

# Luminescence of the optical fiber preforms

S. GĘBALA

Institute of Physics, Technical University of Wrocław, Wybrzeże Wyspiańskiego 27,  
50-370 Wrocław, Poland.

Luminescence spectra of the optical fiber preform core and cladding have been presented. A luminescence spectrum in a preform is connected first of all with the presence of  $\text{Ge}^{2+}$ . Luminescence on the preform cladding has been measured. The model of energetic bands for  $\text{Ge}^{2+}$  complexes, where the luminescence excitation bands (250, 270 and 330 nm) correspond to transitions  $^1S_0 \rightarrow ^1P_1$ ,  $^3P_2$ ,  $^3P_1$ , has been suggested. On the other hand, luminescence bands with the maxima of 290, 396 and 430 nm correspond with the transitions  $^3P_2$ ,  $^3P_1$ ,  $^3P_0 \rightarrow ^1S_0$ . The UV influence in  $\text{Ge}^{2+}$  absorption band on the luminescence intensity change has been shown. The examples of  $\text{Ge}^{2+}$  luminescence intensity changes have been presented as a function of the radius for different lengths of the exciting wave and for different thicknesses of the plates.

## 1. Introduction

A preform is an initial form for the production of optical fibres by the MCVD method. For the preform core generation the  $\text{GeO}_2\text{-P}_2\text{O}_5\text{-SiO}_2$  composition is most frequently used. The radial distribution of the refractive index value as in a preform is determined by  $\text{GeO}_2$  concentration. In earlier papers the main emphasis was put on the refractive index distributions. Other optical properties of the preforms have become the subject of the recent interest. Among these properties the absorption and luminescence are worth mentioning.

In a preform core, apart from  $\text{GeO}_2$ , also its reduced form ( $\text{Ge}^{2+}$ ) may be observed. The absorption band with the maximum of about 250 nm and the blue colour luminescence with the maximum of about 396 nm [1-4] are connected with  $\text{Ge}^{2+}$  ions complexes. A very weak absorption band near 325 nm [5] is also ascribed to  $\text{Ge}^{2+}$  ions. In glasses, similarly as in crystals,  $\text{Ge}^{4+}$  ions may occur in two types of coordinations. The first type has tetrahedral coordination and is isostructural with  $\alpha$ -quartz. The second type has octahedral coordination and is isostructural with rutile. The first form occurs in a glassy  $\text{GeO}_2$ , while the second one appears in the presence of other oxides, for example, alkalic ones.  $\text{Ge}^{4+}$  ions in octahedral coordinations reach the maximum at definite concentrations of oxides [1-3, 6-8]. The presence of  $\text{Ge}^{4+}$  in octahedral coordination is connected with a considerable increase of the refractive index [1-4, 7, 8], as well as with the absorption bands 5.35 eV (232 nm), and 6.0 eV (207 nm) and the yellow colour luminescence [3, 4, 9]. In tetrahedral coordination, however,  $\text{Ge}^{4+}$  ions, analogically to  $\text{Si}^{4+}$ , have the absorption band in a similar coordination with a certain shift in a long-wave direction (2.3 eV), the luminescence

properties are not observed [1–3]. The complexity of Ge ion forms was investigated in germanium glasses, however, has not yet been studied in the preforms.

Spatial distributions of  $\text{Ge}^{2+}$  luminescence in the optical fiber preforms and the distributions of refractive index were investigated by PRESBY et al. [10–12]. These investigations were performed in the plates and the whole preforms [13, 14]. In the present paper the results concerning spectral properties of luminescence will be presented.

## 2. The measurement method

The optical fiber preforms used for measurements were produced years ago at the Maria Skłodowska-Curie University, in Lublin. The plates of different thicknesses cut perpendicularly to the core and core and cladding parts, separately, were used for measurements. Spectral measurements of luminescence were carried in standard systems. The setup for measurements consisted of the following elements: monochromator UM 2 or SPM 2, photomultiplier M12FC51, recorder G1B1 and power supply ZWN 2,5. The setup for the luminescence excitation spectra measurements consisted of the following elements: monochromator SPM2 with a quartz prism, illuminator with a deuterium lamp, photomultiplier M12FC51, recorder G1B1 and power supply ZWN 4,1. The luminescence excitation spectra were recorded with the range of 200 nm to 400 nm. The spectral ranges of luminescence were chosen by the optical filters. The optical system for measurements of luminescence spatial distributions was presented in the paper [14].

