Radiation optical effects in commercial SiO_2:Ge fibers

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Abstract. Present work is dedicated to investigation of radiation optical properties of SiO_2:Ge glass fibers produced by Fujikura and Corning Glass. Distribution of Ge dopant characteristics in core and cladding of quartz fibers have been determined. Ge dopant rings shaped luminescence in optical fibers has been observed. New method of determination the Ge dopant distribution in core and cladding cross sectional profile of silica glass fibers is presented. The thermoluminescence and light storage processes in fibers affected by x-ray radiation have been investigated. The photoluminescence investigations shows that there are two bands of luminescence with 400 nm and 550 nm maxima, which appear in different temperature stimulation conditions. Obtained results are discussed.

1. Introduction

For over than 40 years doped quartz optical fibers were used in optical communication systems and different optical fiber devices. On the basis of these devices the fiber-optic gyroscopes and distributed fiber-optic sensors of external physical effects for continuous monitoring of controlled parameters are produced [1–14]. Fiber technologies are increasingly used for registration of ionizing radiation [15]. Largest research centers in Russia, Europe, USA, China, Japan, as well as manufacturers of fiber optical devices search for solution to the fiber optics problems. Quartz optical fibers doped with Ge, P, F, N, Cr, Bi and other transition metals are being studied and developed. While germanium doped quartz glass is most widely used, however, some properties of these glass fibers have been researched insufficiently.

This paper is focused on photo-, radio-, cathodo- and thermoluminescence properties of germanium doped Fujikura and Corning silicate glass fibers. Our studies have been performed by taking into account the distribution of germanium dopant profile in the core center and cladding in glass fibers basing on the original method [16].

2. Samples and research methodology

Germanium dopant distribution profile of the core center and cladding of quartz fiber s research was carried out for a number of samples of germanium glass fibers Fujikura LWP and Corning SMF-28e+. The fiber samples were cut into a length of about 5 cm formed in the fiber bundles of the certain type and placed in a cylindrical form with epoxy resin. After the hardening process, one of the cylinder

surfaces of epoxy resin was grinded and polished until the surface was of the required quality. Then conductive carbon layer of thickness no more than 5 nm was deposited on the polished side by vacuum plasma spray on the device Quorum 150T.
Profile measurements and map of the dopant ion distribution in the glass fibers were acquired using an electron microscope Zeiss Sigma VP equipped with energy dispersive analysis attachment INCA Oxford Instruments. The accelerating voltage of the electron beam was equal 20 kV at beam current 20 nA. Image registration was carried out using secondary electron detector SE2, backscattered electron detector CZ BSD and cathode luminescent detector CL (spectral range of 200–850 nm).
Fujikura LWP and Corning SMF-28e+ fiber glass samples were cleaned of polymer coating and treated with acetone to investigate luminescence properties. Then the fiber was grinded in agate mortar to obtain homogeneous fine powder which was deposited on a metal substrate with ethanol.
Photoluminescence (PL) and photoluminescence excitation spectra (PLE) of the glass fibers formed as fine fibers were measured using Perkin Elmer LS55 spectrophotometer equipped with a Hamamatsu photomultiplier R928. A pulsed xenon lamp was used as the excitation source. The signal registration was carried out in fluorescence mode.
Thermoluminescence (TL) was recorded using the same Perkin Elmer LS55 spectrophotometer upgraded with built-in high-top box for measurements at linear heating at the range of 300–770 K. The original quartz fiber powder samples were annealed beforehand at 770 K, and then irradiated with X-ray Oxford Instruments Eclipse IV device with dose of 15 Gy at 300 K. Registration of TL was carried out at a constant heating rate of 2 K/s. Three-dimensional spectral distribution of TL was registered in the range of 290–650 nm with a scan rate of 800 nm/min at a heating rate of 0.1 K/s. The sample temperature was varied for 4 K during the measurement of one spectrum.

