Luminescent Monitoring of Eu^{3+}-Doped 13-93 Bioactive Glass Fiber Degradation

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Abstract—Bioactive 13-93 glass fibers were doped with 0.2 and 2% mol of Eu^{3+} ions and drawn using a traditional method. The study examined the degradation rate using the proposed optical method and to analyze the influence of the dopant on the degradation process. The fibers were immersed in SBF for 48 hours, with simultaneous and continuous measurement of the change in the luminescence spectrum ($\lambda_{exc.}$= 394 nm) at 611 nm. The morphology of the fibers was also investigated. The optical time constant analysis demonstrated that bioactive glass fibers doped with 2% moles of Eu^{3+} decomposed more slowly than 13-93_02Eu.

Larry Hench pioneered the development of the first bioactive glass named Bioglass® 45S5 in 1969 [1], which found widespread application in medicine due to its great bioactive properties. The increasing demand for biomaterials that exhibit high levels of biocompatibility and biodegradability has prompted researchers to focus on modifying fundamental bioactive glasses to facilitate the production of fibers. Bioactive glass fibers are a rapidly growing area of research aimed at developing new materials to support tissue regeneration and biomedical engineering applications. However, the process of drawing fibers using conventional methods presents significant challenges. This resulted in developing new or modified compositions with enhanced properties, facilitating the fabrication of bioactive glass fibers, such as the widely studied 13-93 bioactive glass [2]. These fibers, characterized by their superior mechanical and biological properties, can be used as reinforcing elements in composite materials [3–4].

Nowadays, materials doped with lanthanide ions are widely used in various scientific fields, from photonics to biomedical applications. Their luminescent properties have become particularly valuable in sensor technologies, offering multiple potential applications. An interesting rare earth element in terms of biological properties is europium. In preliminary studies, glasses and nanofibers doped with Eu^{3+} showed no toxic properties, and their bioactivity was not inhibited [5]. Moreover, the present work [6–7] has been demonstrated that Eu^{3+} promotes the mechanisms of angiogenesis, i.e., the formation of new blood vessels, which is a key process in wound healing.

There is currently no universal technique to evaluate the degradation of bioactive glass fibers. Existing approaches primarily involve measuring weight loss, monitoring pH variations, or analyzing the solution ion concentrations of particular elements. However, optical methods offer a promising alternative for fiber assessing the extent of fiber degradation, providing potential advantages in terms of precision and efficiency.

In the present study, an optical [8] method was used to monitor the degradation of bioactive fibers composed of 13-93 glass doped with varying concentrations of europium ions. The luminescence properties of the fibers were also analyzed, and microstructure studies were conducted using SEM+EDS to confirm the changes occurring on the surface of the fibers under investigation.

The glass samples were synthesized using the conventional melt-quenching technique. Europium oxide was introduced as a dopant to replace part of the silicon dioxide. The initial molar composition is detailed in Table 1. Homogenized reagent mixtures were transferred into a platinum crucible and subsequently melted at 1400°C for 60 minutes in an air atmosphere using an electric furnace. The molten material was cast into stainless steel molds, forming cylindrical glass rods with a diameter of 10 mm. To reduce thermal stress, the samples were annealed at 520°C for 12 hours in an electric furnace.

Table 1. The initial molar composition of different glasses.

Glass name	SiO_2	P_2O_5	MgO	CaO	K_2O	Na_2O	Eu_2O_3
	[%mol]						
13-93	54.6	1.7	7.7	22.1	7.9	6.0	-
13-93_02Eu	54.4	1.7	7.7	22.1	7.9	6.0	0.2
13-93_2Eu	52.6	1.7	7.7	22.1	7.9	6.0	2.0

The bioactive glass preform was introduced into a tube furnace (SG Control, Newton, UK) operating within a precisely controlled temperature range. Glass fiber production was carried out using an SG Control drawing tower with a height of 7.5 m. The glass preform feed rate was controlled between 0.2 and 1.6 mm/min. The glass rod was melted during processing and flowed through the furnace outlet. A rotating drum was used to draw the molten glass stream into fibers, with the final fiber

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diameter determined by the combined control of drum speed and preform feed rate. Depending on the glass composition, the drawing temperature was maintained in the 1000 to 1100°C range.

