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THE EFFECT OF ZINC CONTENT ON THE ENHANCEMENT Er^{3+}–Yb^{3+} LUMINESCENCE PROPERTIES IN THE SILICATE GLASS MATRIX

#SOŇA VYTYKÁČOVÁ*, STANISLAV STANĚK*, BLANKA ŠVECOVÁ*, MARTIN MÍKA*, JIŘÍ OSWALD**, ANNA MACKOVÁ***,****, PETR MALINSKÝ***,****, ROMAN BÖTTGER*****, ROMAN YATSKIV******, PAVLA NEKVINDOVÁ*

*University of Chemistry and Technology, Technická 5, 166 28 Prague, Czech Republic
**Institute of Physics, Czech Academy of Sciences, v.v.i., Cukrovarnická 10/112, 162 00 Prague, Czech Republic
***Department of Physics, Faculty of Science, J.E. Purkinje University,
Ceske Mladeze 8, 400 96 Usti nad Labem, Czech Republic
****Nuclear Physics Institute, Czech Academy of Sciences, v. v. i., 250 68 Řež, Czech Republic
*****Helmholtz-Zentrum Dresden-Rossendorf, Institute of Ion Beam Physics and Materials Research,
Bautzner Landstraße 400, 01328 Dresden, Germany
******Institute of Photonics and Electronics, Czech Academy of Sciences, v.v.i.,
Chaberská 57, 182 51 Prague, Czech Republic

#E-mail: Sona.Vytykacova@vscht.cz

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Glasses doped with Er and Yb show strong luminescence around 1530 nm, which makes them attractive luminophores for the preparation of multifunctional optical components. This article is focused on the influence of ZnO on the optical and luminescence properties of Er–Yb zinc-silicate glasses. The influence of silver doping on the resulting luminescence properties of the prepared glasses has also been investigated.

Three types of silicate glasses containing different amounts of ZnO and RE ions (Er and Yb) were prepared. For all the glasses prepared, their density, glass-transformation temperature and refractive index were determined. Moreover, these glasses were doped with silver using two methods – ion implantation and ion exchange. The presence of silver metal nanoparticles was observed using optical absorption in the UV-VIS range. Photoluminescence spectroscopy was used to observe the effect of the presence silver or zinc oxide on the intensity of luminescence.

The results have shown that the enhancement of ZnO content positively influenced erbium luminescence at 1530 nm without affecting the transparency or homogeneity of the glass matrix. Moreover, the presence Ag^{+} ions in this special type of glass matrix positively contributed to the enhancement of erbium photoluminescence.

INTRODUCTION

The study of the possibilities of improving the optical and luminescence properties of glasses for use as materials for photonics devices has attracted steadily growing interest. Silicate glasses doped with erbium have been used as a suitable material for photonics because of their strong luminescence in the near infrared region, their optical and mechanical properties, chemical stability and compatibility with the silica optical fibres used. Trivalent erbium is an ideal luminescent centre in visible and mid- and infrared spectra thanks to its well-described transitions {$^2H_{11/2} \rightarrow {}^4I_{15/2}$ (539 nm), $^4S_{3/2} \rightarrow {}^4I_{15/2}$ (557 nm), $^4F_{9/2} \rightarrow {}^4I_{15/2}$ (675 nm), $^4S_{3/2} \rightarrow {}^4I_{13/2}$ (852 nm), $^4I_{13/2} \rightarrow {}^4I_{15/2}$ (1500 nm), $^4I_{11/2} \rightarrow {}^4I_{13/2}$ (2900 nm)} and to the fact that it can be pumped easily in the visible as well as near-infrared ranges of the spectra Trivalent ytterbium is one of the best co-dopants for significantly increasing absorption and pumping efficiency around 980 nm. This element can subsequently help to increase luminescence intensity as a result of the excitation of the energy level $^4I_{11/2}$ of Er^{3+} thanks to the energy transfer between the mentioned energy level of Er^{3+} and the energy level of Yb^{3+} ($^2F_{5/2}$). The increase in the amount of rare-earth elements (REs) in the glass substrate is limited due to the concentration quenching effect and relatively bad solubility of RE in silicate glasses [1,2].

