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New radiation colour centre in germanosilicate glass fibres

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Abstract. **We have investigated radiation-induced absorption (RIA) of light in five optical fibres with a germanosilicate core and a light-reflecting cladding made of undoped silica glass in the visible and near-IR ranges under γ-irradiation to a dose of 1 kGy at temperatures from –60 to +60 °C. The concentration of GeO_2 in the cores of the studied fibres ranged from 3.5 to 50 mol%. It is found that the RIA dependences on temperature for optical fibres having been lightly or heavily doped by germanium are different. An increase in RIA with increasing temperature for heavily doped fibres is associated with an increase in the absorption intensity of the GeX centre due to thermal decay of Ge(1) centre. It is found that, in fibres lightly doped by germanium, RIA in the near-IR range is determined mainly by a previously unknown radiation colour centre (RCC) called the GeY centre, with a maximum of the absorption band at a wavelength of ~900 nm (1.38 eV), a half-width of 495 nm (0.71 eV), and an activation energy of 0.15 eV. It is established that the concentrations of GeX and GeY centres differently depend on the irradiation temperature and the content of germanium in silica glass: the concentration of GeX centres increases and the concentration of GeY centers, on the contrary, decreases with increasing temperature and GeO_2 concentration in the core. Thus, in accordance with its spectral position, the GeY centre represents the main RCC limiting the radiation resistance of standard telecommunication fibres with a small addition of germanium (3.5 mol% of GeO_2).**

Keywords: *radiation-induced light absorption, radiation colour centres, germanosilicate optical fibres, radiation resistance.*

1. Introduction

Silica-glass fibres with a germanium-doped core and an undoped light-reflecting cladding (germanosilicate fibres) represent the most common and popular type of optical fibres for optical communication and many other areas of science and technology. However, these fibres have a relatively low radiation resistance due to the colour centers formed under the action of ionising radiation in the fibre glass network and absorbing the light signal at an operating wavelength [1–4].

Most radiation colour centres (RCCs) containing germanium have their absorption bands in the UV range [1, 3]. In the visible and near-IR ranges, the radiation-induced absorption (RIA) of light decrease monotonically with increasing wavelength. The Ge (1) and GeX centres are the most probable RCCs, the absorption bands of which can contribute in the near-IR region. The Ge(1) centre represents a germanium atom with a trapped electron, four-coordinated by oxygen, =Ge•= (• is an unpaired electron). The absorption band maximum of the Ge(1) centre is located at a wavelength of ~282 nm (4.4 eV) [1, 3]. The GeX centre has an absorption band with a maximum at a wavelength of ~475 nm (2.61 eV) [1, 5]; however, the structure of this RCC is not reliably known.

In addition to the short-wavelength RIA in the near-IR range, radiation resistance can be limited by the long-wavelength absorption with a centre in the region λ = 1.7–1.8 μm [6–8], the nature of which also remains questionable.

Note that Girard et al. [9] have shown the impossibility of approximating the RIA spectrum of a germanosilicate fibre using the RCC absorption known in the literature. It is suggested that there is another unknown RCC that can make a significant contribution to the RIA directly in the near-IR range.

The proportion of the short-wavelength and long-wavelength RIA in germanosilicate fibres in the range λ = 1300–1550 nm may vary depending on the GeO_2 concentration, and also depending on the temperature during irradiation due to the different thermal stability of the RCCs determining these absorption bands.

Figure 1 presents the results of published studies on RCCs in germanosilicate fibres at various temperatures. For optical fibres with the GeO_2 concentration of less than 10 mol%, the

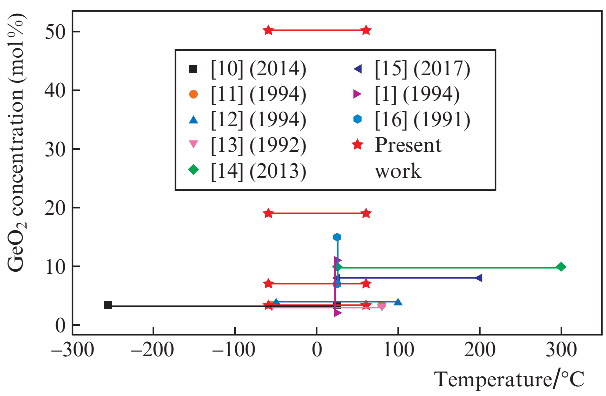

Figure 1. Results of studies on the RIA of optical fibres doped with germanium and irradiated at different temperatures (horizontal lines show the temperature range of fibre irradiation; vertical lines are the range of GeO_2 concentrations).