3. Experiment Results

3.1. Cathodoluminescence and germanium dopant distribution profile

Cross-sectional images of the fiber surface of Fujikura LWP and Corning SMF-28e+, obtained by CZ BSD detector, are presented in figure 1. The figure shows quartz cladding of diameter of 125 μm and a polymeric protective coating of diameter of 224 μm. The region of the fiber core center of 9 μm diameter is clearly visible due to the contrast in atomic number of the chemical elements produced by registered CZ BSD backscattered electron detector. Cross-sectional surface is dotted with small recesses and cavities formed during samples grinding and polishing. EDS-detector ion concentration measurement of glass fiber core and cladding of Fujikura LWP and Corning SMF-28e+ fibers proves that their composition is almost identical to each other. The ion concentrations are shown in table 1 in mass and atomic fractions. Slight impurity content of chlorine ions has been detected in Fujikura LWP fiber sample which might have occurred as the remainder of the batch used in the preparation process.

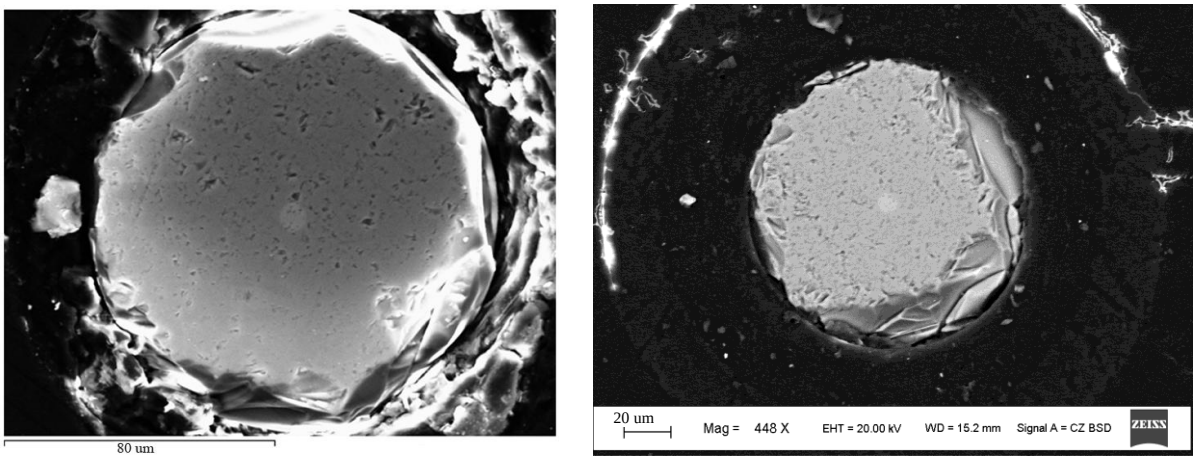

Figure 1. Fujikura LWP(a) and Corning SMF-28e+ (b) silica core general view.

Table 1. FujikuraLWP silica fiber core ion concentration

Element	Core		Cladding	
	Mass fraction, %	At. fraction, %	Mass fraction, %	At. fraction, %
Fujikura LWP				
O	53.80	67.91	53.87	67.21
Si	43.54	31.31	46.13	32.79
Cl	0.14	0.08	–	–
Ge	2.52	0.70	–	–
Corning SMF-28e+				
O	51.89	66.20	53.09	66.52
Si	45.50	33.07	46.91	33.48
Ge	2.61	0.73	–	–

Figure 2 represents the Fujikura LWP and Corning SMF-28e+ fiber samples polished sections image registrations resulted in cathodoluminescence microscopy channel under the influence of the electron beam. Complex glow distribution profile formed as concentric circles near the center of the quartz core is observed in images. The profile includes three areas differing in luminescence intensity: central weakly luminescent area in diameter of 8–10 μm, strongly luminescent halo with the thickness of ~5 μm, and Fujikura LWP fiber sample ring with the thickness of ~5 μm in diameter and ~30 μm with low intensity glow. It is worth to note that the luminescence distribution profiles of the different fiber types are the same in the central area and different at the edge.