## 3. Results of measurements

The curves of optical densities are given in Figure 1 in the range of 200–400 nm. The curve 1 represents the optical density for a plate with a thickness of 1 mm measured in the external part of the preform core. In this curve the band with the maximum of about 240 nm is visualized. The curve 2 shows the optical density for  $d = 20$  mm. In this curve a weak and washed out absorption band is observed between 320 and 340 nm.

In the works [13, 14] the spectral measurements were made for the whole preform, i.e., for both the core and cladding. In this paper they are presented separately. Figure 2 shows the results obtained for the blue luminescence ( $\text{Ge}^{2+}$ ) measured in the preform core. The luminescence emission spectrum is presented in the curve 1. This luminescence excited by the wavelength of 250 nm, has two bands: the first one – intense with the maximum of about 396 nm, and the second one – weak with the maximum of about 290 nm. Luminescence excitation spectrum was measured by interferential filter ( $\lambda = 400$  nm) excited by deuterium lamp via monochromator SPM 2. The excitation spectrum is shown in curve 2. This curve has two bands: the first one – very intense with the maxi-

mum between 245 and 250 nm, and the second one - of low intensity with the maximum of about 330 nm. For luminescence comprising the long-wave and visible parts of spectrum, registered by using the edge filter ( $\lambda > 560$  nm), the excitation spectrum is presented in Fig. 3. In this spectrum there are two bands - one with the maximum of about 218 nm, and the other - with the maxim

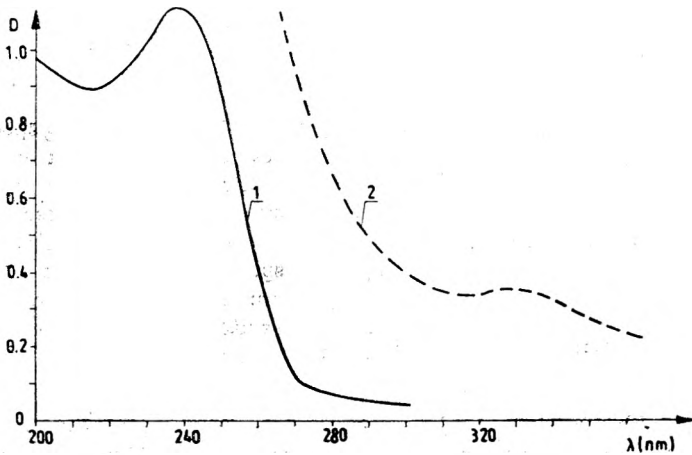


Fig. 1. The dependence of the optical density on the light wavelength for the preform core plate: 1-1 mm and 2-20 mm thick

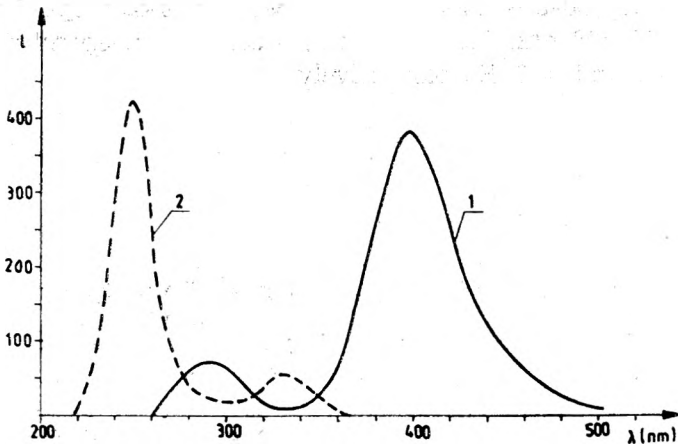


Fig. 2. The blue luminescence spectra of the preform core: 1 - the luminescence emission spectrum ( $\lambda_e = 250$  nm), 2 - the blue luminescence excitation spectrum

um of about 270 nm. The luminescence emission spectrum excited by a wavelength of 220 nm has been also presented. This spectrum has the bands developed within the whole visible spectrum. Luminescence excited in the band of 270 nm has mainly blue component (curve 2).

