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Article

Side-Detecting Optical Fiber Doped with Tb^{3+} for Ultraviolet Sensor Application

Jacek Zmojda, Marcin Kochanowicz, Piotr Miluski and Dominik Dorosz *

Department of Power Engineering, Photonics and Lighting Technology, Faculty of Electrical Engineering, Bialystok University of Technology, 45 Wiejska Street, 15-351 Bialystok, Poland;
E-Mails: j.zmojda@pb.edu.pl (J.Z.); m.kochanowicz@pb.edu.pl (M.K.); p.miluski@pb.edu.pl (P.M.)

***** Author to whom correspondence should be addressed; E-Mail: d.dorosz@pb.edu.pl;
Tel.: +48-85-746-93-62; Fax: +48-85-746-94-00.

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Abstract: In the article a novel construction of a side-detecting luminescent optical fiber for an UV sensor application has been presented. In the fiber, structure phosphate glass doped with 0.5 mol% Tb^{3+} ions was used as a UV sensitive core/ribbon. The luminescence spectrum of glass and the optical fiber was measured under UV excitation using a deuterium lamp. It was found that large energy gap between upper (metastable) and lower (ground) levels of terbium ions incorporated in phosphate matrix leads to the effective emission at wavelengths of 489, 543, 586 and 621 nm, which correspond to $^5D_4 \rightarrow {}^7F_J$, (J = 3, 4, 5, 6) transitions respectively. Phosphate glass doped with optimal (the strongest VIS emission) concentration of Tb^{3+} (0.5 mol%) was used as the active core/ribbon in the construction of UV side-detecting optical fiber.

Keywords: luminescence; Tb^{3+} ions; UV sensor; optical fiber; side-detection

1. Introduction

Specific spectroscopic properties of lanthanides ions allow their applications as active materials in a construction of radiation sensors. Additionally, well known advantages of rare earth (RE) ions are their ease of introducing into the glassy matrix and forming into optical fibers or bulk elements. Fiber-optic sensors have many advantages over conventional optical sensors [1]. The former are small in size, light, electrically safe and resistant to electromagnetic interference. Resistance to electromagnetic interference is especially important during measurements near the UV lamp due to intense electromagnetic fields encountered in its vicinity [2]. Semiconductor UV detectors are expensive and require advanced supply circuits. In luminescent fiber optic sensors the phenomenon of the energy conversion by excited RE ions enables to apply silicon detectors in sensing applications. Nowadays, some UV sensing constructions based on the optical fiber coated with polymer layers doped with phosphors are well described [3–5]. However, the efficiency of detection is significantly reduced due to strong density of energy from UV radiation regime, which leads to the degradation of polymers bonds. Another approach to the construction of the UV sensor is the use of side-emitting optical fibers, which can absorb radiation by side surface and then propagates it inside the fiber. Moreover, fiber-optic sensors offer the possibility of distributed and localized measurements along the whole sensor length, providing in this way radiation measurements over an interval and in a point [5].

In order to provide the possibility of a good transmission in UV range the selection of a suitable host system is a key factor in fabricating the optical fiber. Phosphate glasses are good to be used to fabricate optical fibers due to high transmission in the range of UV-VIS-NIR, low refractive index ($n = 1.5$), dispersion, thermal stability, mechanical resistance and good solubility of high concentration of RE ions [6,7]. High solubility of rare earth ions in phosphate glasses enables the construction of short fiber amplifiers and fiber lasers [8–10]. On the other hand, the absorption edge in the range of short wavelengths at 200 nm enables to use them as active materials for the detection of UV radiation. When considering the fabrication of such sensor based on phosphate glasses the maximum phonon energy of the matrix, which is approx. 1200 cm^{-1}, leads to the increase of the probability of multiphonon transitions between closely located energy levels of the RE elements. The solution is to choose lanthanide ions with absorption bands in the range of UV radiation and a wide gap between the metastable and ground levels, enabling to achieve the efficient spontaneous emission with partial elimination of the non-radiative transition. Among the lanthanides, which meet criteria above, one of the most appropriate is Tb^{3+} ion. Due to its optical properties, terbium is used in many optoelectronic devices such as mass storage with high capacity, 3D displays, photovoltaic applications and sources of radiation in the visible range [11–14]. The expanded structure of energy levels corresponds to the four-level quantum scheme, hence Tb^{3+} ions are characterized by effective emission at the wavelength of approx. 500 nm corresponding to the $^5D_4 \rightarrow {}^7F_5$ transition. Moreover, Tb^{3+} ions are characterized by a long radiative lifetime of the $^5D_4 \rightarrow {}^7F_5$ transition (approx. 3 ms), hence this is important in case of memory effect in sensing systems.