Despite the fact that silicate glasses have relatively low solubility of RE, it is feasible to shift the limit of solubility simply by adding of P_2O_5, Al_2O_3, or just by ZnO, which make it possible to increase the resulting intensity of the luminescence of silicate glasses in the near infrared region [3-5]. This fact that the presence of zinc oxide (in comparison with calcium or magnesium oxides) positively influences the intensity of luminescence can be ascribed to the decreasing of basicity of silicate glass and to the basicity close to the value of phosphate glasses [6, 7].

Another possibility to increase the luminescence of RE doped silicate glasses to enhance their efficiency is doping with silver [8-10]. This can be done by the presence of silver in glass matrix. Possible mechanism of this phenomenon can be surface plasmon resonance (SPR) of silver metal nanoparticles (Ns), but it has been shown that this effect can also be observed in glasses containing silver present in the oxidation state +I [11, 12].

In this paper, three novel types of zinc-silicate glasses with various ZnO content were prepared and the effect of ZnO addition in glass on Er^{3+} luminescence enhancement around 1530 nm was investigated.

We focused on the improvement of luminescence efficiency around 1530 nm in erbium-doped silicate glasses. To achieve a higher intensity, we used two different ways – adding and increasing of zinc oxide content to the glass matrix and doping prepared glass with silver. The emphasis was laid to the explanation of mechanism, how the presence of added metal elements can improve the luminescence and optical properties. We also concentrated to the oxidation state of doped elements, changes in glass matrix caused by presence of zinc and by doping process of silver, coordination number of dopants in resulting arrangement of glass matrix and their influence on the resulting optical and luminescence properties.

EXPERIMENTAL

The preparation of the samples

For the investigation of the influence of ZnO presence on the resulting properties of Er–Yb glasses, a new set of three glasses containing different amounts of ZnO was prepared. The chemical composition of the prepared glasses was the following: 65 - 75 mol. % of SiO_2, 12 - 16 mol. % of Na_2O, 0.3 - 2 mol. % of Al_2O_3, 5 mol. % Yb_2O_3, 0.25 mol. % Er_2O_3 and 12, 15 or 18 mol. % of ZnO. The specific compositions were chosen based on our previous research [6, 7, 12], and zinc oxide substituted for silica oxide. The glasses were synthesised by the standard melting process, which had been designed to achieve the desired optical homogeneity, at a temperature of 1550°C. In order to remove inner tension in the glass matrix, the melted glasses were annealed at temperatures in the range of 450 - 560°C for several days. The samples of the molten glass were cut into 3-mm-thick wafers, which were then polished. All the prepared glasses showed high homogeneity and transparency, and finally very high purity, with the content of impurities (mainly reduction oxides) being lower than 0.01 wt. %.

Two metods were used for preparing of silver-rich thin layers: ion exchange and ion implantation. Silver-ion implantation was performed in collaboration with the Helmholtz-Zentrum Dresden Rossendorf, Germany, on a Tandetron accelerator. The energy of the implanted Ag^+ ions was 1.2 MeV or 1.7 MeV using an ion fluence of 1×10^{16} cm^{-2} according [12]. The ion-exchange process proceeded as follows: before the process, the clean glass substrate was tempered. The $Ag^+ \leftrightarrow Na^+$ ion exchange was performed on all glass substrates using a three-component melt containing 23.72 wt. % of $AgNO_3$, 42.92 wt. % of KNO_3 and 33.32 wt. of % $NaNO_3$. The temperature was set to 280°C and the time of exchange process was set to 50 min.

The characterisation of the samples

First, the properties of molten glasses were characterised. The chemical composition and purity were controlled by XRF analyses, the glass density was determined using a pycnometer, and the glass-transition temperature were determined by thermogravimetric analysis using a termogravimeter TG-DSC Sensys Evo with a Calvet 3D sensor. The refractive-index values were measured on the polished substrates by dark-mode spectroscopy at 633 nm using a Metricon Prism Coupler 2010.