Fifty fibers of each type, 13-93_02Eu and 13-93_2Eu, with an average diameter of 130 μm ± 10 μm, were immersed in simulated body fluid (SBF) prepared by Kokubo's method [9] in a plastic container with their ends exposed to the outside. The effective interaction length of the fibers was approximately 45 mm. The europium-doped glass fibers were excited by a 100 mW continuous wave (CW) laser diode operating at a wavelength of 394 nm. The luminescence signal emitted by the fibers was recorded at their output ends using a BROADCOM Qmini 2 Wide VIS spectrometer (San Jose, California, USA) in the wavelength range 550-750 nm with a resolution of 1 nm. Data were collected at 1-minute intervals over a period of 48 hours. The polypropylene container containing SBF and firmly attached Eu^{3+}-doped bioactive glass fibers was placed on an IKA C-MAG HS 7 heating plate (IKA, Warszawa, Poland) with adjustable temperature control and a thermocouple sensor. The automatic feedback mechanism ensured precise control and stabilization of the liquid temperature throughout the experiment.

The schematic of the measurement setup is presented in Fig. 1.

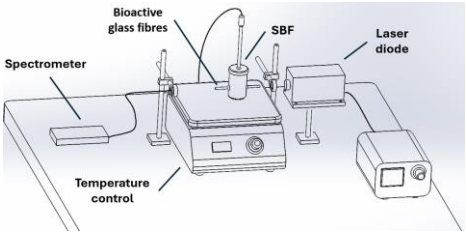
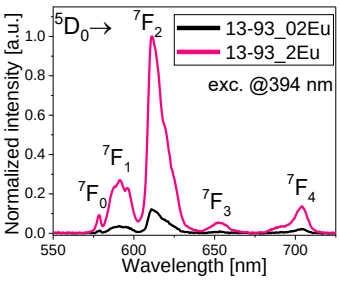


Fig. 1. The measurement setup for the optical evaluation of the bioactive glass fiber degradation process.

The morphologies of the dry fibers were examined by scanning electron microscopy (SEM). The glass fibers were carefully mounted on double-sided adhesive carbon tape, which was attached to aluminum pin discs using tweezers. Imaging was performed with an ultra-high resolution analytical dual beam FIB-SEM system (Scios 2 Dual Beam, Thermo Fisher Scientific, Waltham, MA, USA) equipped with a full range energy dispersive X-ray microanalysis system (NORAN System 7, NS7). Analyses were performed using an electron beam acceleration voltage of 2 kV without applying any additional conductive coating. Magnifications ranging from 500× to 50,000× were used to capture detailed fiber structures. Elemental analyses were performed at 30 kV, with chemical composition measurements made using an elemental range of 10 kV.

This section presents the results of degradation studies carried out on bioactive fibers made of 13-93 glass doped with europium ions, with diameters of 130 μm ± 10 μm, immersed in simulated body fluid (SBF). The fibers were optically excited using a 394 nm laser, and the changes in luminescence intensity were analyzed as a function of incubation time. Initially, luminescence studies were conducted on 13-93 glasses doped with varying concentrations of europium ions. Figure 1 shows that higher levels of dopant (2% mol. Eu^{3+}) lead to higher levels of luminescence. Glass 13-93_02Eu, despite its lower level of luminescence, is valuable for further investigation.

Fig. 2. Emission spectrum of 13-93_02Eu, 13-93_2Eu bioactive glassed excited at λ_{exc}=394 nm.



The luminescence spectra of 13-93 bioactive glass fibers with varying concentrations of Eu^{3+} ions, excited at 394 nm, have been recorded over the spectral range from 555 to 735 nm (see Fig. 3). Fabricated fibers emit luminescence, which corresponds to the initial $^5D_0$ to the lower states ^7F_J, where J = 0, 1, 2, 3, 4. The characteristic luminescence shape of the emission bands at 579, 591, 611, 652, and 704 nm was observed. As demonstrated in Figure 2, the luminescence spectra of bioactive fibers doped with varying concentrations of europium ions were observed before (0 h) and during the degradation process at specific time intervals (4, 8, 24, and 48 h). The $^5D_0 \rightarrow {}^7F_2$ transition, corresponding to 611 nm, demonstrated the highest luminescence intensity. This band recorded changes in luminescence intensity over time due to structural and microstructural changes occurring in the bioactive fibers by interaction with the SBF fluid.