The Main aims of this study was to examine optical properties of fabricated phosphate glass and develop side-detecting optical fiber doped with Tb^{3+} ions intended to be used as the UV radiation sensor. The use of fabricated optical fiber in the detection of arc in medium and low-voltage control boxes, where the time of response is very important to avoid a damage of electrical components, was mostly considered by authors. In short-term processes, such as arc discharges, the response time of detection plays the significant role, which must be considered during the development of security systems. Luminescence fiber sensors offer very short response time (~0.1 ms) depending on energy of UV radiation.

2. Experimental Section

Glasses with molar compositions of (65−x)P_2O_5−8Al_2O_3−10BaO−17(Na_2O−MgO−ZnO)−$x$$Tb_2O_3$ (where x: 0.2, 0.5, 1, 2 mol%) were melted at 1350 °C for 60 min. in a platinum crucible using an electrically heated furnace. All phosphate glasses doped with Tb^{3+} ions were prepared from special high purity agents (99.99%). For dimensions repeatability the melted mass of glass was poured into preheated brass form and annealed at 450 °C for 12 h to remove thermal strains. Transparent and homogenous glasses without crystallization was fabricated. Finally, glass samples were polished in order to carry out the optical measurements. Series of samples with dimensions of 10 × 10 × 3 mm^3 were prepared in order to determine optical properties. The density of fabricated glasses was measured using the hydrostatic weighing method. Refractive indices of active core and cladding at the wavelength of 632.8 nm was determined by a m-line apparatus based on prism coupling technique (Metricon 2010). Characteristic temperatures were determined on the basis of DSC measurements performed at the heating rate of 10 °C/min. using the SETARAM Labsys thermal analyzer. The thermal expansion coefficient was measured using standard dilatometer with a heating rate of 10 K/min. The absorption spectrum of samples was performed in the range of 200–500 nm using the Stellarnet Black-Comet spectrometer. The UV excitation source was the deuterium lamp with maximum power of 30 mW. The visible luminescence spectrum in the wavelength range from 400 to 800 nm was also measured with the Stellarnet spectrometer.

The modified rod-in-tube method was used to fabricate side-detecting optical fiber doped with Tb^{3+}. In the luminescent measurement setup the fabricated fiber was placed in rotating mount 5 cm below the output window of the deuterium lamp located perpendicularly to the side surface of the fiber. Next, in order to maximize the luminescence signal, resulting from absorption of UV radiation, the fiber was rotated around its own axis. The asymmetry of construction reduces the angular range of measurements in a half-space. However, good flexibility of the fabricated fiber increases the possibility of UV detection in difficult conditions. According to measurements, the ability of side-detection of UV radiation was observed.

3. Results and Discussion

Physico-chemical and thermal parameters of fabricated phosphate glasses doped with Tb^{3+} ions are presented in Table 1. Thermal stability of host glass is the essential parameter in optical fiber technology. Values of T_g and T_x are 500 °C and 868 °C respectively. The ΔT, defined as a temperature gap between T_g and T_x, amounts to 368 °C. Thermal stability of fabricated phosphate glasses is relatively high in comparison to tellurite and HMO glasses [15,16].

The ΔT parameter is commonly used as a rough criterion to measure thermal stability of glass. Moreover, the large value of ΔT indicates that glassy matrix is thermally stable and can be used as an active material in optical fiber fabrication.

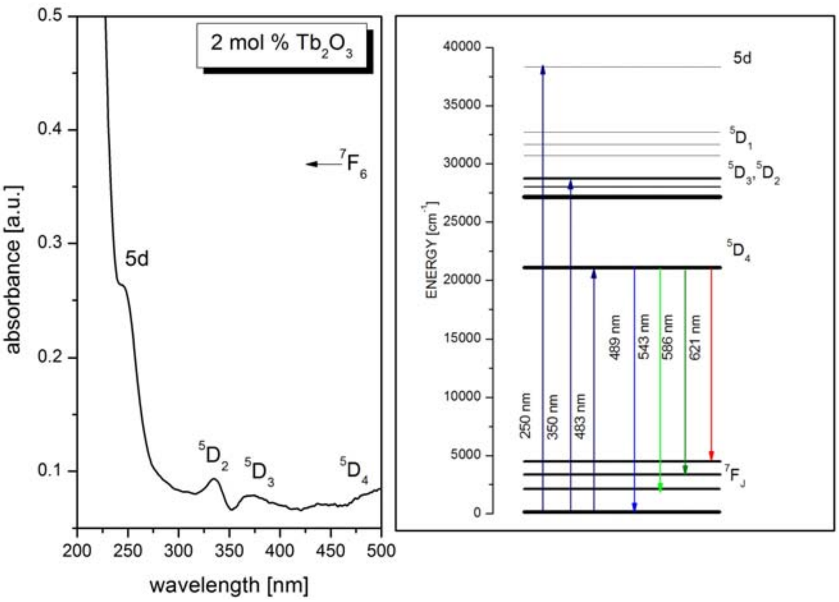
Table 1. Material and thermal parameters of fabricated glasses.