The theoretical simulation of silver penetration in the samples implanted with silver was performed by SRIM 2013 [13]. The chemical composition of the samples after ion exchange was determined by electron microprobe analysis (EMA) using a CAMECA SX-100 electron microprobe from the polished inner edges.

A Cary 50 dual-beam spectrometer in transmission modes or a Specord 210 Analytic Jena spectrometer was used to collect the UV-VIS absorption-transmission spectra in the range of 200 - 1000 nm. Photoluminescence in the range of 1440 - 1650 nm was measured using a semiconductor laser POL 4300, emitting at 980 nm, as an excitation source. The luminescence was detected by a two-step cooled Ge detector J16 (Teledyne Judson Technologies). The 4 K photoluminescence spectra were measured with a set-up comprising a Ar laser (514.5 nm) as an excitation source. The pumping power was 9 mW for visible range and 0.5 mW for NIR range. A grating monochromator Jobin Yvon THR 1000, a closed cycle He optical cryostat, and a GaAs photomultiplier or liquid nitrogen cooled high-purity Ge photodiode were used for detection.

RESULTS

The effect of the content of zinc oxide

In the Table 1 the basic characteristics of Er-Yb doped glasses with different content of ZnO are shown. The table implies that the higher content of ZnO, the higher values of refractive index and the higher density of glasses. On the contrary, the transformation temperature falls to the lower values with higher amount of ZnO.

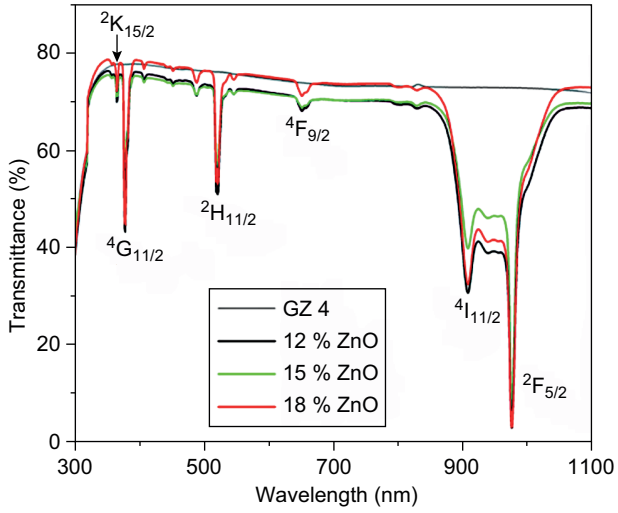
Table 1. The basic characteristics of the prepared Er-Yb zinc-silicate glasses.

ZnO (wt. %)	12	15	18
Refractive index ± 0.0001 [-]	1.5419	1.5502	1.5605
Glass density ± 0.001 (g·cm^{-3})	2.854	3.007	3.051
T_g (°C)	690.1	688.8	686.8

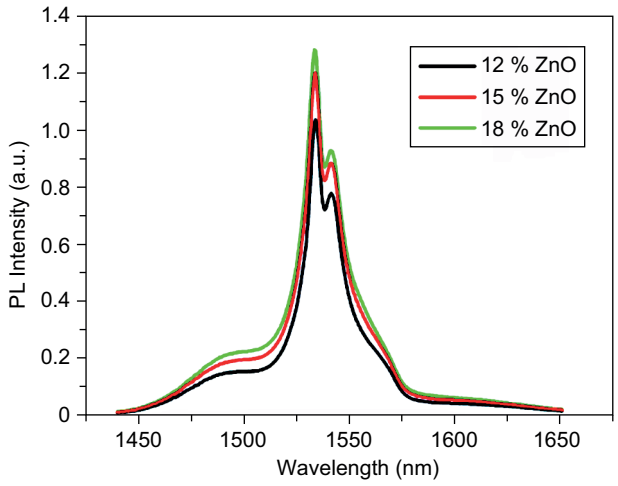
For the prepared set of glasses containing different amounts of ZnO, the absorption spectra were collected in range of 200 - 1100 nm. 4f-4f inner–shell absorption bands of Er^{3+} and Yb^{3+} ions were observed – see Figure 1a. As expected, there are no similar bands in the virgin (without erbium and ytterbium) zinc-silicate glass. When we focus on the range of luminescence pumping of 800 - 1000 nm, we can see the highest value of absorption intensity in glass contains 15 mol. % of ZnO. On the contrary, the lowest absorption intensity is exhibited by the glass with 18 mol. % of ZnO.