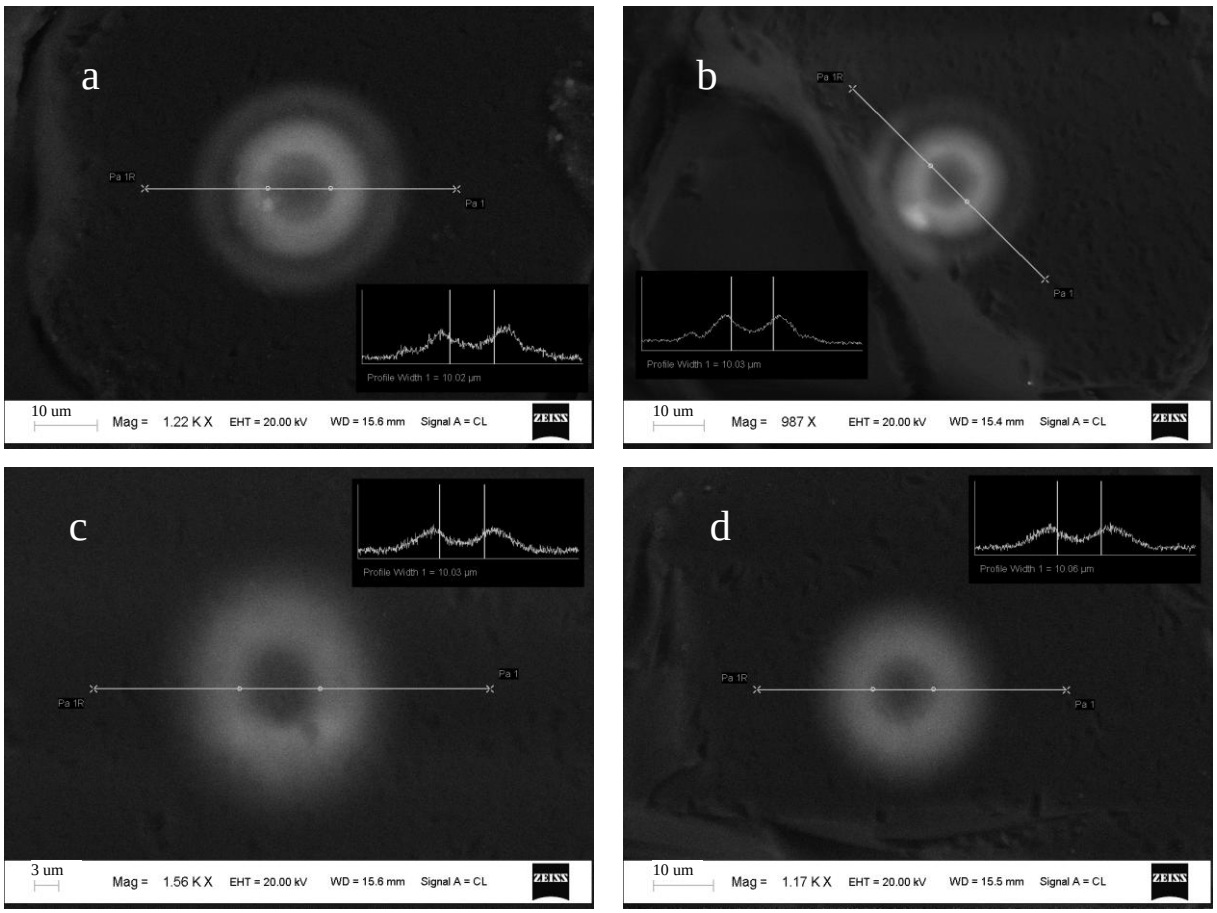

Figure 2. Fujikura LWP (a, b) and CorningSMF-28e+ (c, d) fiber sample CL-channel microscope images. Luminescence intensity distribution profiles measured along a green line are shown.

