Optica Applicata, Vol. XVI, No. 4, 1986

Spatial distributions of the colour centres (POHC) in the optical fibre core*

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1. Introduction

It is well known that in phosphate glasses, including phosphate-silicate ones with PO_4^{2-} defects, there occur absorption bands in the visible range together with EPR spectra characteristic for them, and denoted as POHC [1]. In the optical visible spectrum two absorption bands appear with the maxima within 400–420 nm and 500–550 nm after γ irradiation. The position of the first band is strongly affected by the sort of the other component of the glass [1], [2]. The behaviour of these centres in the presence of rare earths ions was also examined. Under the action of the radiation these ions play the competitive role in relation to the phosphate centres, in "catching" the holes and electrons.

The author of this paper has examined the glasses which contain germanium dioxide in addition to phosphor and silicon oxides. These glasses are used for the production of the optical fibres. Their common feature is that the concentration of GeO_2 varies gradiently, while the P_2O_5-concentration is stable. This fact allows determining the intensity disribution of colour centres in the glass of POHC type when irradiating the glass with γ radiation [3].

The purpose of this work is to determine the main conditions under which this defect occurs.

2. Method and results of examinations

An experimental preform produced by the Maria Skłodowska-Curie University in Lublin was used in the examinations. The preforms prepared there, although unsatisfactory for the production of optical fibres, are very good for the examinations being the subject matter of this work. The content of P_2O_5 amounts there to about 1–2%, while the concentration of GeO_2 changes from zero outside the core to a maximum inside the core, which amounts to about 10%. The germanium occurs there mainly as a 4-valency ion (Ge^{4+}), and in small quantities as Ge^{2+}.

The samples in the form of plates of d = 1–2 mm thickness were indispensable

* This work was sponsored by the Research Project CPBP 01.06.

to carry the examinations out, and were obtained by cross-cutting of the preform. These plates were irradiated with γ radiation in the doses of 2.0×10^5 rads.

In the first place, the measurement of optical absorption spectrum was performed by means of a Specord UV VIS spectrophotometer. The results have been shown in Fig. 1. Two wide bands with maxima of about 400–420 nm and 500–550 nm can be seen in the optical density (D) graph.

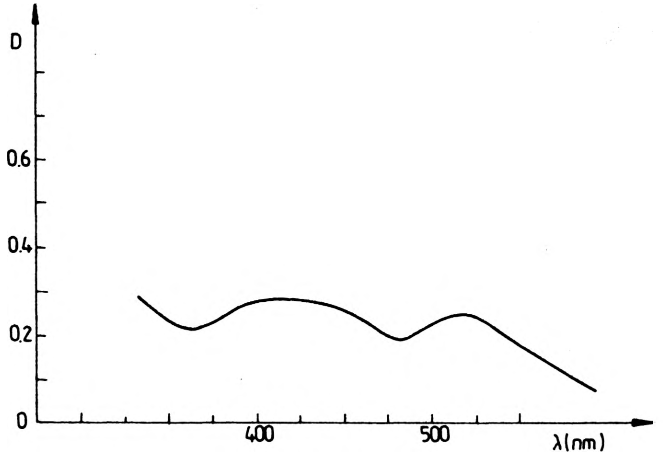

Fig. 1. Dependence of the optical density (D) of the preform irradiated by γ radiation on the light wavelength ($d = 1$ mm)

The EPR spectrum of the paramagnetic defect of POHC type has been presented in Fig. 2. The core was irradiated with γ radiation of 2.0×10^5 rad dose at room temperature. The measurements in the range of 300–400 mT were also taken at room temperatures. The core sample for measurements was used in the powder shape.

Next, the distribution of optical density in the irradiated preform plate was examined, which is shown in Fig. 3. In visual observations and colour