In the luminescence spectra measured at room tem-perature under 980 nm excitation (Figure 1b), luminescence of erbium is noticeable around 1530 nm pumped with a 980-nm laser of the three types of Er-Yb-Zn-silicate glasses. On the contrary in the relation of absorption intensity, we can see that in the luminescence spectra, the content of ZnO influenced the resulting intensity of luminescence. As expected, the highest content of ZnO positively influences the photoluminescence of the prepared glasses and leads to the increasing intensity of the luminescence of erbium until 1.3 times.

Figure 2a shows the emission spectra of prepared glasses measured at 4.2 K under 514 nm excitation in visible region. There are 4 emission bands centered at 524, 545, 660 and 850 nm, which corresponds with

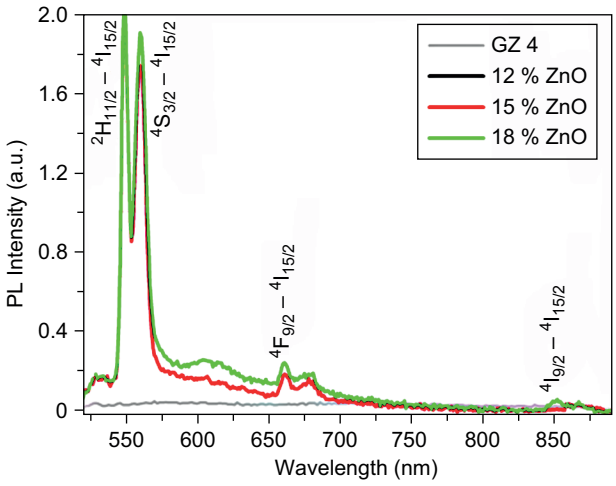


a) absorption spectra

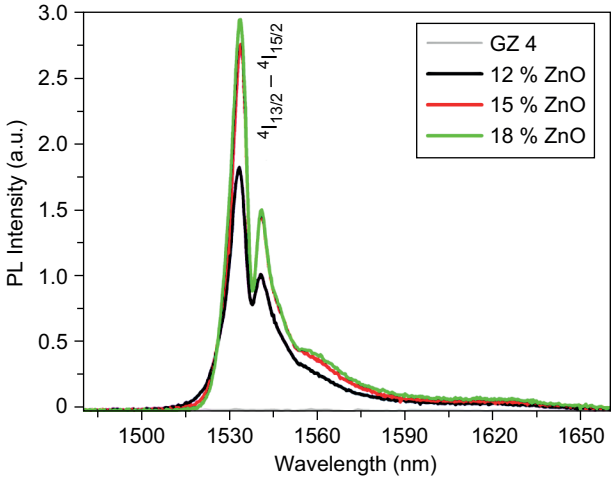


b) luminescence spectra

Figure 1. The absorption (a) and luminescence (b) spectra of three different types of glasses determined at room temperature under 980 nm excitation. GZ4-reference samples without Er-Yb co-doping.



a) visible range



b) NIR range

Figure 2. 4.2 K photoluminescence spectra of the Er-Yb zinc-silicate glasses with different content of ZnO under 514 nm excitation in visible range (a) and in NIR range (b). GZ4-reference samples without Er-Yb co-doping.

absorption spectra. The photoluminescence intensity of emission bands slightly increases with higher content of zinc oxide. Figure 2b demonstrates photoluminescence spectra of mentioned glasses measured under same excitation wavelength at 4.2 K in near IR range. Despite different excitation wavelength and temperature of measurement, this spectra are fully agreeable with those measured at room temperature. We can observe two band with local maxima at 1530 and 1545 nm corresponding with $^4I_{13/2} \rightarrow {}^4I_{5/2}$ transition, which positions are given by surrounding of Er^{3+} ions in glass matrix.

