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Photosensitivity of heavily GeO_2-doped fibres in the near UV range between 300 and 350 nm

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***Abstract*. The photosensitivity of a fibre doped with GeO_2 with a molar concentration of 97 % is studied in the near-UV region. It is found that the refractive index induced in this fibre exposed to low-intensity (150 W cm^{-2}) radiation at wavelengths of 305.5 and 333.6 nm achieves a high value ($\sim 1.5 \times 10^{-3}$). It is shown that the photosensitivity increases with decreasing the irradiation wavelength.**

Keywords: *photosensitivity, Bragg gratings, germanosilicate fibre.*

1. Introduction

Optical fibres with a core heavily doped with GeO_2 are promising for the development of Raman fibre lasers (wavelength converters) [1]. One of the main elements of a Raman laser are fibre Bragg gratings (FBGs) forming the laser resonator, which can be written in germanosilicate fibres due to their high photosensitivity providing a permanent change in the refractive index of the fibre exposed to UV radiation. FBGs are usually written in germanosilicate fibres by UV radiation in the 190 – 360-nm range, typically from an ArF and KrF excimer lasers emitting at 193 nm and 248 nm, respectively, or frequency-doubled argon laser at 244 nm. Germanosilicate fibres have a high photosensitivity at these wavelengths. The FBG writing through a polymer coating is of technological interest. At the same time, the transparency region of a standard acrylate polymer coating is limited in the short-wavelength spectral region by the wavelength ~ 300 nm [2]. Therefore, the study of the photosensitivity of new heavily doped germanosilicate fibres in the wavelength region above 300 nm is an urgent problem.

2. Experimental

We studied the photosensitivity of two germanosilicate fibres doped with GeO_2 at the molar concentration (fraction) in the fibre core 97 % (fibre I) and 22 % (fibre II). The fibre preforms were prepared by the modified chemical vapour deposition (MCVD) method. The fibres were drawn at a temperature of 1905 °C. A part of fibres were kept in the hydrogen atmosphere for 16 h at a temperature of 100 °C and pressure 120 atm. In such a way, the fibres were loaded with molecular hydrogen.

The induced refractive index n_{ind} was determined by measuring the parameters of a FBG written in the fibre core [3]

$$\Delta n_{\text{ind}} = \lambda_{\text{Br}} \ln\left(\frac{1+\sqrt{R}}{1-\sqrt{R}}\right) \Big/ 2\pi\eta L, \qquad (1)$$

where λ_{Br} is the wavelength at which the maximum reflection from the grating is observed; R is the grating reflectivity; L is the grating length; and η is the fraction of the energy of the fundamental HE_{11} mode in the fibre core. FBGs were written by UV radiation from a BeamLock 2085 Spectra Physics argon laser in a scheme with a Lloyd interferometer. This laser emits in the near-UV region the lines at 300.3, 305.5, 333.6, 351, and 363.8 nm. Absorption in a standard polymer coating at wavelengths below 300 nm is a few hundreds of inverse centimetres [2], while the photosensitivity of germanosilicate fibres at a wavelength of 364 nm is already two orders of magnitude lower than that at 333.6 and 305.5 nm [4]. Because of this, we studied here the photosensitivity of fibres only at three wavelengths 305.5, 333.6 and 351 nm.

FBGs were written in fibre regions with a polymer coating removed preliminary. Laser radiation was focused to the fibre core with a cylindrical lens to provide the radiation power density ~ 150 W cm^{-2}. The length of FBGs written in fibres was 2 mm. The grating period was ~ 0.5 μm, corresponding to $\lambda_{\text{Br}} \sim 1.5$ μm. The transmission spectrum of a fibre was recorded during FBG writing with an AQ6317B Ando optical spectrum analyser with a spectral resolution of 0.1 nm. The accuracy of measuring the induced refractive index with this experimental setup was 10^{-4}.