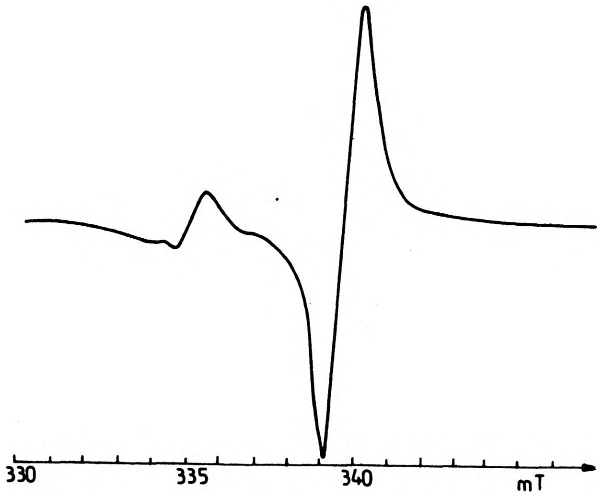

Fig. 2. EPR spectrum of POHC paramagnetic defect in the preform core

photographies the core seems to be of nearly red colour. An automatic scanning device, built for measurements of optical fibre preforms, was used for examinations of distributions. The measurement results were recorded on a plotter. The measurements were performed for $\lambda = 400$ nm (curve 1) and for $\lambda = 500$ nm (curve 2). The impossibility to apply considerable magnifications for nonuniform plates was an obstacle here. Therefore, smoothing procedure was involved in the

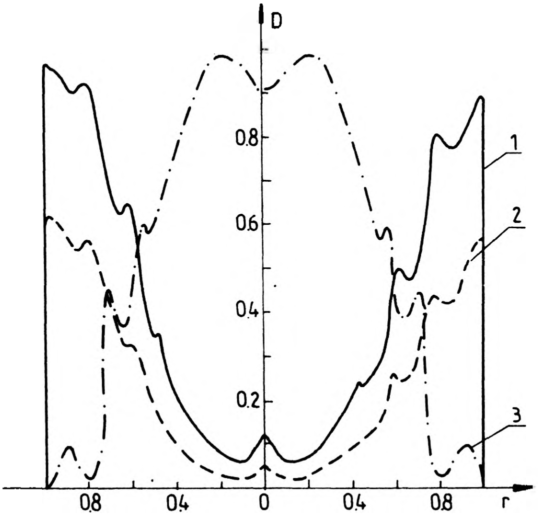

Fig. 3. Optical density distribution in the irradiated plate as a function of its radii for: $\lambda = 400$ nm (1), $\lambda = 500$ nm (2), and relative distribution of germanium (3)

measurements due to partial integrating of the light signals from the neighbouring layers of the core by the detector. The nonuniformity of the preform was advantageous for these types of examinations, the more because the measurements of relative germanium distribution were also made. These measurements were based on countings of the X-ray spectrum characteristic for germanium (Ge–L). They were performed with the Stereoscan 180 Scanning Cambridge Instruments microscope, equipped with a Link systems device for X-ray microanalysis. The result of the relative distribution of germanium concentration is shown in Fig. 3 (curve 3). It turns out, that the observed deviations are similar with the only difference that when on the germanium concentration curve a maximum occurs, the concentration of colour centers (POHC) diminishes.

In Figure 4 a comparison of the normalized curve of transmittance of the plate ($d = 1$ mm) after having been irradiated by the γ radiation (curve 1) with a similar normalized distribution of the luminescence due to Ge^{2+} was made as the function of the radius (r). The luminescence was excited by the 265 nm Hg line while luminescence emission was recorded via an interference filter 400 nm. Non-irradiated sample was used to the luminescence measurements. The measurements were performed in the scanning device. There exists such a general relation, that at the places of higher luminescence, due to Ge^{2+}, there occurs a lower transmittance in the POHC band (500 nm). This should be understood that at the places of higher quantity of Ge^{2+} a decrease of paramagnetic POHC defects occurs.

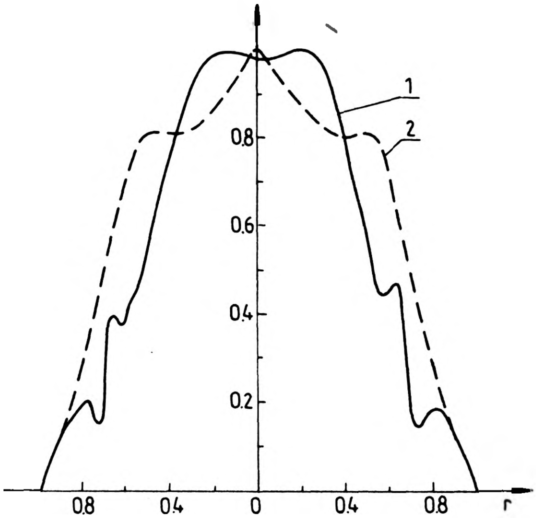

Fig. 4. Normalized distribution of transmissivity in the plate of the core vs radius (r) for: 1 – λ = 500 nm, 2 – normalized distribution of the blue luminescence (Ge^{2+})