In the quartz glass and the elements made of it available to the author, luminescence properties identical with those presented in the literature, were stated within their whole volume. The luminescence effects in the preform cladding are localized on its surface. The curves of luminescence spectra for

the quartz glass (curve 1) and for the preform cladding (curve 2) are presented in Fig. 4. The excitation spectra have the maximum of about 242–245 nm, while the emission bands have the maximum of about 400 nm. The diagrams of the quartz technical glass are similar to those for the preform cladding.

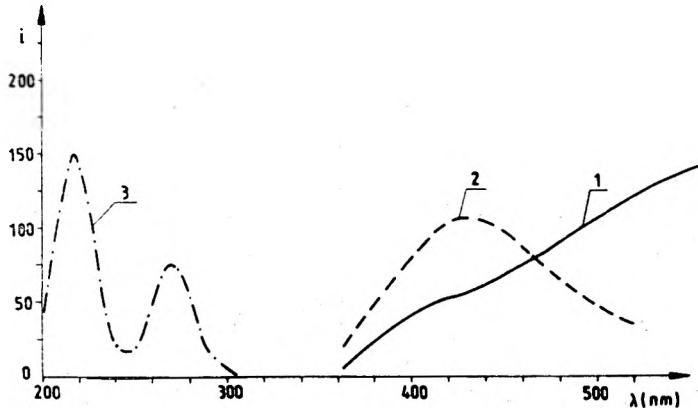


Fig. 3. The remaining spectra of the preform core luminescence: 1 – the emission spectrum, excited at 220 nm, 2 – the emission spectrum, excited at 270, nm, 3 – the luminescence excitation spectrum above 560 nm

The curves of luminescence excitation spectrum measured by the blue glass filter (BG 12) before (curve 1) and after (curve 2) UV-irradiation (Hg-lamp exposure for 2 h) are presented in Fig. 5.

Figure 6 represents the temperature-dependent changes of excitation spectra measured in the range of 420–500 nm. The curves: 1, 2 and 3 correspond to the temperature of 293, 343 and 423 K, respectively.

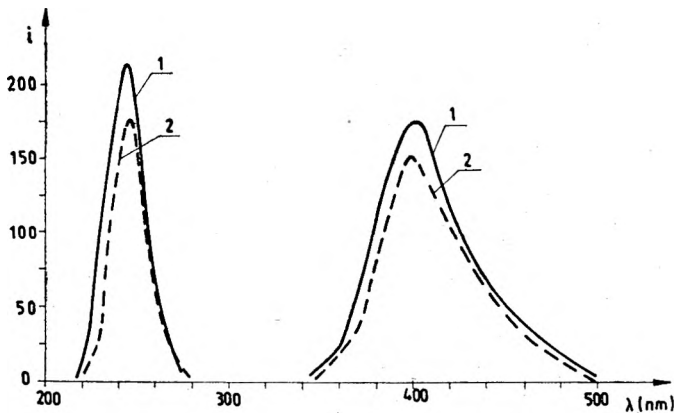


Fig. 4. The preform cladding luminescence spectra: 1 – the emission spectrum and the excitation spectrum for the quartz glass, 2 – the emission spectrum and the excitation spectrum for the preform cladding

Figure 7 shows the luminescence intensity distributions measured in a plate of a thickness of 2 mm as the radius function. These curves are averaged with respect to the preform layers. The aperture leading to photomultiplier with a blue glass filter was about 0.5 mm. Just in front of it the plate investigated was being shifted. Luminescence was excited by deuterium lamp via monochromator SPM2 with the quartz prism.

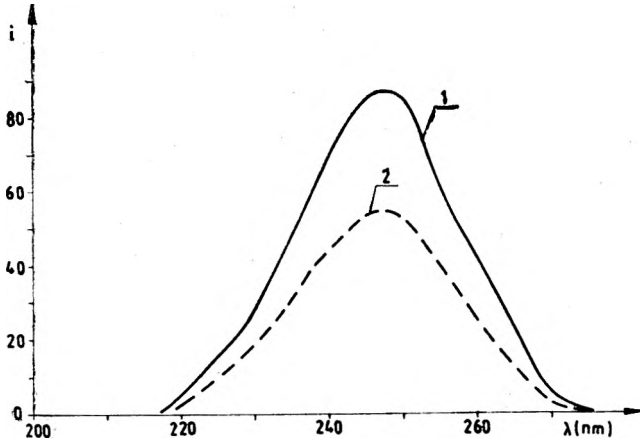


Fig. 5. The blue luminescence excitation spectrum: 1 - the spectrum before exposure, 2 - the spectrum after a 2 h. exposure to Hg-lamp