EDS ion distribution in the observed luminescence area was held using the results of measurements carried out in the CL-channel microscope. Thus, the ion concentration distribution profiles along a line passing through the center of the luminescence region have been measured and also element concentration distribution maps have been constructed. Figure 3 shows that the central region corresponding to the quartz core center provides the maximum amount of germanium dopant, to the center of the core edge its concentration decreases sharply. Highest germanium concentration region (about 0.7 at.%) has low luminescence intensity (central area). Maximum luminescence intensity is achieved in the core-cladding edge area of the quartz core in the ring width of 5 μm; the germanium concentration is reduced in this area to the limit values of EDS-spectrometer sensitivity (figure 3, c, f).

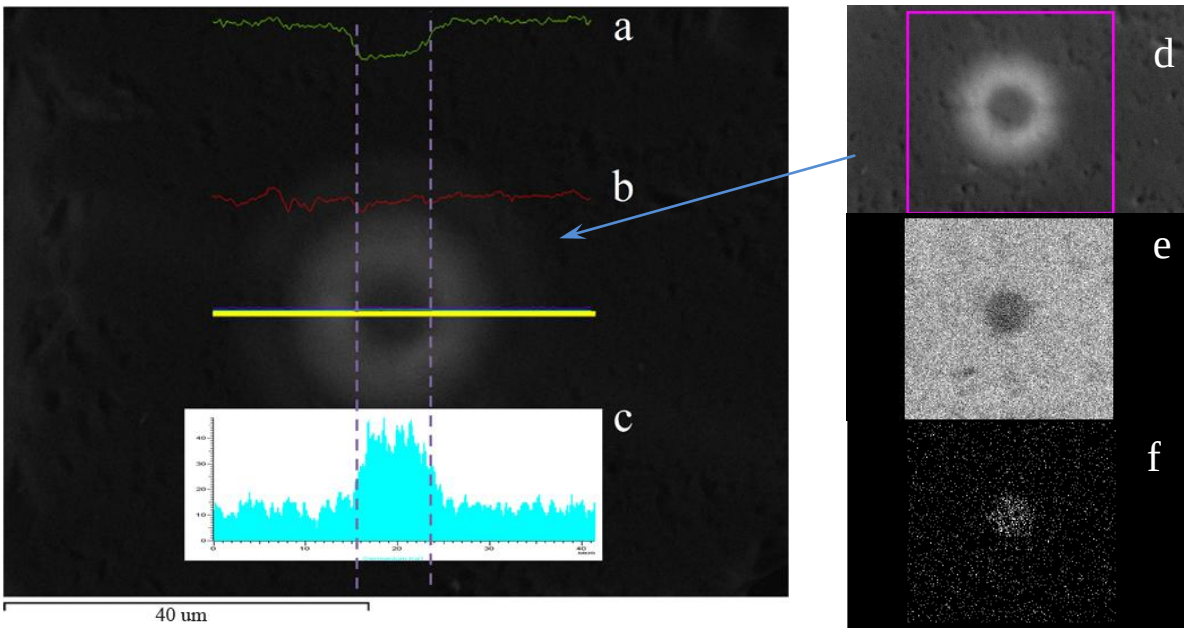

Figure 3. Typical distribution profiles (a, b, c) and distribution images as an element concentration distribution maps (d, e, f) of fibers under investigation measured with EDS-method: a, e – Si; b – O; c, f – Ge; d – mapping area is marked. For a direction of yellow line which element concentration distribution profiles were measured.

3.2. Photoluminescence

PL and PLE spectra of grinded optical fiber Fujikura LWP and Corning SMF-28e+ are the same. The typical luminescence spectrum of the Fujikura LWP fiber has a complex profile, which is a superposition of two bands (Figure 4). The PL spectrum component decomposition into the Gaussian shape bands is plotted in Figure 4c. Two luminescence bands are uniquely determined with maxima at 450 and 400 nm (which correspond to photon energy of 2.77 and 3.12 eV respectively).