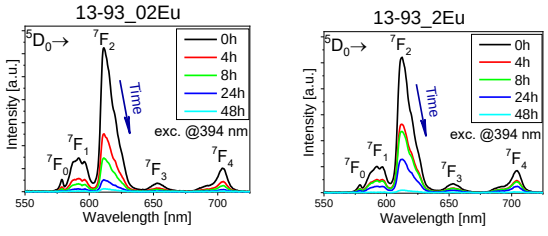


Fig. 3. Emission spectrum of a) 13-93_02Eu, b) 13-93_2Eu bioactive glass fibers immersed in SBF for 0, 4, 8, 24, 48h.

The changes in luminescence intensity were fitted using a two-exponential function of the form:

$$I(t) = A_1 exp\left(\frac{t}{\tau_1}\right) + A_2 \exp\left(\frac{t}{\tau_2}\right) \quad (1)$$

where $\tau_{1,2}$ is time constant, $A_{1,2}$ fitting constant. A single-exponential function was found to be inadequate to fit the data, as indicated by a poor coefficient of determination ($R^2 < 0.9$).

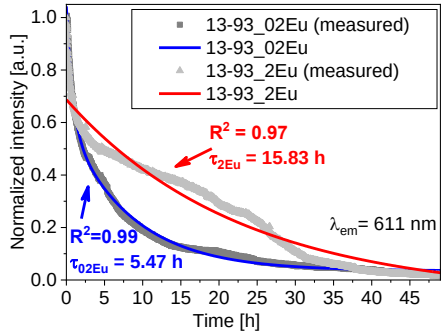


Fig. 4. Characteristics of luminescence changes at 611 nm for 13-93 bioactive glass fibers doped with 0.2 and 2 %mol Eu_2O_3.

As the bioactive fibers were incubated in simulated body fluid (SBF), a reduction in luminescence intensity was observed. This phenomenon was caused by the degradation of the glass surface of the fibers and the formation of a hydroxyapatite layer in the simulated body fluid (SBF) environment. The progressive leaching of ions from the glass matrix, along with structural deterioration—manifested as cracks, the formation of cavities, and the crystallization of the apatite layer on the surface—reduced the luminescence signal intensity. These findings are confirmed by scanning electron microscopy (SEM) images of the fibers (Fig. 5). As demonstrated in Fig. 4, the changes in luminescence intensity were observed to exhibit a faster rate of change for the 0.2% mol Eu_2O_3 doped sample in comparison to the 2%. This can also be evidenced by the calculated differences in the decay time constant, which resulted in values of 5.47 and 15,83 for fibers 13-93_02Eu and 13-93_2Eu, respectively.

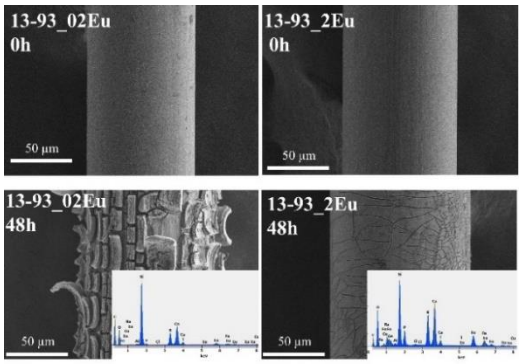


Fig. 5. The measurement setup for the optical evaluation of the bioactive glass fiber degradation process.

This study introduces a new approach to the characterization of bioactive glass fibers. The luminescent and microstructural properties of 13-93 glass fibers doped with europium ions at concentrations of 0.2 and 2%mol were investigated. The findings demonstrate that the luminescent behavior of these fibers can serve as an effective tool for monitoring the degradation process of bioactive glass fibers under in vitro conditions. Europium ions have been shown to exhibit sufficient luminescence intensity to detect changes in intensity over time. The findings of this study demonstrate a direct correlation between the rate of change in luminescence intensity and the dopant concentration. The results indicate that increasing the amount of europium ions within the fibers reduces the degradation rate.

It can be inferred that structural changes in the glass and glass fibers are a consequence of the polymerization process. This is supported by the observed reduction in bioactivity, indicating alterations in the glass network. These changes are associated with the influence of lanthanide ions on the glass fiber structure and the modulation of ion release rates, which are essential for forming the bioactive apatite layer.

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