Parameter	Value
Refractive index n_{core} (@ 632.8 nm)	1.529
Refractive index $n_{cladding}$ (@ 632.8 nm)	1.623
Mass density ρ [g/cm^3]	2.98
Thermal expansion coefficient α_{100}^{400} [10^{-7} 1/K]	55.9
Dilatometric softening point T_s [°C]	482
Transformation temperature T_g [°C] (DSC)	500
Crystallisation temperature T_x [°C] (DSC)	868
Maximum of phonon energy $h\omega_{maax}$ [cm^{-1}]	1280

3.1. The Absorption Spectrum and the Energy Diagram

The absorption spectrum of phosphate glass doped with terbium (Tb^{3+}) with the wavelength range of 200–500 nm is shown in Figure 1. The highest broadband at the wavelength of 248 nm is associated with the $4f^8 \rightarrow 4f^75d$ transition. Moreover, weak narrow bands located at 338, 375 and 483 nm are respectively assigned to the transitions from the ground state to $^5D_2$, $^5D_3$ and $^5D_4$ energy levels.

Figure 1. Absorption spectrum of phosphate glass doped with 2 mol% Tb_2O_3 and the simplified energy levels diagram with observed transitions.

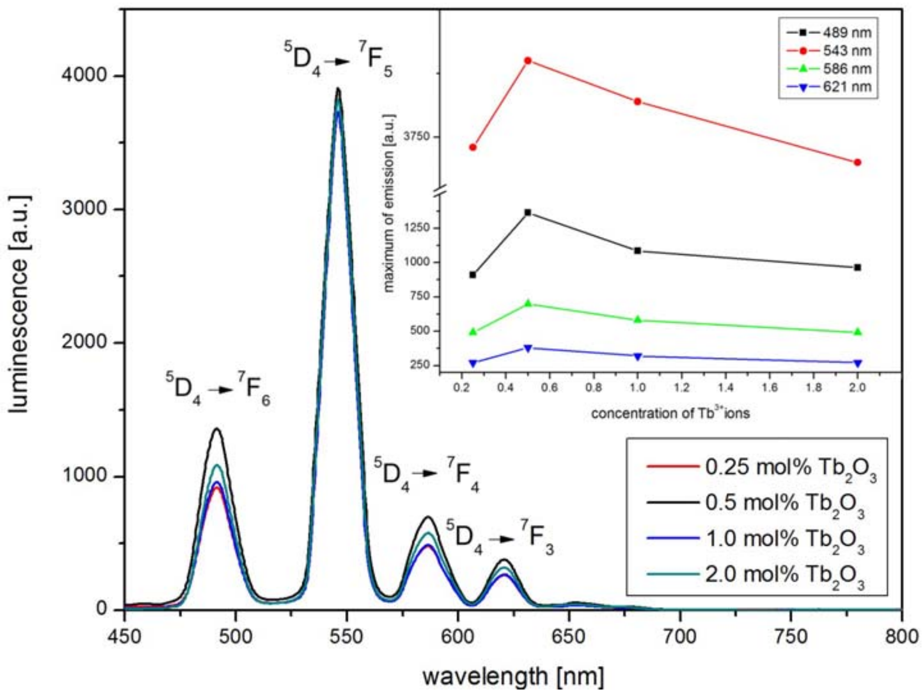


Appropriate selection of glass-forming components in fabricated glasses allows to obtain the absorption edge in the range of middle-ultraviolet. The absorption band around 248 nm of Tb^{3+} ions indicates that fabricated glass can be efficiently excited by UV radiation.

3.2. The Analysis of the Luminescence Spectrum

Using deuterium lamp, luminescence in the visible range with characteristic green colour emission was obtained as a result of optical pumping of glass doped with Tb^{3+} (Figure 2). In the range of 450–700 nm the maximum of luminescence intensity was obtained with the wavelength within the band of 543 nm corresponding to the $^5D_4 \rightarrow {}^7F_5$ transition. The other three $^5D_4 \rightarrow {}^7F_J$ transitions, where J = 3, 4, 6 correspond to the emission at 489, 586 and 621 nm respectively. The influence of Tb^{3+} concentration on the luminescence spectrum of fabricated glasses is presented in the inset in Figure 2. The maximum of emission was obtained in glass doped with 0.5 mol% Tb_2O_3.