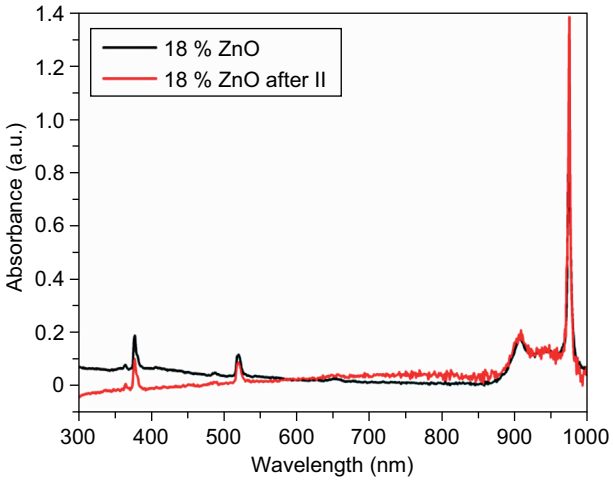
The effect of the content of silver

Ion implantation

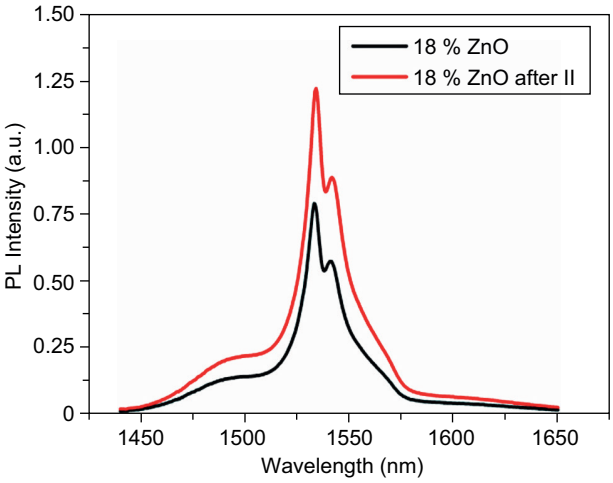
A set of six glasses containing three different amounts of ZnO was implanted with silver ions using different ion implantation energies (1.2.a 1.7 MeV) and the same fluence. According to [12], the silver depth profiles were predicted by SRIM simulation. Since the density of the prepared glasses was almost the same as in [12], the R_p was about 480 nm (ΔR_p about 124 nm) for the fluence of 1.2 MeV and about 700 nm (ΔR_p about 168 nm) for the fluence 1.7 MeV.

Before and after the ion-implantation process, the absorption spectra were collected. It is noticeable from the obtained spectra that in all the cases, the absorption spectrum of the samples after ion implantation is similar to the spectrum of non-implanted samples, i.e. the bands are in the same position. However, we can see the differences in the intensity of absorption before (black curve) and after (red curve) ion implantation – a significant increase of absorption around 980 nm was found after ion implantation. This absorption band is related with $^4I_{11/2}$ and $^2F_{5/2}$ energy levels of Yb^{3+} ions. For glass with 18 mol. % of ZnO, this is illustrated in Figure 3a. It is possible to discern slightly lower absorption between 300 and 500 nm (the same effect has been found for different content of ZnO). These changes in absorption can be associated with the resulting higher refractive index of the doped glasses. There is no evident band at about 400 nm in any of the samples prepared, which corresponds to the SPR of silver metal nanoparticles. This means that after the ion-implantation process, silver is present in the glasses mainly in the oxidation state Ag (+ I).