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RCC studies were performed in a wide range of temperatures: from –250 to 300 °C [10–15]. In almost all cases, the RCC increases with decreasing irradiation temperature, which is associated with a decrease in the rate of thermal decay of the colour centers.

For fibres with a GeO_2 concentration of more than 10 mol%, RIA studies were mainly conducted at room temperature [1, 16], and until now nothing is known about the temperature dependence of RIA for fibres with a higher GeO_2 concentration in the core.

The aim of this work is to study the RIA in germanosilicate fibres in a wider range of irradiation temperatures and GeO_2 concentrations. We have studied the RIA spectra directly in the process of γ-irradiations for fibres with a GeO_2 concentration in the core from 3.5 to 50 mol% at a temperature from –60 to +60 °C, which made it possible to reveal a new RCC in the near-IR range.

2. Experiment

We have investigated five germanosilicate fibres with different GeO_2 concentrations in the core. All the fibres had an undoped light-reflecting silica-glass cladding, with the exception of fibre 4, in the core and cladding of which a small amount of fluorine (0.3 at.%) was added uniformly over the cross section. The main difference between the fibres is the different GeO_2 concentration in the core, which gradually increased from 3.5 mol% (fibres 1 and 2) to 50 mol% (fibre 5). Some studies on RIA in fibre 5 were previously performed in work [8, 17, 18]. Characteristics of the studied fibres are presented in Table 1.

Table 1. Characteristics of investigated optical fibres.

Fibre number	GeO_2 concentration (mol %)	Special features
1	3.5	Standard telecommunication fibre of SMF-28 type
2	3.5	J-FIBER radiation-resistant fibre
3	6.9	Panda polarisation-maintaining fibre
4	19	0.3 at. % fluorine is added into the core and cladding of fibre
5	50	–

Gamma irradiation of fibres was carried out at the Kurchatov Institute using a GUT 200M installation with a ^{60}Co active source.

The fibres with a length from 3 to 200 m (the length was varied depending on the irradiation temperature and the spectral range under study) were wound on coils, which were alternately placed in a thermostat located at the same dose-calibrated point inside the irradiation chamber. Radiation-resistant fibres, connected through biological shielding to the light source and recording equipment, were fusion spliced to both ends of the fibre samples under study.

After lifting the cobalt rods from the underground storage, γ-irradiation of fibres was conducted for 15.5–17.5 min to attain an absorbed dose of ~1 kGy (dose rate was 0.95–1.10 Gy s^{-1}). After a dose of ~1 kGy was accumulated, irradiation was stopped, and the RIA relaxation for 15 min took place. Throughout the experiment, the temperature in the thermostat was maintained at one of five levels: –60, –30, 0, +30 and +60 °C with an accuracy of ±1.5 °C.

The RIA spectra in the near-IR range were recorded using spectrometers based on the InGaAs Avantes NIR-128 (λ = 1100–1700 nm) or NIR Quest 512 (Ocean Optics) (λ = 900–1750 nm) diode arrays. In all these experiments, an HL-2000 halogen lamp was used as a light source. To minimise the effect of RCC photobleaching, the short-wavelength part of the spectrum (λ < 900 nm) was cut off by an IKS-3 filter. In this case, the radiation power in the fibre did not exceed 0.5 μW. For studies on RIA in the visible range, an USB-2000 (Ocean Optics) CCD spectrometer (λ = 200–850 nm) was used. In order to minimise the effect of RCC photobleaching, the radiation source was switched on for only 5 s to record a successive spectral point. In each experiment, a previously unirradiated fibre length was used. The setup and scheme of the experiment are described in more detail in work [19].

3. Results and discussion

Figure 2 shows the RIA dependences on the irradiation temperature T at λ = 1550 nm for all the samples studied. It is seen that, with increasing the GeO_2 concentration in the core, the behaviour of the dependence changes. If for lightly doped fibres 1 and 2, a decrease in temperature from +60 to –60 °C results in the RIA increase by more than an order of magnitude, then for fibres with a concentration of GeO_2 in the core exceeding 7 mol% (fibres 3–5), the RIA temperature dependence proved to be much weaker. It should be noted that a rather low RIA level for fibre 4 is apparently caused by the presence of a small fluorine additive, which, as is known [20], reduces the RCC concentration associated with germanium.