Figure 2. The emission spectra of phosphate glasses doped with (0.25, 0.5, 1, 2) mol% Tb_2O_3. (the inset) The maximum intensity of luminescence as a function of terbium content.

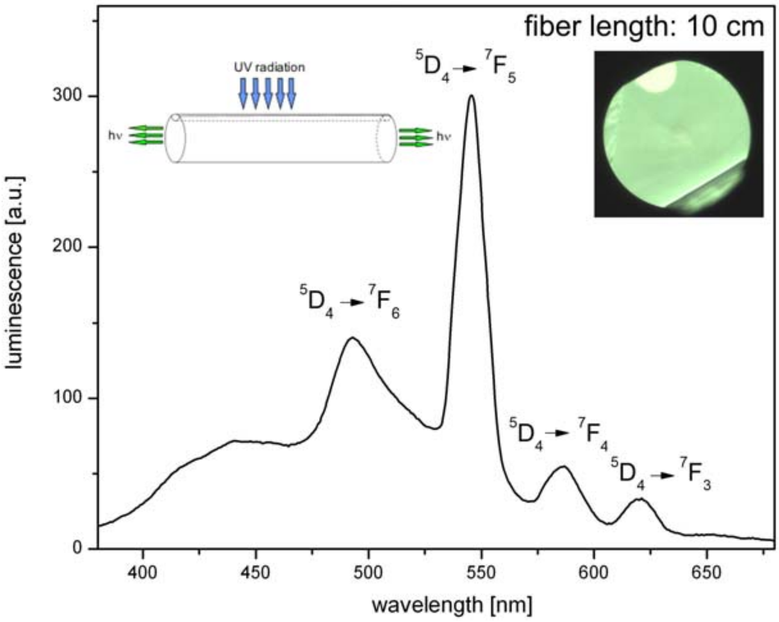


3.3. The Side-Detecting Optical Fiber Doped with Tb^{3+}

The fabricated optical fiber is based on specially designed sensing construction with active core/ribbon located on the side of the fiber. A modified structure of the side-emitting fiber allows coupling of optical signal from the core/ribbon to the undoped cladding area of the optical fiber. The cladding area was made of glass with a higher refractive index (n = 1.623), hence the signal of luminescence is transmitted from the core/ribbon to the undoped clad and propagates inside due to total inner reflection. The fiber diameter is 350 µm and the radius of the active, semi-circular core/ribbon, which is located in the fiber side surface, is 50 µm. In addition, the absorption edge of fabricated phosphate glass at 200 nm enables efficient absorption of UV radiation by the Tb^{3+} ions.

Figure 3 shows the photograph of the fabricated fiber and the luminescence spectrum obtained as an effect of UV excitation. As a result of the absorption of UV radiation from the side surface of the optical fiber it was possible to measure the luminescence of Tb^{3+} ions at the end of the fiber (the scheme inside the set of Figure 3). The asymmetry of geometry of fabricated fiber enables effective UV absorption in a half-space. The maximum intensity of green emission was recorded in the opposite position of the active core/ribbon and the output window of the deuterium lamp. The luminescence signal was collected at the end of the 10 cm long optical fiber.

Figure 3. The emission spectrum of phosphate side-detecting optical fiber doped with 0.5 mol% Tb_2O_3. (the inset) Photograph of cross-section of fabricated fiber and scheme of measurement set.



4. Conclusions

In this work new sensing optical fiber construction with the core/ribbon doped with Tb^{3+} was presented. The active layer was made of developed thermally stable phosphate glass with the $65P_2O_5$–$8Al_2O_3$–$10BaO$–$17(Na_2O$–MgO–$ZnO)$ molar composition, characterised with different molar concentration of Tb_2O_3. The selection of glass composition enabled the shift of the absorption edge to the UV-C range. Strong absorption band at the wavelength of 248 nm (Tb^{3+}) enables detection of UV radiation. Strong emission band in the characteristic green colour emission resulted from the $^5D_4 \rightarrow {}^7F_5$ transition of terbium ions was achieved in fabricated glass excited by UV radiation. Glass characterized by the highest intensity of luminescence (0.5% mol Tb_2O_3) was used as the core/ribbon in the fabricated side-detecting optical fiber. Luminescence measurement of the fabricated optical fiber confirms its ability to selective detection of the radiation in the UV range and can be used in the construction of luminescence UV sensors.

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Author Contributions

J.Z. and M.K developed the manufacturing technology of side-detecting optical fiber doped with Tb^{3+} ions and prepared the experiments. P.M. collected the data and carried out the analysis of absorbance and luminescence spectra of fabricated glass and fiber. J.Z., M.K., P.M. and D.D. prepared the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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