Effect of the temperature on the luminescence profile of photonic materials for biological applications

Karolina Sadowska,* Jacek Żmojda

Faculty of Electrical Engineering, Bialystok University of Technology, Wiejska 45D, 15-351 Bialystok

Received November 28, 2023; accepted December 29, 2023; published December 31, 2023

Abstract—Temperature significantly impacts the luminescence profile of photonic materials for biological applications. This paper presents the effect of temperature on the luminescence profile of three different photonic materials in the range of the second biological window. The effect of temperature on luminescence properties is shown on glass, glass-ceramics, and phosphors co-doped with $Eu^{3+}/Nd^{3+}/Yb^{3+}$ under UV laser diode excitation. Each sample has been analyzed for temperature effects on optical parameters in biological window ranges. Moreover, the effect of temperature on mechanisms of energy transfer $Eu^{3+} \rightarrow Nd^{3+} \rightarrow Yb^{3+}$ in all fabricated photonic materials was analyzed.

Recently, there has been a noticeable surge in research focused on using nanophosphors in medicine as advanced instruments for fluorescence imaging, drug delivery, and image-guided therapy. This aspect holds particular significance in applications where the efficient permeation of fluorescent nanoparticles across physiological barriers is crucial [1–3].

Phosphors are chemical compounds that exhibit strong luminescence when exposed to external optical radiation. Usually doped with trivalent lanthanides, they have relatively narrow emission bands [4–5]. Phosphors stand out by the high sensitivity of detection and increased optical ranges of tissue penetration, giving them a distinct advantage in biomedical applications, particularly within a second (NIR-II: 950–1350 nm) near-infrared biological window. Compared to the visible spectrum or the first biological window, NIR-II has superior tissue penetration depth and reduced scattering, as scattering tends to decrease with increasing wavelength in nearly all biological tissues [6–8].

Based on literature studies, it can be concluded that high-power LED chips generate large amounts of heat, which alters the luminescent properties of the phosphors. The quantum efficiency (QE) is reduced, and thus the probability of non-radiative transitions increases. An important aspect is the analysis of the effect of the temperature on the emission profile and the probability of the energy transfer mechanism depending on the selected photonic materials [9–10]. In recent years, there has been a focus on investigating photonic materials that leverage the unique properties of rare-earth (RE) ions. Due to the distinctive characteristics of Ln^{3+} ions, including extended excited-state lifetimes, significant Stokes shifts, and rich 4f electronic energy level structures, they are used in lighting, displays, solar cells, lasers, sensors, and bioimaging. Rare-earth ions are characterized by narrow emission bands [1, 11].

Also, to increase the signal-to-excitation (noise) ratio, the optical materials are co-doped with two or three RE ions. It is known that using UV active donor ions makes it possible to observe downshifting emissions occurring by energy transfer mechanisms. Europium ions have strong absorption at the wavelength of 395 nm, which allows UV diodes to excite it efficiently. Using europium ions as a donor shows the possibility of obtaining efficient energy transfer between europium and neodymium, and then between neodymium and ytterbium [12–14].

In the experimental part, we fabricated three different photonic materials – glass, glass-ceramic, and phosphor. The glass sample with the chemical composition: (40-x) P_2O_5-30GeO_2-20Sb_2O_3-5Al_2O_3-5Na_2O (PSG), where x=0.5Eu_2O_3-0.5Yb_2O_3-0.25Nd_2O_3 (in mol%) was prepared by standard melting and quenching methods. All reagents were characterized by high purity (Sigma-Aldrich, 99.99%). A synthesized powder was placed in the platinum crucible and melted at 1450°C. Next, the molten glass was poured into a stainless form and kept in the furnace at 450°C to reduce thermal stress. Based on DSC measurements, the crystallization temperature was indicated at 715°C. Glass ceramics were obtained after 15 minutes of heat treatment of the parent glass. Based on previous research [13, 15], the co-precipitation method was chosen to fabricate $LaPO_4$ nanophosphors co-doped with 5% mol of Eu_2O_3, 5% mol Yb_2O_5, and 2% mol of Nd_2O_3. To synthesize the phosphors were used: La_2O_3, Eu_2O_3, Yb_2O_3, Nd_2O_3 (Sigma-Aldrich, 99.99%), nitric acid (V), $NH_4H_2PO_4$ (Chempur), and glycerol (Sigma-Aldrich, 99.5%). First, rare earths were dissolved in nitric acid, and nitrates were mixed with 75 mL of deionized water and 25 mL of glycerin. Then, the mixture was stirred until a temperature of 50°C and 50 ml of aqueous ammonium phosphate solution was dropped. The next step was to stir and centrifuge the suspension. In the end, the precipitate was washed three times with deionized water and once with ethanol. The sediment was placed in