3. Results and discussion

No FBG writing was observed in fibres I and II, which have not been preliminary loaded with hydrogen and were exposed to the 351-nm radiation for 50 min (the irradiation dose was ~ 500 kJ cm^{-2}). However, even short-time irradiation (for 1 min) of fibres I at 305.5 and 333.6 nm

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(the irradiation dose was ~ 10 kJ cm^{-2}) resulted in the production of FBGs with the refractive-index modulation 0.2–0.5 dB corresponding to the induced refractive index $(1.5-2.5) \times 10^{-4}$. One can see from Fig. 1 [curve (*1*)] that the dependence of the induced refractive index on the irradiation dose saturates rather rapidly. Note that no FBG writing was observed in fibre II (the induced refractive index was lower than 10^{-4}).

The loading of fibres with molecular hydrogen resulted in a considerable increase in their photosensitivity [curves (*2–5*) in Fig. 1]. One can see that the induced refractive index in fibre I equal to 10^{-3} was achieved for the irradiation dose ~ 10 kJ cm^{-2} at a wavelength of 305.5 nm [curve (*2*)] and ~ 200 kJ cm^{-2} at a wavelength of 333.6 nm [curve (*3*)]. The production of the induced refractive index approximately equal to 10^{-3} is a practically important result because this value is quite sufficient for writing highly reflecting FBGs ($R > 99.9\,\%$) in the fibre core.

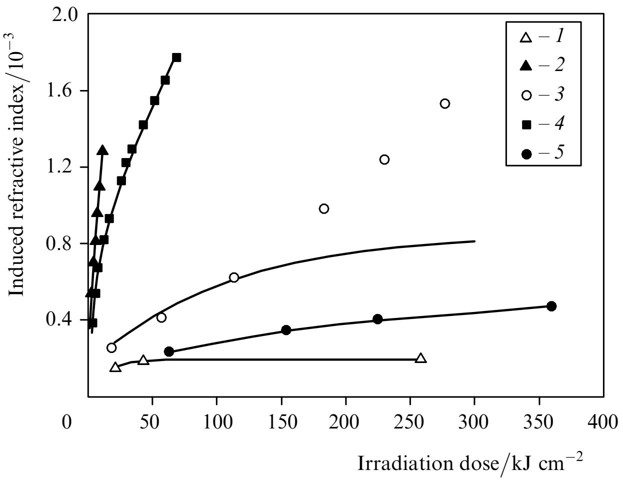

Figure 1. Dose dependences of the refractive index induced by UV radiation at different wavelengths λ for fibres with different molar concentrations N of germanium oxide: (*1, 2*) $\lambda = 305.5$ nm, $N = 97\,\%$; (*3*) $\lambda = 333.6$ nm, $N = 97\,\%$; (*4*) $\lambda = 305.5$ nm, $N = 22\,\%$; (*5*) $\lambda = 333.6$ nm, $N = 22\,\%$; dependences (*2–5*) are obtained for hydrogen-loaded fibres.

An important feature of our experiments is the use of low-intensity laser radiation for FBG writing. The refractive index is usually induced in germanosilicate fibres by the $10^3 - 10^5$ W cm^{-2} cw radiation at wavelengths above 300 nm [4, 5]. However, the exposure of a standard polymer coating to radiation of such high intensity for a few seconds results in its destruction (inflammation). The premature destruction of a polymer coating can be avoided by decreasing the incident radiation intensity [2]. Thus, we demonstrated in this paper the induction of a rather large refractive index ($\sim 10^{-3}$) by the near-UV cw radiation of intensity $\sim 10^2$ W cm^{-2}.

The dose dependences of the induced refractive index for hydrogen-loaded fibres show that a fibre with a higher concentration of GeO_2 has a higher photosensitivity for the same irradiation wavelength. This conclusion is valid both for irradiation at a wavelength of 333.6 nm [curves (*4*) and (*5*)] falling at the maximum of the triplet absorption of germanium oxygen-deficient centres [6] and at a wavelength of 305.5 nm [curves (*2*) and (*3*)] located between the 242-nm singlet and 330-nm triplet absorption bands. It follows from Fig. 1 that irradiation at a wavelength of 305.5 nm instead of 333.6 nm results in the enhancement of the refractive-index induction efficiency by an order of magnitude.