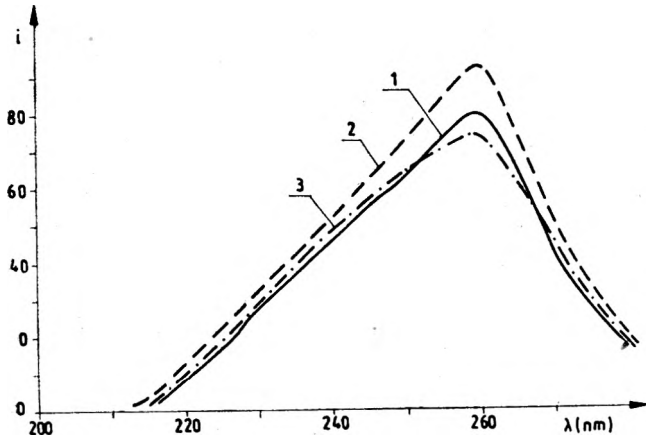


Fig. 6. The temperature-dependent changes of luminescence excitation spectra (420-500 nm) at: 1-293 K, 2-343 K, 3-423 K

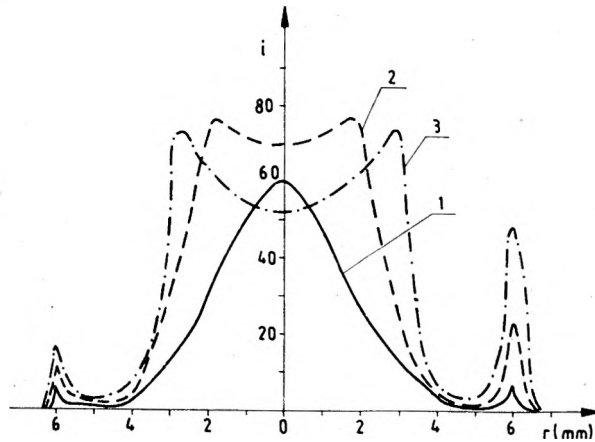


Fig. 7. Luminescence intensity as a radius function of the plate 2 mm thickness: 1 -  $\lambda_e = 265$  nm, 2 -  $\lambda_e = 250$  nm, 3 -  $\lambda_e = 230$  nm

Analogical curves for the excitation by a wavelength of 252 nm and for 3 thicknesses of the plates are shown in Fig. 8 (curve 1 for  $d = 1$  mm, curve 2 for  $d = 2$  mm, while curve 3 - for  $d = 10$  mm). The shape of the curves depends on luminescence excitation wavelength and on the plate thickness. It is possible to find the wavelength for a plate with a given thickness below

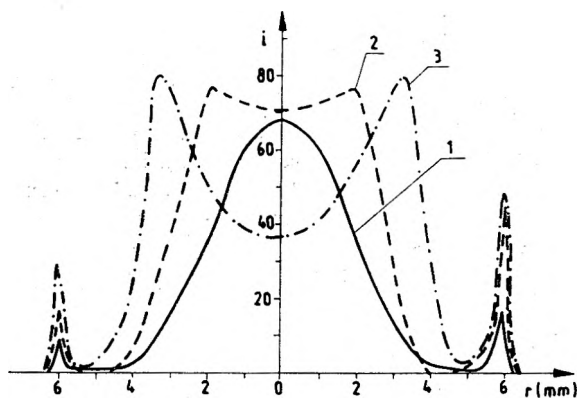


Fig. 8. Luminescence intensity as a radius function of the plate at excitation  $\lambda_e = 252$  nm: 1 -  $d = 1$  mm, 2 -  $d = 2$  mm, 3 -  $d = 10$  mm

which the distribution curve will have the complex character, i.e., luminescence effects will be affected by absorption. On the preform cladding edge the sharp maxima correspond to the surface irradiation. Inside the plate there occurs the increased luminescence coming from defects. To reproduce the presence of "dip", a suitable narrow filter is needed.