For this set of glasses, also photoluminescence properties were measured in the range of 1420-1650 nm. The behaviour of samples containing different amounts of ZnO is identical. Spectrum for glass with 18 mol. % of ZnO is ilustrated in Figure 3b (black curve). After the ion-implantation process (red curve), we can see an increase in the intensity of luminescence around 1530 nm. The intensity of photoluminescence after ion implantation for glass containing 18, 15 and 12 mol. % of ZnO is 1.5 times higher than in the case of the non-implanted sample.



a) absorption spectra



b) luminescence spectra

Figure 3. An example of the absorption (a) and photoluminescence (b) spectra of Zn silicate glasses (18 mol.% of ZnO) non-implanted and implanted with silver ions (the energy of 1.7 MeV and the fluence of 1×10^{-16} ion cm^{-2}).

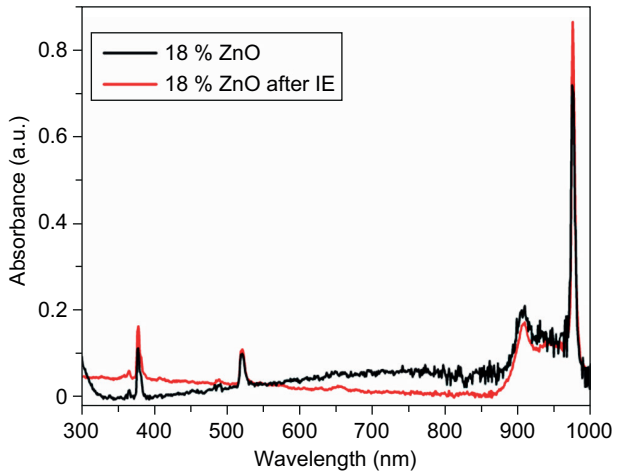
Ion exchange

The $Ag^+ \rightarrow Na^+$ ion exchange was performed in three glasses containing three different amounts of ZnO. According to [14], the silver concentration – depth profile was characterised by EMA analysis. The depth of the silver-containing layers was about 6 μm and the surface concentration of silver was about 8 mol. %.

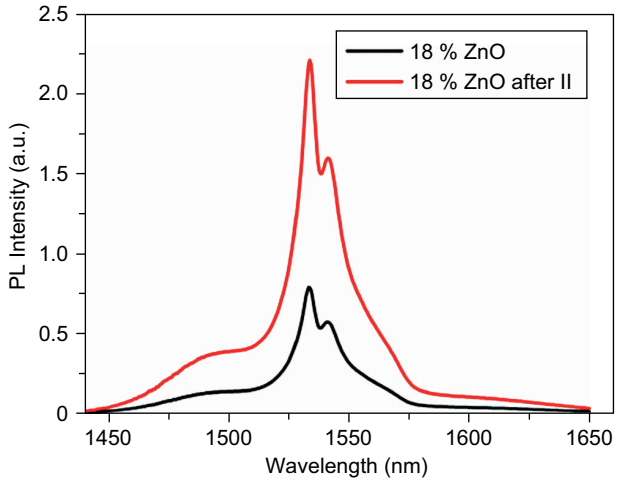
The spectroscopic and luminescence properties of the prepared samples were determined after the ion exchange process. Figure 4a shows the absorption spectra before (black curve) and after (red curve) ion exchange for glass containing 18 mol. %, again as an example of the behaviour of all the samples. Equally to the ion-implantation process, neither in this case can we see any increase in absorption around 400 - 500 nm,

which indicates the presence of silver metal nanoparticles. Also in this case, changes in the intensity of absorption can be caused by changes in the refractive index after the ion-exchange process.

The luminescence spectra were measured for the mentioned glasses as well. Figure 4b shows the photoluminescence spectra for glasses with 18 mol. % of ZnO before (black curve) and after (red curve) the ion-exchange process. Only minor changes in the intensity of luminescence after the ion exchange process were observed between glasses containing different amounts of ZnO and the luminescence spectra of all the glasses are comparable (not shown). All luminescence measurements showed two local maxima, at 1530 and 1540 nm, corresponding to the emission of erbium $^4I_{13/2} \rightarrow {}^4I_{15/2}$. After the process of ion exchange, it was possible to observe an increase in the luminescence intensity around 1530 nm (2.7 times). The results imply that the increase in the luminescence of erbium could be caused by the presence of silver in the oxidation state Ag (+I).



a) absorption spectra



b) luminescence spectra

Figure 4. An example of the absorption (a) and photoluminescence (b) spectra of Er-Yb-Zn silicate glasses (18 mol. % of ZnO) before and after silver-ion exchange (at a temperature of 280°C for 50 min.)

