Broadband near-infrared emission in barium gallo-germanate glasses co-doped with bismuth, chromium and erbium ions

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Abstract—This work presents barium gallo-germanate glasses co-doped with Bi^+/Er^{3+} and Cr^{3+}/Er^{3+} ions for NIR luminescence. The addition of Al_2O_3 content in the glass matrix made it possible to obtain luminescence corresponding to the $^3P_1 \rightarrow ^3P_0$ transition of Bi^+ ions. Co-doping with the Bi^+/Er^{3+} system resulted in a broad luminescence spectrum of 1.0–1.6 μm, and Cr^{3+}/Er^{3+} co-doping in selected glass matrix resulted in luminescence in 0.9-1.6 μm band. However, the luminescence of the Cr^{3+} ions is much lower than that of Er^{3+} ions.

Optical amplification and the development of new ultra-broadband amplified spontaneous emission (ASE) sources present a research challenge. Near-infrared emission in the range of 1.0–1.6μm is widely studied due to potential applications in WDM systems for telecommunications [1]. While 1.5μm band amplification and ASE sources are commercially available and realized with erbium-doped amorphous materials, there is a problem with the 1.3 μm band. Research in this band for active glasses focuses on transition metals, bismuth, and quantum dots [2–5]. The main problem with using Ni^{2+} ions as dopants is the requirement of a nanocrystal environment for these ions to obtain luminescence in the 1.3 μm band. Moreover, glass-ceramics can be characterized by increased attenuation due to scattering losses caused by nanocrystal structures. Chromium ions, conversely, are characterized by luminescence in the 1.1μm and 1.3μm bands, depending on the divalent state (Cr^{3+}, Cr^{4+}) [6]. However, obtaining emission in the desired 1.3 μm band for Cr^{4+} ions is still a research challenge. Many different works have appeared on glasses doped with bismuth ions. Bi^+ ions do not require crystal structures to obtain luminescence around 1.3μm. However, their luminescence bands can vary depending on the glass matrix. In the case of lead-aluminum-germanate (PAG) glasses, the emission peak reaches 1250nm [4]. On the other hand, aluminum gallo-germanate glasses show luminescence at 1200nm or 1350nm, depending on the pump excitation [7]. The same phenomenon was observed for lithium alumino-sillicate glasses [8]. In the case of Bi^+/RE co-doped glasses, Bi^+/Er^{3+} silicate glass-ceramics and lanthanum-aluminosilicate glasses were reported with broad emission in the 1.0–1.6μm range [9–10]. However, there is still a lack of solutions for low phonon energy glasses doped with Bi^+/Er^{3+} for optical fiber applications. This letter presents the fabrication and luminescent properties of barium gallo-germanate (BGG) glasses doped with bismuth, chromium, and erbium ions characterized by near-infrared emission with suitable properties for optical fiber drawing.

Barium gallo-germanate (BGG) glass samples doped with bismuth and rare-earths ions had the following molar composition: $(50–x–y)GeO_2–25Ga_2O_3–10BaO–15Na_2O–xAl_2O_3–0.5Bi_2O_3–yEr_2O_3$, where x=0, 5, y=0, 0.05. The second set of BGG glasses doped with chromium and erbium ions had the following molar formula: $(50–n–m)GeO_2–25Ga_2O_3–10BaO–15Na_2O–nCr_2O_3–mEr_2O_3$ where n=0.35, 0.5 and m=0, 0.05. Glass samples were prepared by standard melting and quenching method. The homogeneous set was melted in platinum crucible for 30 minutes at 1500°C. Molten glass was poured into a stainless steel form and then annealed at 600°C for 6 hours. After slowly cooling to room temperature, glass samples were polished to get appropriate optical properties with a thickness of 3mm. Absorbance spectra of glass samples were measured using the Stellarnet Green-Wave spectrometer in a range of 300nm to 1000nm. Luminescence properties were measured with Acton 2300i monochromator under 808 nm pump excitation.

The influence of aluminum oxide content on the absorbance spectra of glass samples doped with 0.5 mol% Bi_2O_3 is presented in Fig. 1. For glass sample without Al_2O_3, we can observe a shift of the absorption edge towards longer wavelengths. In the case of the sample containing aluminum oxide, we can observe the absorption

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edge at the wavelength of 350nm. Additionally, we found two bismuth absorption bands around 475nm and 725nm. The band at 475nm can be attributed to the red luminescence of Bi^{2+} ions, while the second band at 725nm corresponds to Bi^{+} emission in near-infrared. Moreover, bismuth was described as "the wonder metal" by Dianov in 2012 because no other element produces such a variety of products (Bi^{5+}, Bi^{3+}, Bi^{2+}, Bi^{+}) depending on the temperature of melting, so the absorbance spectra may depend on glass matrix and temperature of melting [11]. Changes in absorbance spectra after introducing Al_2O_3 content are connected with a modified field around bismuth [12].