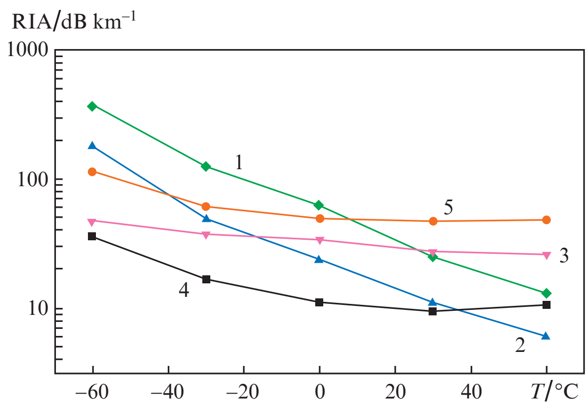

Figure 2. RIA dependences of optical fibres 1–5 on irradiation temperature at λ = 1550 nm during irradiation with an absorbed dose of 1 kGy.

Consider in more detail the RIA spectra in the temperature range from –60 to +60 °C for fibres 2 and 4 (Fig. 3) with a GeO_2 concentration in the core of 3.5 and 19 mol%, respectively, which clearly indicate the qualitative difference in temperature dependences of RIA for lightly and heavily doped fibres with germanium oxide. It can be seen that for both fibres the RIA behaviour in the range under study is determined mainly by the short-wavelength 'tail' of the RCC absorption bands with maxima in the spectral region λ < 1100 nm. For fibre 2 (Fig. 3a), we can observe a monotonic increase in RIA with decreasing temperature over the entire range of 1100–1700 nm. However, for a heavily doped fibre 4 (19 mol% of GeO_2), we obtained a qualitatively different temperature dependence of RIA, especially in the short-wavelength

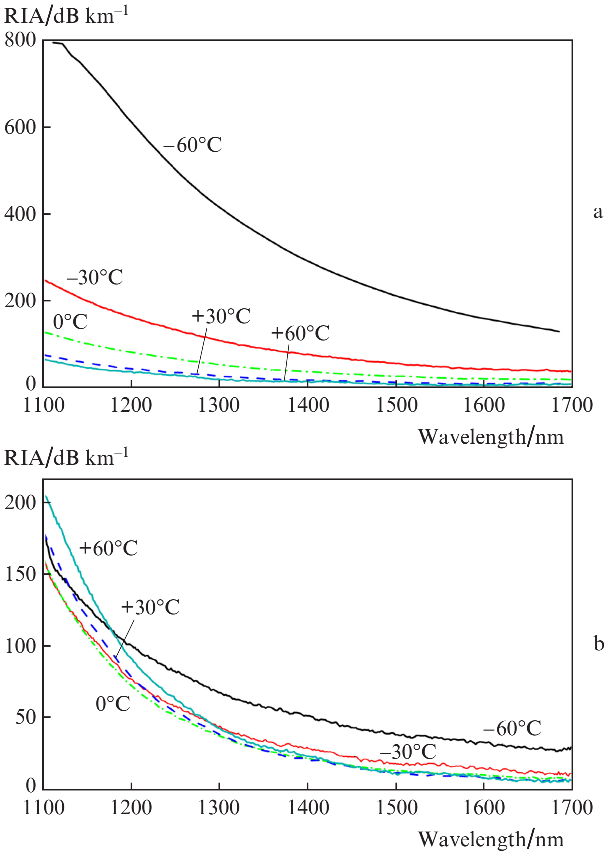

Figure 3. RIA spectra for optical fibres (a) 2 and (b) 4 in the temperature range from −60 to +60 °C, measured during irradiation at an absorbed dose of 1 kGy.