* E-mail: karolina.sadowska@pb.edu.pl

the furnace for 48 hours at 80°C for 42 h. Then, the finished product was annealed in an oven at 1000°C for 2 hours.

All samples were grounded and the powders were formed into pellets to perform luminescence measurements. Measurements of optical properties in the temperatures range 303–573 K for three types of samples were realized in the range of 925–1100 nm by using an Acton 2300i monochromator (Acton Research Corporation, Acton, MA, USA) equipped with an InGaAs detector. We used a reflection mode setup with laser radiation at the wavelength of 395 nm as the excitation source and multimode optical fiber with 200 μm diameter as the detection head.

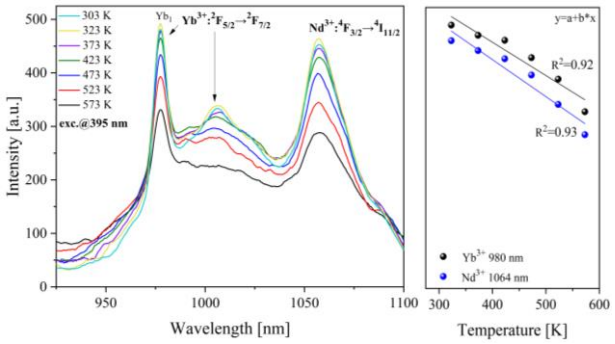

Fig. 1. Luminescence spectra of PSG glass (λ_{exc} = 395 nm) (left) and intensity of selected emission bands as a function of temperature (right).

Figure 1 shows the luminescence spectra of PSG glass under 395 nm laser excitation in the range of the second biological windows. In this case, we observed three characteristic luminescence bands at the wavelengths 980 nm, 1005 nm, and 1064 nm corresponding to transition $^2F_{5/2} \rightarrow {}^2F_{7/2}$:$Yb^{3+}$ and $^4F_{3/2} \rightarrow {}^4I_{11/2}$:$Nd^{3+}$. Luminescence intensity decreases as the temperature increases, with the lowest emission intensity at 573 K.

Luminescence spectra of glass-ceramic under UV excitation are shown in Figure 2. Analogously, after measurement, the highest intensity was observed for the temperature at 303 K and the lowest at 573 K. However, the shape of the glass-ceramic luminescence has two characteristic emission bands at 980 nm corresponding to $^2F_{5/2} \rightarrow {}^2F_{7/2}$:$Yb^{3+}$ and 1064 nm ($^4F_{3/2} \rightarrow {}^4I_{11/2}$:$Nd^{3+}$).

From the luminescence measurements for $LaPO_4$:Eu^{3+}/Nd^{3+}/Yb^{3+} (Fig. 3), there are four main bands: 980 nm, 991 nm, 1005 nm and 1033 nm ($^2F_{5/2} \rightarrow {}^2F_{7/2}$:$Yb^{3+}$) and 1064 nm ($^4F_{3/2} \rightarrow {}^4I_{11/2}$:$Nd^{3+}$).

The highest luminescence intensity in the studied range is seen in the case of $LaPO_4$:Eu^{3+}/Nd^{3+}/Yb^{3+} nanophosphor, while the lowest is in the case of glass-ceramic. According to intensity changes resulting from temperature exposition, we determined the sensibility as S=dI/dT after linear fitting. The values of sensitivity of luminescence decline for 980 nm, 991 nm, and 1064 nm in the three samples are shown in Table 1.