It was found [7] that the refractive index is mainly induced in heavily doped, hydrogen-loaded germanosilicate fibres exposed to the near-UV radiation not by photochemical processes involving oxygen-deficient centres but by reactions of hydrogen atoms with the glass-forming bonds $\equiv \mathrm{Ge-O-Ge} \equiv$ and $\equiv \mathrm{Ge-O-Si} \equiv$. These reactions lead to the formation of new structural defects in the glass network. The structural variations caused by these reactions can result in the refractive-index induction in the glass.

It was assumed in [8] that defects are produced in the germanosilicate glass network exposed to UV radiation due to one- or two-stage reactions. According to this hypothesis, changes in the concentrations of the initial (A), intermediate (B), and final (C) defects during the two-stage process of their formation can be written in the differential form

$$\dot{A} = -k_1[A],$$

$$\dot{B} = k_1[A] - k_2[B], \tag{2}$$

$$\dot{C} = k_2[B],$$

where k_1 and k_2 are the rate constants of photochemical reactions $A \xrightarrow{k_1} B$ and $B \xrightarrow{k_2} C$ corresponding to the first and second stages of the defect formation. In the case of one-stage defect production, expression (2) is simplified to the form

$$\dot{C} = k_3[A], \tag{3}$$

where k_3 is the rate constant of the one-stage photochemical reaction $A \xrightarrow{k_3} C$. According to [8], the induced refractive index Δn can be represented as a sum of two refractive indices induced in one-stage (Δn_1) and two-stage (Δn_2) reactions:

$$\Delta n = \Delta n_1 + \Delta n_2,$$

$$\Delta n_1 = n_1^0(1 - \mathrm{e}^{-k_3 t}), \tag{4}$$

$$\Delta n_2 = n_2^0\left[1 + \left(\frac{k_1 \mathrm{e}^{-k_1 t} - k_2 \mathrm{e}^{-k_2 t}}{k_2 - k_1}\right)\right],$$

where t is the irradiation time; n_1^0 and n_2^0 are the maximum values of the refractive index achieved upon saturation of the dependences $\Delta n_1(t)$ and $\Delta n_2(t)$. By using expressions (4), we approximated numerically the experimental dose dependences shown in Fig. 1. The results are presented in Table 1. One can see from this table that the coefficients k_1, k_2 and n_2^0 for the irradiated fibre not loaded with hydrogen, which characterise the two-stage process of defect production, are negligibly small ($\sim 10^{-6}$). Therefore, we can assume that the refractive index is induced in the irradiated hydrogen-unloaded germanosilicate fibre only due to the one-stage transformation of defects. On the contrary, irradiation of a hydrogen-loaded fibre stimulates

Table 1.

Fibre types	Hydrogen loading	Irradiation wavelength/nm	k_1/s^{-1}	k_2/s^{-1}	k_3/s^{-1}	n_1^0	n_2^0
I	no	305.5	2×10^{-6}	10^{-6}	7.85×10^{-2}	1.9×10^{-4}	10^{-6}
I	yes	305.5	1.0914	0.2661	5.65×10^{-2}	2.29×10^{-3}	2×10^{-4}
I	yes	333.6	15	1	9.5×10^{-3}	7×10^{-4}	1.5×10^{-4}
II	yes	305.5	0.219	0.0148	9.5×10^{-3}	2.56×10^{-3}	5.4×10^{-4}
II	yes	333.6	18	0.7	4.4×10^{-3}	4.3×10^{-4}	1.3×10^{-4}

two-stage reactions accompanied by the formation of intermediate defects. In this case, the refractive index induced in one-stage reactions proves to be several times greater (by factors of ~ 10 and ~ 5 for fibres I and II, respectively) than that induced in two-stage reactions. In addition, the rate constants k_1, k_2, and k_3 for the dose dependences obtained for hydrogen-loaded fibres satisfy the inequalities $k_1 \gg k_2 > k_3$. The same relation was obtained in [8] for the dose dependences of the refractive index induced by radiation at 244 and 193 nm. By comparing the values of n_1^0 and n_2^0 corresponding to the same fibre at different wavelengths, we can obtain another interesting dependence: n_1^0 and n_2^0 increase with decreasing the radiation wavelength.