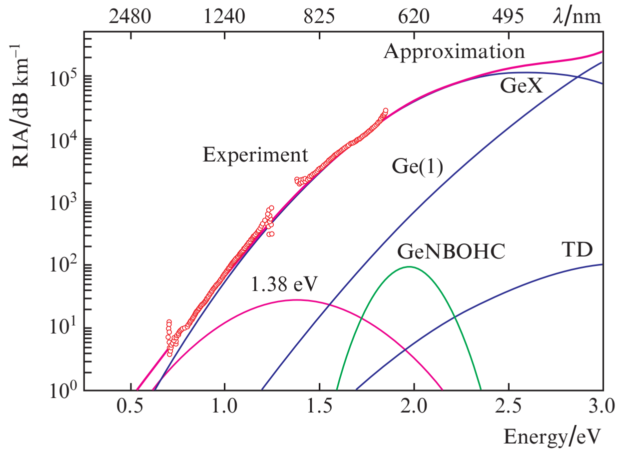

Figure 4. RIA spectrum of fibre 4 measured during irradiation at T = +30 °C and an absorbed dose of 1 kGy, and its Gaussian expansion. GeNBOHC is the nonbridging oxygen atom bound to germanium; TD (transient defect) is a short-lived RCC in germanium-silicate fibres [9]. Parameters of the known RCC absorption bands are taken from [1, 9].

region with λ < 1300 nm (Fig. 3b). As the irradiation temperature increases from −60 to 0 °C, the RIA decrease, and a further increase in temperature from 0 to +60 °C leads to an increase in the short-wavelength RIA 'tail'.

Note that a similar RIA behaviour for a germanosilicate fibre was recorded by Girard et al. [14], but this fact was left without explanation.

In order to analyse this dependence in more detail, the RIA spectra in the visible range were investigated. In this case, the spectra were considered as a superposition of individual absorption bands of the Gaussian form (Gaussian expansion). Figure 4 indicates that, for a heavily doped fibre 4 at T = +30 °C, the main contribution to RIA is made by the GeX centre having an absorption maximum at a wavelength of 475 nm (2.61 eV). It is known from [1] that, as a result of thermal decay of the Ge(1) centres, the concentration of the Ge(X) centres increases after irradiation. Thus, it can be assumed that for heavily doped fibres, an increase in RIA with increasing temperature is also caused by this process, i.e., as irradiation temperature increases, the thermal decay rate of the Ge(1) centre and its transition to the GeX centre increase, which leads to an increase in RIA in the region λ < 1100 nm (see Fig. 3b).

An interesting fact is that, in order to enhance the expansion accuracy (see Fig. 4), we had to introduce another RIA band centred at a wavelength of ~900 nm (1.38 eV) and a FWHM of 475 nm (0.71 eV) [21]. This band belongs to an unknown RCC, the existence of which was discussed by Girard et al. [9]. By analogy with the already known GeX centre, we called this RCC the GeY centre. If, for heavily doped fibres, the absorption band of the GeY centre makes a rather small contribution to the total RIA (see Fig. 4), then for fibres with a low GeO_2 content, including standard telecommunication optical fibres, this band represent one of the main RCCs limiting radiation resistance in the near-IR range (Fig. 5). For example, at a wavelength of λ = 1550 nm with an absorbed dose of 1 kGy, the contribution of this band to the total RIA of fibre 2 with a standard GeO_2 concentration (3.5 mol%) is more than 90% (see Fig. 5).

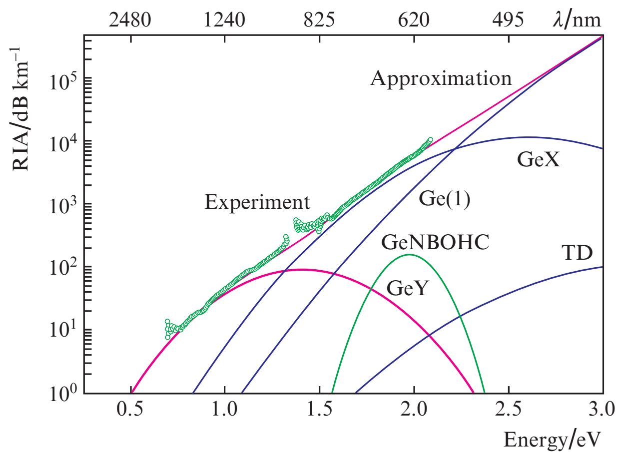

Figure 5. The same as in Fig. 4, but for fibre 2.

Now we should take a closer look at the properties of the GeY centre. Comparing the dependences of the natural logarithm of induced absorption α_{max} (α_{max} corresponds to the amplitudes of the absorption bands of GeY and GeX centres) on T^{-1} for heavily doped fibre 4 (Fig. 6), it is seen that they differ in behaviour. While the absorption intensity of the GeX centre increases with temperature, GeY centres have a 'normal' temperature dependence for the majority of RCCs, i.e., their concentration decreases with increasing irradiation temperature.

