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Observation of radiation-induced absorption of self-trapped holes in Ge-doped silica fiber in near infrared range at reduced temperature

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ABSTRACT

Short-lived radiation-induced absorption (RIA) of light peaking at wavelengths > 1700 nm has been revealed in a γ-irradiated (≤1 kGy) heavily (50 mol% GeO_2) Ge-doped silica optical fiber (Ge-doped fiber) at low temperatures (≤ −30 °C). This RIA is found to closely resemble in properties the known RIA due to inherent self-trapped holes (STHs) in undoped-silica-core optical fibers (same spectral range, low thermostability, non-monotonic evolution with dose, shift of the peak wavelength with temperature, Arrhenius dependence on temperature, growth of the activation energy in the course of irradiation and recovery). The STH-like RIA is found not to occur in more lightly Ge-doped fibers and in a Bi-codoped Ge-doped fiber with the same (50 mol%) GeO_2 concentration. A possible microscopic structure of the STH in heavily Ge-doped fibers is discussed.

1. Introduction

Being exposed to ionizing radiation, amorphous SiO_2 (silica) bulk samples as well as undoped-silica-core optical fibers exhibit, among other radiation-induced color centers (RICC), self-trapped holes (STHs) [1–7]. It is worth briefly recalling the existing knowledge of STH.

Initially in 1989, Griscom observed two types of ESR spectra in irradiated bulk silica samples at liquid nitrogen temperature (LNT) which he attributed to STHs [1]. A few months later, Chernov with coauthors [2] revealed STHs in γ-irradiated undoped silica optical fibers at LNT in the optical domain as a wide non-Gaussian radiation-induced absorption (RIA) band centered at the wavelength of ~1600 nm (0.77 eV), which was named therein "low-temperature infrared absorption" (LTIRA). This RIA band was attributed to STH based on computer simulation and on the similarity of its thermal annealing and that of trapped positive charges in X-ray-irradiated silica thin films investigated previously in ref. [7]. LTIRA intensity was found to monotonically decrease nearly to zero with increasing temperature to room temperature (RT) [2]. In the course thermal annealing or photobleaching, the wavelength of the LTIRA maximum was found to decrease concurrently with a reduction of its amplitude [2].

In 1992, based on the ESR-spectra analysis, Griscom proposed the microstructure of two STH types [3]: STH_1 is constituted by a radiation-induced hole localized on the non-bonding *p*-orbital of a single bridging oxygen atom, whereas STH_2 by a hole delocalized over the non-bonding *p*-orbitals of two neighboring bridging oxygen atoms of the same SiO_4 tetrahedron. Two Gaussian bands at 1.88 and 1.63 eV in the RIA spectra of pure-silica core fibers initially observed by Nagasawa [8] and later by Griscom [4–6] were subsequently interpreted as being due to STH_1 and STH_2, respectively [9]. In contrast to the other STH optical manifestations, those bands were found to be metastable even at RT.

In 2003, Sasajima and Tanimura [10], by correlating the ESR signal and RIA, identified STH_1 and STH_2 in bulk silica samples irradiated at LNT by electron pulses, their absorption bands being centered at 2.60 eV (477 nm) and 2.16 eV (574 nm), respectively. That is, these STH bands proved to be somewhat shifted in spectrum with respect to their counterparts observed in fibers at RT (1.88 and 1.63 eV, respectively).

Thus, there exist RIA bands due to STH occurring only at reduced temperature (LNT and somewhat higher) and those metastable even at RT. As this takes place, the STH bands have been observed at RT only in optical fibers, of which the network is more strained than that of bulk silica samples owing to the frozen-in drawing-induced strain [9,11]. Therefore, we proposed to classify STHs into two classes: those inherent in silica and those strain-assisted [9]. The inherent STHs are induced by ionizing radiation in bulk silica samples and in unstrained or weakly strained fragments of the fiber silica network; they are short-lived and of low thermostability. The strain-assisted STHs are induced in strongly strained fragments of the fiber silica network and are relatively long-lived and thermostable. Inherent STHs are responsible for the RIA bands at 2.60 and 2.16 eV (STH_1 and STH_2, respectively [10]), at 0.77, and at ~1 eV, the latter band having been recently observed for the first time [9] Only two RIA bands are known so far to be associated with strain-assisted STHs: 1.88 eV (STH_1) and 1.63 eV (STH_2).

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RIA intensity of both inherent and strain-assisted STHs was found to increase with increasing the drawing-induced strain [9]. However, there appears to exist critical network train separating STHs of the two classes, which feature, evidently, different self-trapping mechanisms of the hole. This difference manifests itself in the different spectral positions of the RIA bands due to STH_1 and STH_2 of the two classes.

A "visiting card" of RIA due to all STHs is non-monotonic evolution with dose [4–6] at least at the irradiation temperatures $\geq -60\,°C$ [9]: RIA quickly goes up at the very beginning of irradiation, reaches maximum, and then smoothly goes down as the irradiation proceeds. The non-monotonic RIA evolution with dose leading, in the long run, to the irreversible STH disappearance is due to the competition of two concurrent opposite processes: STH induction and disruption of Si—O bonds followed by network relaxation to eliminate strain.

In a number of papers [12,13], the ESR signal due to STH has been observed in irradiated bulk germanosilicate glass samples as well. However, just one paper [14] has reported an STH observation in such a sample in the optical domain, where a RIA band due to STH was found to occur at 77–100 K and to be centered at 2.4 eV. In all likelihood, it was a composite band consisting of the inherent STH_1 and STH_2 bands known from the studies of undoped-silica bulk samples and fibers [10]. If so, the STHs occurred, apparently, in the network fragments free of germanium atoms; otherwise, one has to assume that the spectral positions of the RIA bands due to STH remain the same in the presence of germanium, which is less probable.