Thus, the action of radiation at a wavelength of 305.5 nm corresponding to the photon energy of 4.1 eV proves to be a few time more efficient than the action of radiation at a wavelength of 333.6 nm corresponding to the photon energy of 3.7 eV. Therefore, analysis of the results presented in Table 1 once more confirms the hypothesis about the main role of the bonds $\equiv\mathrm{Ge-O-Ge}\equiv$ and $\equiv\mathrm{Ge-O-Si}\equiv$ in photochemical reactions making the largest contribution to the induced refractive index. Hence, these bonds can be treated as initial defects A. It is known that photochemical reactions involving molecular hydrogen give rise to defects containing the hydride and hydroxyl groups [7]:

$$\equiv\mathrm{Ge-O-Ge}\equiv + \mathrm{H}_2 \xrightarrow{h\nu} \equiv\mathrm{Ge-O-H} + \mathrm{H-Ge}\equiv\,. \qquad (5)$$

These defects can be assigned to final defects C. In [9], a model of another photochemical reaction involving H_2 was considered, which produces oxygen-deficient defects and defects containing hydroxyl groups:

$$\equiv\mathrm{Ge-O-Ge}\equiv + \mathrm{H}_2 \xrightarrow{h\nu} =\mathrm{Ge}: + 2\,(\equiv\mathrm{Ge-O-H}). \qquad (6)$$

According to [10], oxygen-deficient defects can then react with H_2, by producing GeH_2 centres:

$$\equiv\mathrm{Ge}: + \mathrm{H}_2 \xrightarrow{h\nu} =\mathrm{GeH}_2\,. \qquad (7)$$

In our case, it is reasonable to consider the model proposed in [9] as the model describing the two-photon process where oxygen-deficient defects play the role of intermediate defects B.

Note that curve (*3*) corresponding to the refractive-index induction dynamics in fibre I irradiated at a wavelength of 333.6 nm has a more complicated form than the rest of the curves. Unlike curves (*1*), (*2*), (*4*), and (*5*), which monotonically tend to saturation with increasing the radiation dose, curve (*3*) exhibits a distinct break at a dose of ~ 100 kJ cm^{-2} after which the slope of curve (*3*) to the abscissa axis changes. This break can be explained by the replacement of one of the mechanisms of refractive-index induction by another with increasing the radiation dose. However, to get a better insight into this effect, it is necessary to perform a complex study of spectral variations induced in the germanosilicate glass network by the near-UV radiation. The transmission, Raman, and EPR spectra of these glasses will be recorded and analysed in our next papers.

4. Conclusions

We have studied for the first time the photosensitivity of heavily GeO_2-doped (97 %) germanosilicate fibres in the near-UV spectral region.

It has been found that even for heavily doped germanosilicate fibres the preliminary loading with hydrogen is necessarily required for efficient FBG writing. Nevertheless, the high photosensitivity ($\Delta n_{\mathrm{ind}} \sim 1.5 \times 10^{-3}$) observed for comparatively low radiation intensities (~ 150 W cm^{-2}) at wavelengths 305.5 and 333.6 nm suggests the possibility of FBG writing in fibres of this type directly through a polymer coating. In this case, the polymer coating should have minimal absorption in the near-UV region.

We have found that the refractive index is induced in hydrogen-loaded germanosilicate fibres by UV radiation both due to one-stage and two-stage photochemical reactions. On the contrary, it seems that in hydrogen-unloaded fibres the refractive index is induced only due to one-stage photochemical reactions.

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