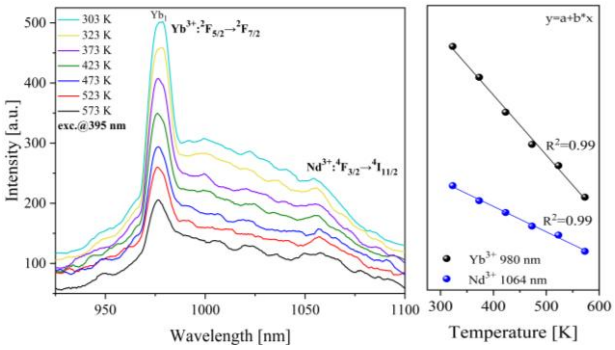

Fig. 2. Luminescence spectra of PSG glass-ceramics (λ_{exc} = 395 nm) (left) and intensity of selected emission bands as a function of temperature (right).

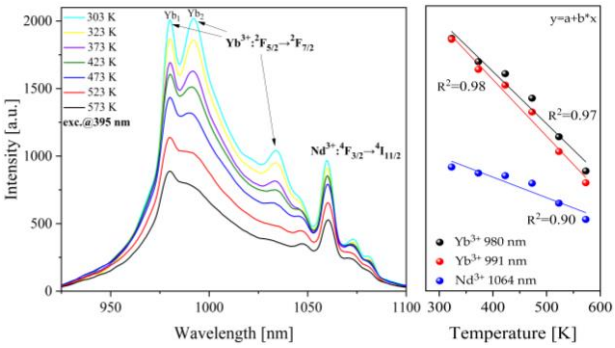

Fig. 3. Luminescence spectra of $LaPO_4$:Eu^{3+}/Nd^{3+}/Yb^{3+} phosphor (λ_{exc} = 395 nm) (left) intensity of selected emission bands as a function of temperature (right).

Table 1. Luminescence quenching

No.	Sample	Sensitivity		
		Yb_1	Yb_2	Nd_1
1	PSG glass	0.5	-	0.61
2	PSG glass-ceramics	1.1	-	0.44
3	$LaPO_4$	3.9	4.3	1.47

The highest sensitivity has been observed for LaPO4 nanophosphor which can be related to the homogenous structure of crystal lattice. In another case, the sensitivity is much lower due to the phase separation, which affects the excitation energy.

Based on luminescence studies in the range of 2nd biological window performed on three samples, it can be seen that in each case, there are 980 nm ($^2F_{5/2} \rightarrow {}^2F_{7/2}$:$Yb^{3+}$) 1064 nm ($^4F_{3/2} \rightarrow {}^4I_{11/2}$:$Nd^{3+}$) transitions. In the case of PSG glass, the 1005 nm band corresponding to the transition $^2F_{5/2} \rightarrow {}^2F_{7/2}$:$Yb^{3+}$ is also pronounced, the intensity decreasing with increasing temperature. The

phosphor sample is additionally characterized by the 991 nm and 1033 nm transitions ($^2F_{5/2} \rightarrow {}^2F_{7/2}$:$Yb^{3+}$), whose intensity is highest at 303 K and disappears as the temperature increases. The $LaPO_4$:Eu^{3+}/Nd^{3+}/Yb^{3+} phosphor sample also has the narrowest luminescent bands, which indicate the presence of crystalline structures. According to luminescence analysis, the possible simplified sensibilization mechanism is presented in Fig. 4. In the first step, the europium ions were excited into the $^5L_6$ energy state and next relaxed rapidly to the $^5D_0$ level by multiphonon transitions. Effective energy transfer can be obtained from the $^5D_0$ level of europium to the $^4G_{5/2}$ level to neodymium. After fast non-radiative transitions to the $^4F_{3/2}$ level, radiative transition at the wavelengths of 1064 nm was observed ($^4F_{3/2} \rightarrow {}^4I_{11/2}$:$Nd^{3+}$). Between neodymium and ytterbium, it is possible to obtain energy transfer from the $^4F_{3/2}$ level for Nd^{3+} ions to the $^2F_{5/2}$ level for Yb^{3+} ions. As a result, it can be observed a radiative transition $^2F_{5/2} \rightarrow {}^2F_{7/2}$:$Yb^{3+}$ and four emissions bands at 980 nm, 991 nm, 1005 nm, and 1033 nm (Fig. 4).