As it follows from the literature [8–14], it is established that the amorphous silicon oxide α-SiO_2, doped germanium, intense luminescence band with a maximum at 400 nm (3.12 eV) can be attributed to the radiative transition in the center of luminescence consisting of two-fold coordinated germanium ion [= Ge:] in coordination of rutile (β band) [14]. Excitation of the band mentioned above is carried out in well-known $B_{2\beta}$ band with a maximum at 240 nm (5.15 eV) which was also detected in the EPL spectrum (Fig. 4a). It should be noted, however, that so-called α_E luminescence band of the center [= Ge:] with a maximum at 288 nm (4.3 eV) as described in [14] was not found.

Low-intensity luminescence band at 450 nm (2.77 eV) can be attributed to radiative transitions in the center of luminescence, which is a two-fold coordinated silicon ion [= Si:]. A detected second type of luminescent centers is suits undoped amorphous quartz [13]. However, due to the low intensity of

light, these centers of luminescence in undoped core cladding of optical fiber in the electron microscope CL-channel are failed to register.

It follows from the above that the glow in the core-cladding border-area inside the center of the core of quartz fiber is determined by the presence of luminescence centers of two-fold coordinated germanium ions type [= Ge:]. However, in the center of the fiber core where the concentration of germanium is the maximum, due to the concentration quenching the intensity of luminescence is low, whereas in the core-cladding border area and in the areas of the cladding surrounding core the luminescence intensity reaches its maximum. Luminescence intensity distribution analysis in such optical fiber is complex and is a subject for the further investigation.

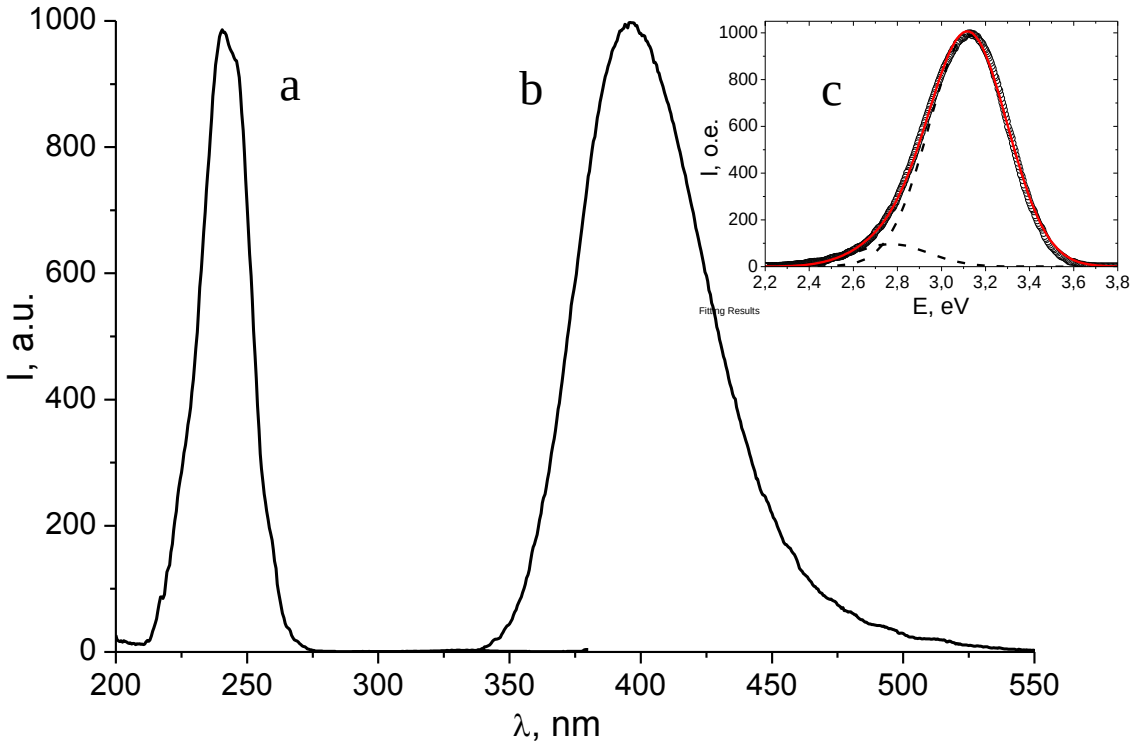

Figure 4. PL excitation spectrum (a) for400 nm and PL spectrum for excitation wavelength of 247 nm (b). PL spectrum component distribution result of the Fujikura LWP fiber powder sample (c).