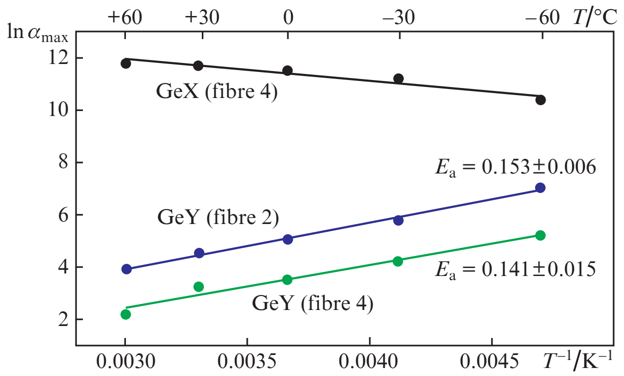

Figure 6. Dependences of the natural logarithm of induced absorption α_{max} of GeY and GeX centres for fibre 4 and GeY centres for fibre 2 on T^{-1}. Approximating straight lines: for the GeY centre (fibre 2), $y = 1777.44x - 1.40$ (the correlation coefficient $R_{xy} = 0.998$); for the GeY centre (fibre 4), $y = 1641.72x - 2.50$ (the correlation coefficient $R_{xy} = 0.982$).

It is also seen from Fig. 6 that the absorption intensity of the GeY centre obeys the Arrhenius dependence with the activation energy ~0.15 eV. It is worth noting that for lightly and heavily doped fibres, we have different concentration of GeY centres with identical activation energy, which indirectly confirms the existence of a new RCC.

No less interesting are the absorption dependences of GeX and GeY centres on GeO_2 concentration in the fibre core (Fig. 7). It can be seen that with an increase in the GeO_2 content, the concentration of GeX centres increases, while the concentration of GeY centres decreases. Thus, the concentrations of the two RCCs have opposite dependences on irradiation temperature and concentration of germanium in the core. In this case, as can be seen from Fig. 7, the GeY centre determines, first and foremost, the radiation resistance of standard optical fibres for optical communication with GeO_2 concentration of 3.5 mol% and therefore is extremely important from a practical viewpoint.

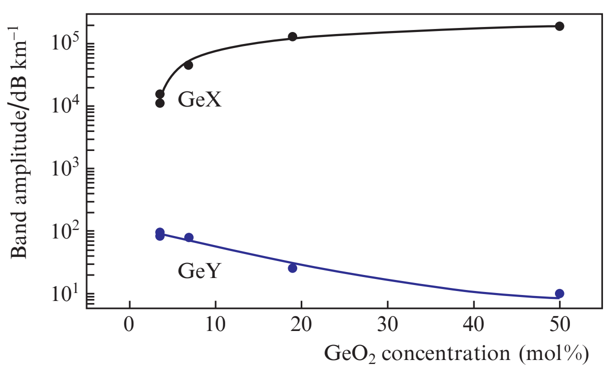

Figure 7. Dependences of the amplitudes of RIA bands of GeX and GeY centres on the GeO_2 concentration in the fibre core at an absorbed dose of 1 Ky and a temperature T = +30 °C.

4. Conclusions

The studies on the RIA of γ-irradiated optical fibres with different GeO_2 concentrations in the core, performed at temperatures from −60 to +60 °C, have shown that the RIA temperature dependences for fibres, lightly and heavily doped by germanium, are different. For heavily doped fibres with a GeO_2 concentration of no less than 19 mol%, the RIA value increases with temperature at wavelengths $\lambda < 1300$ nm. This effect is caused by an increase in the absorption intensity of the known GeX centre due to thermal decay of the Ge(1) centre.

By means of Gaussian decomposition of the RIA spectra of these germanosilicate fibres measured at different temperatures, a previously unknown RCC, namely the GeY centre with a maximum of the absorption band at a wavelength of ~900 nm (1.38 eV), a half-width of 495 nm (0.71 eV), and an activation energy of 0.15 eV has been for the first time identified. It has been established that the concentrations of these GeX and GeY centres have different dependences on the irradiation temperature and germanium concentration: the concentration of GeX centres increases, while that of GeY centres, on the contrary, decreases with an increase in temperature and GeO_2 concentration in the core.

The GeY centre is the main RCC limiting the radiation resistance of standard telecommunication optical fibres in the near-IR range.

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