DISCUSSION

The experiments have shown that the increased amount of zinc in our silicate glasses leads to an increase in the luminescence intensity of erbium at 1530 nm. Similar effects can occur with other ions such as aluminium and phosphorus. Phosphorus is considered to be a glass-network former; on the other hand, aluminium and zinc could act as network formers or as network modifiers. They both create tetrahedral as well as octahedral units [16]. The measurement that confirmed this theory was performed using the EXAFS method [17]. It is often mentioned in the literature that these network-forming elements increase the solubility of RE in glasses. Around RE ions, zinc create octahedral surroundings with the coordination number VI, which is higher than in the SiO_2 matrix (coordination number IV). Consequently, added network formers (Zn) prevent the clustering of REs and their luminescence quenching. One of the important factors to influence the solubility of RE in glasses appears to be the radius of the elements that are incorporated into glass as network formers. We assumed that the effect of zinc (radius 139 pm), whose position in the periodic table, chemical behaviour and radius are similar to those of aluminium (radius 121 pm), would be similar to those of Al or P (radius 106 pm). Our results have confirmed this assumption and shown that the increase in the amount of ZnO from 12 to 18 mol. % leads to the increase in luminescence intensity up to 30 %.

The increasing amount of ZnO in glass could be considered as the next step for the mentioned experiments. However, there are certain limits for the total amount of ZnO in silicate glasses (around 21 wt. % – [15]); above this limit, ZnO clustering or phase separation occur. A question is whether small ZnO clusters could positively influence erbium luminescence intensity.

Because of the possibility of phase separation, we did not increase the amount of ZnO in glass further and attempted to increase luminescence intensity by adding silver to the glass matrix. Similarly to our previous experiments, it has been confirmed also for different amounts of ZnO that the presence of Ag^+ ions positively influences erbium luminescence intensity. In the glass with 18 mol. % of ZnO, luminescence intensity was increased 2.7 times by doping the glass with silver. It has also been observed that luminescence depends on the amount of Ag^+ present in the glass matrix. After ion exchange, when glasses contain about 8 at. % of Ag, the luminescence intensity increased multiple times in comparison with implantation, where the concentration of

Ag was approximately 1 %. These results have confirmed our previous results [12, 14], where the discussion of the luminescence-enhancement mechanism was mentioned.

CONCLUSION

It has been confirmed by our measurements that an increase in the amount of ZnO leads to an increase of erbium luminescence intensity at 1.5 μm. When the amount of ZnO was raised by 6 mol. %, luminescence grew up to 1.3 times. We have not observed the creation of new phases or worse optical quality of the prepared glasses with 18 mol. % of ZnO. It has also been confirmed that the presence of Ag^{+} ions has a definitely positive influence on erbium luminescence intensity. The measurements performed show that the increase of luminescence intensity is closely connected with the concentration of silver in the glass matrix. Ion exchange as a method of doping silicate glasses by silver ions has proved to be a simple and suitable method to increase erbium luminescence intensity. We have also achieved 2.7 times higher luminescence intensity at 8 mol. % surface concentration of silver.