3.3. Thermally stimulated luminescence

Properties investigation of light storage in silica optical fibers was conducted by measuring the TL curves in conjunction with the measurement of TL spectra. In the result of measurements a three-dimensional distribution of TL curves with spectral resolution in the range of 290–650 nm was constructed (figure 5). Under thermoluminescence emission two glow bands are observed with maxima at 400 and 550 nm, appearing at the temperature ranges of 320–600 and 300–400 K, respectively. It should be mentioned that the band with a maximum at 550 nm was not observed while measuring photoluminescence spectra.

To determinate accurately the spectral composition of TL the TL-distribution section of the wavelength distribution (figure 6) at different temperatures of stimulation were built. As the result of TL-spectra approximation, the following parameters of emission bands were determined. At stimulation temperature of 440 K one luminescence band of Gaussian shape with a maximum 3.12 eV (398 nm) and half-width of 0.54 eV were found. At stimulation temperature of 330 K two luminescence bands with maxima at 2.26 (549 nm) and 3.09 eV (401 nm) and half-widths of 0.25 and 0.55 eV, respectively were detected.

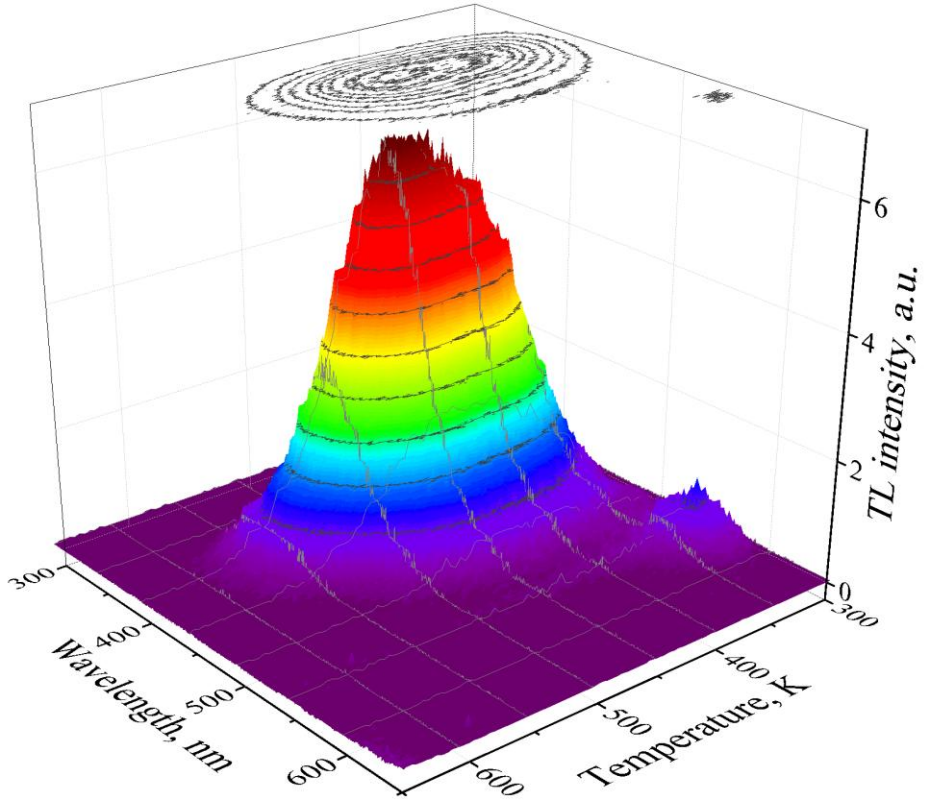

Figure 5. Three-dimensional TL distribution with spectral resolution of the Fujikura LWP optical fiber powder sample.