#### 4. Conclusions

Spectral investigations on the optical fiber preforms luminescence are being carried out by the author. The experimental materials in this paper make a part of results concerning preforms luminescence. A complete identification of the excitation bands and luminescence emission is at this stage of work very difficult because of frequently occurring overlapping luminescence effects, and coming from  $\text{Ge}^{2+}$ ,  $\text{Ge}^{4+}$  in octahedric coordination as well as from the defects of the core and of the quartz cladding. Complete and explicit identification requires an additional selection of experimental material and of properly specified measuring programme.

$\text{Ge}^{2+}$  ions have an electron configuration  $d^{10}s^2$ , similar to those of  $\text{Tl}^+$ ,  $\text{Sn}^{2+}$ ,  $\text{Bi}^{3+}$  ions. The electron transition are of  $s^2 \rightarrow sp$  type. For  $\text{GeO}$  in a gaseous state the following transitions take place: singlet-singlet transition  $x^1\Sigma^+ \rightarrow A^1\Pi$  (265 nm) and two singlet-triplet transitions  $x^1\Sigma^+ \rightarrow a^3\Pi$  (313 nm), and  $x^1\Sigma^+ \rightarrow a'^3\Sigma^+$  (364 nm) [5].

In a crystalline cubic field ( $O_h$ ) in excited state the energetic levels are:  $^3P_0$ ,  $^3P_1$ ,  $^3P_2$ ,  $^1P_1$ , and the following transitions: singlet-singlet transition ( $^1S_0 \rightarrow ^1P_1$ ), and forbidden singlet-triplet transitions ( $^1S_0 \rightarrow ^3P_2$ ) and ( $^1S_0 \rightarrow ^3P_1$ ) occur.

The levels  ${}^3P_0$  and  ${}^3P_2$  are the trap levels. Luminescence occurs at transitions to the ground level, mainly from the level  ${}^3P_1$  and  ${}^3P_0$  [15]. In optical fiber preforms the luminescence and absorption excitation bands are ascribed by the authors to the respective transitions between  $\text{Ge}^{2+}$  levels. There is no doubt that the luminescence excitation band with the maximum of about 250 nm (4.96 eV) and the analogical absorption band correspond to a transition  ${}^1S_0 \rightarrow {}^1P_1$ , i.e., to the transition between singlet states. Since this transition is allowed it has a high intensity. The second excitation band of luminescence and absorption with the maximum of about 330 nm (3.76 eV) with the very low intensity is connected with a transition  ${}^1S_0 \rightarrow {}^3P_1$ . It is the transition from the singlet state to the triplet one and belongs to the forbidden transitions. Luminescence excitation band with the maximum of 270 nm (4.58 eV) should be also ascribed to transition  ${}^1S_0 \rightarrow {}^3P_2$ . The band is localized in a long-wave part of the intensive singlet band wing, which can be selected with the help of luminescence excitation spectra.

Luminescence emission band with the maximum of 396 nm (3.13 eV) is connected with a transition  ${}^3P_1 \rightarrow {}^1S_0$ . Beside this band there occurs a second luminescence emission band from the long-wave side about 430 nm (2.88 eV), which is ascribed to the transitions  ${}^3P_0 \rightarrow {}^1S_0$ . The level  ${}^3P_0$  is the trap level and an additional thermal excitation causes the increase in the band intensity. This explains the effects observed in Fig. 6. The luminescence emission band with the maximum of about 290 nm (4.27 eV) is ascribed to the transitions from the level  ${}^3P_2$  to the ground level  ${}^1S_0$ . This luminescence is excited in the same band as the emission band with the maximum of 396 nm.

Other negative phenomena are also connected with the presence of  $\text{Ge}^{2+}$  ions in the optical fiber preforms. The occurrence of  $\text{Ge}^{2+}$  ions (apart from  $\text{Ge}^{4+}$  ions) in the preforms indicates the possibilities of non-stoichiometric structure. Therefore, the increased light scattering should be expected.

The other negative property connected with the presence of  $\text{Ge}^{2+}$  ions is the easiness of exciting the preforms by UV-radiation and temperature. This possibility is shown in Fig. 5. This effect was known earlier [1, 4]. In consequence, in the preform there occur not only the changes of luminescence and absorption but also of the refractive index value in the whole spectrum range. Hence, the presence of  $\text{Ge}^{2+}$  in the optical fiber preforms is evidently their fault.

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