 dB mm^{-1}, which led to deformation of the Raman spectra in our ~ 20 cm long fibres. Since the dose dependence of the induced absorption reached saturation quite rapidly, even at doses less than 1 kJ cm^{-2} (Fig. 3b), a further increase in the dose increased the 'boson' peak intensity.
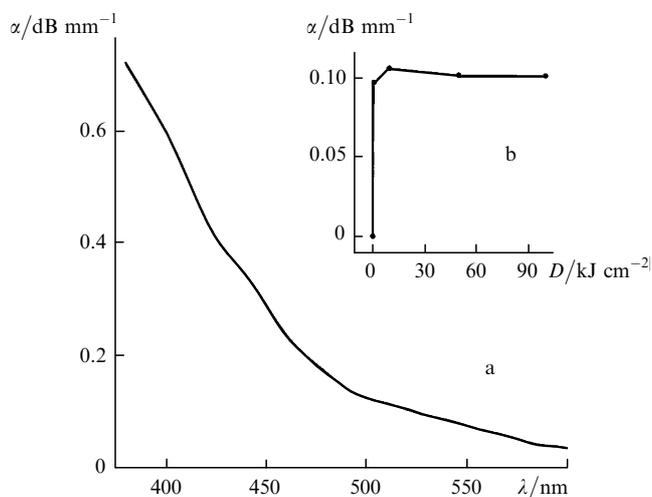

Figure 3. Spectral dependence of the absorption in a fibre D induced by irradiation with 244 nm in a dose of 7.5 kJ cm^{-2} (a) and the dose dependence of the absorption induced at 514.5 nm (b).

Fig. 4 shows the Raman spectra of a fibre (D) before and after UV irradiation with various doses at the 244 nm wavelength. The changes in the Raman spectra were observed at lower and higher (compared with Ref. [6]) radiation doses, right up to 100 kJ cm^{-2}, and an increase in the dose produced a further enhancement of changes in the Raman spectra. However, these changes were less striking than those reported in Ref. [6]. This was probably related to the efficiency of the action of pulsed radiation on the GOD centres and on the glass structure, which was higher than the efficiency of cw radiation.
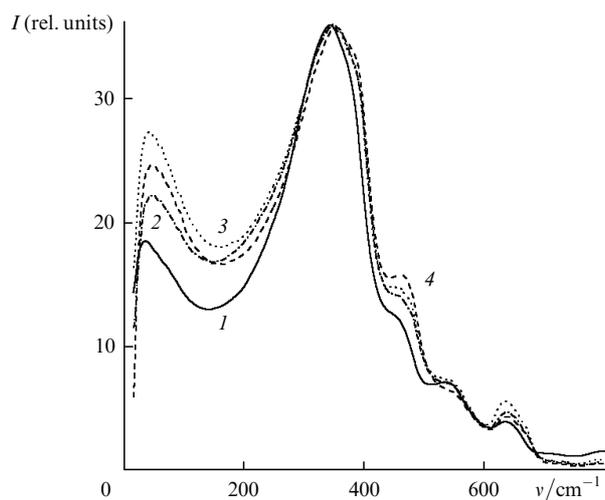

Figure 4. Raman spectra of fibre D before (1) and after UV irradiation with 244 nm in doses of 1 kJ cm^{-2} (2), 10 kJ cm^{-2} (3), and 100 kJ cm^{-2} (4).

The increase in the intensity, the broadening, and the increase in the frequency of the maximum of the 'boson' peak in the Raman spectra could indicate broadening of the distribution of the sizes of the regions in the glass characterised by an increased refractive index. These regions could be the rings themselves or regions with a higher (than the average of the volume of the glass) concentration of the Ge – O – Ge bonds formed by UV irradiation of the germanosilicate glass cores of the fibres.

An analysis of the Raman spectra of the irradiated fibres also showed that, in addition to the changes reported earlier [6], there was a shift and broadening of the band near 800 cm^{-1} and a redistribution of the band intensities at 800 – 1600 cm^{-1}. The results of investigations of changes in the Raman spectra of germanosilicate fibres in this frequency range will be reported in subsequent communications.

4. Conclusions

The UV-induced changes in the Raman spectra of fibres with a pure germanosilicate core thus occur as a result of pulsed and cw irradiation at wavelengths corresponding to the singlet and triplet absorption bands of the GOD centres. The photoinduced changes in the Raman spectra increased with increase in the concentration of germanium oxide in the glass and with the radiation dose, and did not reach saturation up to a dose of 100 kJ cm^{-2}.

The changes in the Raman spectra were of the same nature for all the types of the UV irradiation employed in the present study and they can be explained by destruction of the GOD centres and modification of the glass network near these centres, so as to reduce the concentration of multifold tetrahedron rings and increase the concentration of the fewfold rings.

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