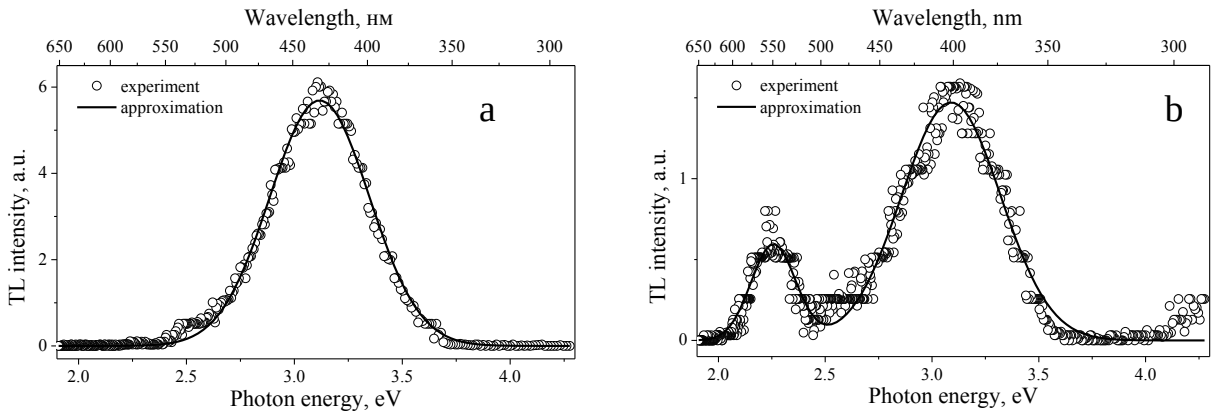

Figure 6. Thermally stimulated luminescence spectra approximation results 440 (a) and 330 K (b)

Green luminescence band with the maximum at 550 nm (2.2–2.3 eV) was previously described in [10, 13, 14]. According to [14] said band is found in newly-implanted by the germanium ions samples of the amorphous silica. After annealing, the luminescence intensity of this band is significantly reduced and practically does not appear in the luminescence spectra. In our experiments the band within the area at 550 nm appears after irradiation of the samples by X-rays. From the above it can be concluded that green luminescence band at 550 nm is to be associated with additive defects in the matrix without germanium ions. This conclusion is also confirmed in [13], where the luminescence band at 550 nm appears under mechanical indentation and laser irradiation on a sample of non-doped amorphous silica. Studies of the nature of the green band are currently underway.

TL curves obtained in our experiments have a complex profile and consist of more than two components. In contrast to the results obtained in [15], attempts of approximation TL curve by the general order theoretical curves did not lead to adequate results, which we believe is due to the presence of fading at low temperatures areas of curves. Restoring the true shape of the TL curves and the parameters determination of the trapping centers requires further experimental studies.

4. Conclusion

The parameters of cathodo-, photo-and thermoluminescence of samples of Fujikura LWP and Corning SMF-28e+ germanium doped silicate glass fibers are described taking into account the profile of germanium dopant distribution in the core and cladding of glass fiber. It is found that the maximum luminescence intensity of observed luminescence [= Si:] and [= Ge:] centers in optical fibers is shown at the area near the fiber core in the cladding. In the core the intensity of luminescence is lower than at cladding area. The experiments shows that the Ge-doped optical fiber has the intensive thermoluminescence and as can be seen from the results of measurements of the three-dimensional spectral distribution of TL in the range 290–650 nm there are two emission bands at 400 (3.1) and 550 nm (2.2–2.3 eV) involved in the energy storage processes. These bands can be attributed at two-fold coordinated [= Ge:] and [= Si:] luminescence centers in optical quartz glass fibers, respectively. It was found that the band at 550 nm ([= Si:] centers) is shown only after the external ionizing radiation damage in the optical fiber. Fiberglass of Fujikura and Corning are potentially suitable for using there as a TL radiation fiber sensors. In this paper we has been described the new investigation method of the distribution dopant germanium profile on the core-cladding border-area inside the center of the glass fiber which potentially suitable for final inspection and adjustment process in the manufacture of optical fiber.

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