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REFERENCES

1. Najafi S.I. (1992). Introduction to Glass Integrated Optics, Artech House. Boston-London.
2. Miniscalco W. J. (1991): Erbium-doped glasses for fiber amplifiers at 1500 nm. *Journal of Lightwave Technology, 9(2)*, 234-250. doi: 10.1109/50.65882.
3. Yan Y. C., Faber A. J., Waal de H., Kik P. G., Polman A. (1998): Erbium-doped phosphate glass waveguide on silicon with 4.1 dB/cm gain at 1.535 μm. *Applied Physics Letters, 71(20)*, 2922-2924. doi: 10.1063/1.120216.
4. Bradley J. (2009): Al_2O_3-Er as a gain platform for integrated photonics, *Doctoral thesis*.
5. Saitoh A., Matsuishi S., Se-Weon Ch., Nishii J., Oto M., Hirano M., Hosono H. (2006): Elucidation of Codoping Effects on the Solubility Enhancement of Er^{3+} in SiO_2 Glass: Striking Difference between Al and P Codoping. *The Journal of Physical Chemistry B, 110*, 7617-7620. doi: 10.1021/jp060702w.
6. Ondracek F., Jagerska J., Salavcova L., Mika M., Spirkova J., CtyrokyJ. (2008): Er–Yb Waveguide Amplifiers in Novel Silicate Glasses. *IEEE Journal of Quantum Electronics*, *44*(6), 536-541. doi: 10.1109/JQE.2008.918302.
7. Svecova B., Spirkova J., Janakova S., Mika M. (2008): Ion-exchanged optical waveguides fabricated in novel Er3+ and Er3+/Yb3+-doped silicate glasses: Relations between glass composition, basicity and waveguide properties. *Materials Science and Engineering: B*, *149*(2), 177-180. doi: 10.1016/j.mseb.2007.11.019.
8. Malta O., Santa-Cruz P. A., De Sá G. F., Auzel F. (1985): Fluorescence enhancement induced by the presence of small silver particles in Eu3+ doped materials. *Journal of Luminescence, 33(3)*, 261-272. doi: 10.1016/0022-2313(85)90003-1.
9. Strohhöfer C., Polman A. (2002): Silver as a sensitizer for erbium. *Applied Physics Letters*, *81*(8), 1414-1416. doi: 10.1063/1.1499509.
10. Speranza G., Bhaktha S N B., Chiappini A., Chiasera A., Ferrari M., Goyes C., Jestin Y., Mattarelli M., Minati L., Montagna M. (2006): Nanocomposite Er–Ag silicate glasses. *Journal of Optics A: Pure and Applied Optics, 8 (7),* 450–454. doi: 10.1088/1464-4258/8/7/S21.
11. Li J. J., Chen J. D., Wei R. F. Guo H. (2012): Combined White Luminescence from Eu^{3+}, ML–Ag Particles and Ag^{+} in Ag–$Eu^{3+\ Co}$-Doped H_{3BO3}–BaF_2 Glasses. *Journal of the American Ceramics Society*, *95*(4), 1208–1211. doi: 10.1111/j.1551-2916.2012.05112.x.
12. Stanek S., Nekvindova P., Svecova B., Vytykacova S., Mika M., Oswald J., Mackova A., Malinsky P., Spirkova J. (2016): The influence of silver-ion doping using ion implantation on the luminescence properties of Er–Yb silicate glasses. *Nuclear Instruments and Methods in Physics Research Sect. B 371*, 350-354. doi: 10.1016/j.nimb.2015.09.078.
13. Ziegler J. (2015). *The Stopping and Range of Ions in Matter.* www.srim.org.
14. Stanek S., Nekvindova P., Svecova B., Vytykacova S., Mika M., Oswald J., Barkman O., Spirkova J. (2017): The influence of silver ion exchange on the luminescence properties of Er-Yb silicate glasses. *Optical Materials*, *72*, 183–189. doi: 10.1016/j.optmat.2017.05.053.
15. Volf M.B. (1978). *Chemie skla*. SNTL Praha.
16. Peters P.M., Houde-Walter S. N. (1998): Local structure of Er^{3+} in multicomponent glasses. *Journal of Non-Crystalline Solids*, *239*(1-3), 162-169. doi: 10.1016/S0022-3093(98)00733-9.
17. Arai K., Namikawa H., Kumata K., Honda T. (1986): Aluminum or phosphorus co-doping effects on the fluorescence and structural properties of neodymium-doped silica glass. *Journal of Applied Physics*, *59*(10), 3430–3438. doi: 10.1063/1.336848.