In some papers [15,16], long-wavelength RIA observed at RT in undoped- and Ge-doped-silica-core fibers peaking in the region $\lambda > 1800$ nm was also interpreted as being due to STH. In fact, it occurs in the same spectral region as LTIRA, and the evolution of its shape in the course of thermal annealing [17,18] is also similar (shift of the peak wavelength towards shorter wavelengths during thermal annealing). However, the former RIA is exceptionally thermostable and monotonically grows with dose; for this reason, its being due to STH is, in our opinion, open to question.

We are not aware of any reports of an observation of "classical" STHs in Ge- or otherwise doped silica-core fibers (except F-doped-silica-core ones [19]) either at reduced temperature (inherent STHs), or at RT (strain-assisted STHs). In this paper, we report, for the first time to our knowledge, an observation of RIA due to STH in a Ge-doped silica fiber peaking in the spectral region > 1700 nm and occurring only at reduced temperatures ($\leq -30\,°C$).

2. Experimental details

2.1. Samples

The parameters of the fibers studied are given in Table 1. They had a Ge-doped silica core and undoped-silica cladding, except fiber *4*, of which the core and the cladding were, in addition, uniformly co-doped with a small amount of fluorine (0.3 at.%). The Cl-content in the fibers and preforms was not measured.

The main difference of the fibers was the GeO_2 concentration, which successively increased from 3.5 mol% (fibers *1* and *2*, Table 1) to 50 mol% (fibers *5* and *6*). The latter two fibers differed only in that the core of fiber *6* contained a small admixture of bismuth (0.018 wt%). RIA in fiber *6* was studied earlier in ref. [20, 21] with the aim to assess radiation-resistance of the novel active bismuth-doped fibers. The technological regimes of preforms and fibers *5* and *6* were exactly the same, except for adding a bismuth-containing reagent into the vapor-gas mixture when synthesizing the core of preform *6* by the MCVD-process.

Looking ahead, it should be noted that a low-temperature STH was revealed in fiber *5* only. Therefore, below we consider mainly this fiber, invoking fibers *1* and *6* for comparison.

2.2. Experiment

RIA spectra in the fibers were measured in the near-IR range in the process of γ-irradiation to the dose of 1 kGy from a ^{60}Co-source and during post-irradiation recovery at temperatures in the range ± 60 °C with a step of 30 °C. Experiments on different fibers and at different temperatures were carried out individually on pristine fiber lengths.

The experimental set-up was described in ref. [9]. A fiber length was wound on a plastic reel and embedded in a thermostat, which was positioned each time in the same calibrated place in the ^{60}Co-source room. The lengths of fibers *1–5* was 30–200 m, of fiber *6*, 5 m. Radiation-resistant undoped-silica-core fiber pigtails were fusion spliced to both ends of the fiber tested and went to the light source and spectrometer to behind the biological shielding. After lifting up the cobalt rods from its underground lead housing, the fibers were exposed to γ-radiation at a dose rate of 0.95–1.10 Gy/s. The irradiation lasted for 15.5–17.5 min until the total absorbed dose reached ~1 kGy. After that, the irradiation was terminated and the fibers recovered during 15 min, the fiber temperature remaining constant during the irradiation and recovery to the accuracy of ± 1.5 °C.

The RIA spectra were measured in the process of irradiation and post-irradiation recovery with a time step of 0.5 min with the help of an InGaAs-based diode-array NIR128 spectrometer of Avantes (1100–1700 nm) and NIRQuest-512 spectrometer of Ocean Optics (900–1700 nm). The probe light source was an HL-2000 halogen white-light lamp of Avantes, which was kept on continuously during the irradiation and recovery. The short-wavelength part of the lamp spectrum ($\lambda < 0.9\,\mu m$) was cut off by a filter. The total light power in the fiber did not exceed 0.5 μW.

Note that we performed all the RIA measurements in the conditions of varying both the irradiation temperature and the temperature of post-irradiation recovery. At the same time, in most preceding papers on STH thermostability [2–4,10], the irradiation temperature was fixed, whereas isothermal or isochronal annealing of the samples was performed already on finishing the irradiation. Girard with co-worker [22] showed that the properties of some RICC observed immediately in the course of irradiation can differ from those revealed in the course of post-irradiation recovery.

Table 1
Parameters of the fibers studied.

Fiber no.	Δn, 10^{-3}	Core diameter (± 0.1 μm)	Cladding diameter (± 1 μm)	Cutoff wavelength (± 0.01 μm)	GeO_2 content (mol. %)	Preform fabrication technique	Comments
1	5.0 ± 0.1	8.2	125	1.26	3.5 ± 0.1	OVD	Standard fiber for optical communication similar to SMF-28
2	5.0 ± 0.1	8.2	125	1.26	3.5 ± 0.1	MCVD (?)	Radiation-resistant fiber of j-fiber
3	10.5 ± 0.3	6.4	80	1.45	6.9 ± 0.2	MCVD	Polarization-maintaining fiber of the PANDA type
4	26.0 ± 0.5	3.1	125	1.12	19.0 ± 0.5	MCVD	Fluorine in the amount of ~0.30 ± 0.05 at.% uniformly added to the core and the cladding
5	70.0 ± 1.5	2.0	125	1.17	50.0 ± 1.0	MCVD	–
6	70.0 ± 1.5	2.0	125	1.17	50.0 ± 1.0	MCVD	Bismuth added to the core (0.018 ± 0.005 wt%)