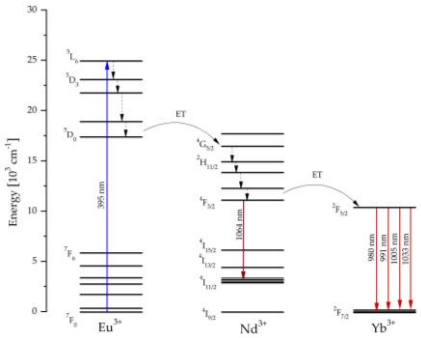

Fig. 4. Simplified mechanism of energy transfer between Eu^{3+}, Nd^{3+}, and Yb^{3+} ions.

In summary, we have shown the effect of temperature on the luminescence profile of photonic materials for biological applications. It was presented that luminescence intensity (at excitation 395 nm) decreases as the temperature increases, with the highest emission intensity occurring at 303 K in the three materials tested and the lowest at 573 K. The highest luminescence intensity in the studied range is seen in the case of $LaPO_4$:Eu^{3+}/Nd^{3+}/Yb^{3+} nanophosphor, while the lowest is in the case of glass-ceramic. Comparing the characteristics of the luminescence bands, there is an apparent change in the shape of the luminescence for the glass, glass-ceramics, and $LaPO_4$:Eu^{3+}/Nd^{3+}/Yb^{3+} nanophosphor co-doped europium, neodymium and ytterbium. Thus, the effect of temperature on the luminescence profile and the excitation energy transfer is crucial in the future application of fabricated materials as an emitter in 2nd biological window.

The work was supported by the Bialystok University of Technology granted based on decision No. WI/WE-IA/13/2023.

References

[1] J. Zhou, J.L. Leano Jr., Z. Liu, D. Jin, K.-L. Wong *et al*., Small **14**, 1801882 (2018).
[2] Z. Li, Y. Zhang, G. Han, Springer Series in Biomaterials Science and Engineering **6**, 139 (2016).
[3] A. Zhang, Z. Sun, M. Jia, *et al*., Chem. Engineering J. **365**, 400 (2019).
[4] M.-F. Tsai, S.-H.G. Chang, F.-Y. Cheng, V. Shanmugam, Y. Cheng *et al.*, ACS Nano **7**, 5330-5342 (2013).
[5] S. Ding, L. Lu, Y. Fan, F. Zhang, J. Rare Earths **38**, 451 (2020).
[6] U. Rocha, K.U. Kumar, C. Jacinto, I. Villa, F. Sanz-Rodriguez *et al.*, Small **10**, 1141 (2014).
[7] M. Jia, Z. Sun, H. Xu, X. Jin, Z. Lv *et al*., J. Mat. Chem. C **8**, 15603 (2020).
[8] H. Lin, T. Hu, Y. Cheng, M. Chen, Y. Wang, Laser Phot. Rev. **12**, 1700344 (2018).
[9] H. Su, Y. Nie, H. Yang, D. Tang, K. Chen, T. Zhang, J. Eur. Ceram. Soc. **38**, 2005 (2018).
[10] K.Y.Duan, B. Liu, Adv. Mat. **30**, 1802394 (2018).
[11] M.L. Debasu, H. Oliveira, J. Rocha, L.D. Carlos, J. Rare Earths **38**, 483 (2020).
[12] L. Pavasaryte, A. Katelnikovas, V. Klimavicius, V. Balevicius, A. Krajnc *et al*., Phys. Chemi. Chem. Phys. **19**, 3729 (2017).
[13] K. Sadowska, P. Awramiuk, I Zgłobicka, K Rećko, J. Żmojda, Photon. Lett. Poland **14**, 28 (2022).
[14] P. Lei, J. Feng, H. Zhang, Nano Today **35**, 100952 (2020).
[15] K. Sadowska, T. Ragiń, M. Kochanowicz, P. Miluski, J. Dorosz *et al.*, Materials **16**, 1588 (2023).