In Figure 5 the behaviour of the absorption bands of the hole defect (POHC) has been shown after annealing of the samples. The samples were heated up to the given temperature at which they were kept during 10 min and then cooled. The curve 1 concerns absorption band with the maximum of about 400 nm, and the curve 2 shows the bands over 500 nm. A two steps discoloration is observed: below 500 K a slow capturing of electrons by the hole defects occurs, while above 500 K – a quick decay of defects is observed. Such changes are most probably due to the presence of other defects like phosphor of lower valency [1] and germanium, as well as to the sequence of electron trapping holding in such cases.

In Figure 6 the time-dependence of the changes of optical density while irradiating the preform sample with XBO 101 xenon lamp has been shown. The

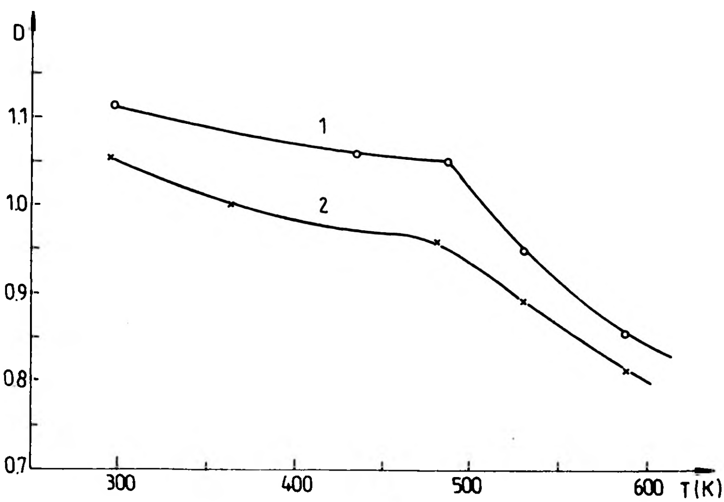

Fig. 5. Changes of optical density vs the annealing temperature for: 1 – λ = 400 nm, 2 – λ = 500 nm

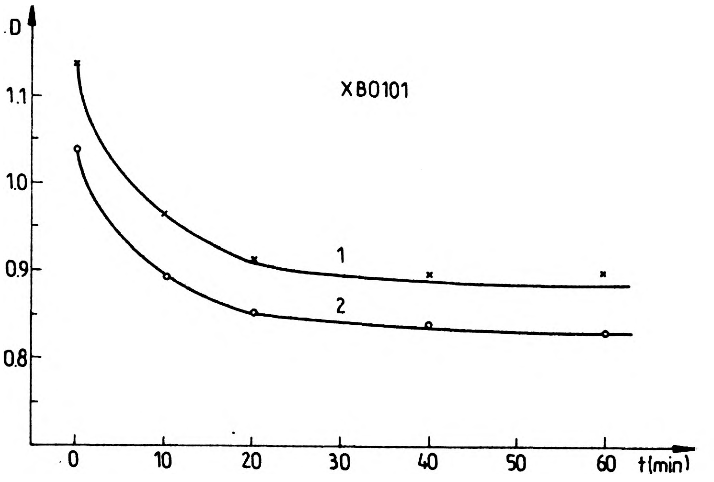

Fig. 6. Change of optical density in irradiated preform vs the exposure time for XBO xenon lamp

sample was earlier irradiated by γ radiation (2×10^5 rad). The curve 1 refers to the 400 nm band while the curve 2 to the 500 nm one. The centres suffer from dislocation too, when irradiated by other light sources.

3. Conclusions

Summing up, it may be univocally concluded that there exists an essential connection between the concentration of GeO_2 and that of POHC defects. When a concentration of phosphor is steady this relation is of inverse proportionality type, which confirms that GeO_2 (especially Ge^{2+}) is an exceptionally good competitor in relation to phosphor in "catching" the holes and electrons. If a preform has a correct distribution of germanium, the normalized distributions of transmissivity in the preform with POHC defects is obtained and the curve representing these distributions is similar to that of the refractive index.

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Received July 18, 1986