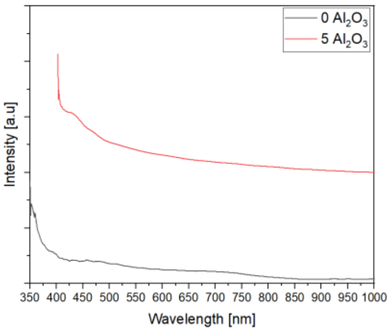

Fig. 1. Stacked absorbance spectra of BGG glass samples doped with 0.5 mol% Bi_2O_3.

The influence of Al_2O_3 content on luminescence properties of glass samples doped with 0.5 mol% Bi_2O_3 under 808 nm pump excitation is presented in Fig. 2. The luminescence spectrum of the sample without aluminum oxide was multiplied by 10 to show the difference in luminescence intensity between both glass samples. After adding Al_2O_3 to the glass matrix, it was possible to obtain strong luminescence of Bi^{+} ions corresponding to the $^3P_1 \longrightarrow ^3P_0$ at the wavelength of 1300nm. The influence of Al_2O_3 on the luminescence properties of bismuth-doped glasses was not fully investigated. However, it may reduce the non-radiative transitions between Bi^{n+} ions [13].

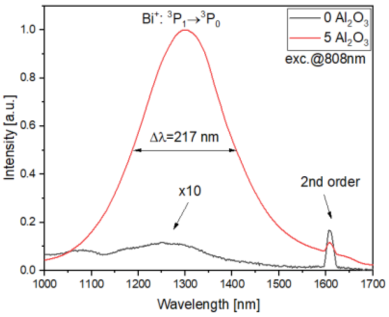

Fig. 2. Luminescence spectra of BGG glass samples doped with 0.5 mol% Bi_2O_3 and with varying content of Al_2O_3.

The calculated value of FWHM was 217nm. As mentioned before, Al_2O_3 content is a crucial factor in the analyzed BGG glass matrix in order to obtain luminescence of Bi^{+} ions.

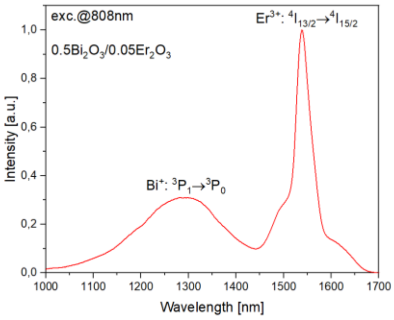

Fig. 3. Luminescence spectra of BGG glass samples co-doped with Bi^{+} and Er^{3+}, containing 5 %mol Al_2O_3.

After investigating the influence of Bi_2O_3 and Al_2O_3 content on luminescence properties, we decided to examine broadband emission using co-doped Bi^{+}/Er^{3+} BGG glass. The introduction of Er^{3+} allows to extend luminescence band to range from 1.0µm to 1.6µm. Figure 3 presents the luminescence spectrum of this sample. In the case of sample co-doped with Bi^{+} and Er^{3+} ions, we observed 1.0–1.65 µm broadband emission being the superposition of two luminescence bands corresponding to the $^3P_1 \longrightarrow ^3P_0$ transition of bismuth ions and $^4I_{13/2} \longrightarrow ^4I_{15/2}$ of erbium ions.

In the next step, we investigated BGG glasses doped with Cr^{3+} ions. The luminescence properties of glass samples are presented in Fig. 4 under 808nm pump excitation.

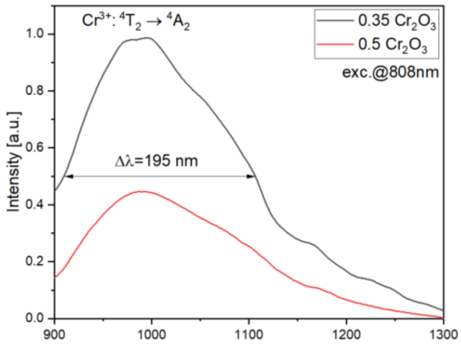

Fig. 4. Luminescence properties of BGG glass samples doped with Cr^{3+} ions.

We obtained a higher luminescence intensity for the sample doped with 0.35 mol% Cr_2O_3. Increasing Cr_2O_3 content to 0.5 mol% resulted in a significant decrease in luminescence intensity. Obtained emission spectra can be assigned to the $^4T_2 \longrightarrow ^4A_2$ transition of Cr^{3+} ions. At the same time, we did not notice a luminescence band corresponding to the $^3T_2 \rightarrow {}^3A_2$ transition of Cr^{4+} ions. FWHM value for the sample doped with 0.35 mol% Cr_2O_3 reached 195nm.

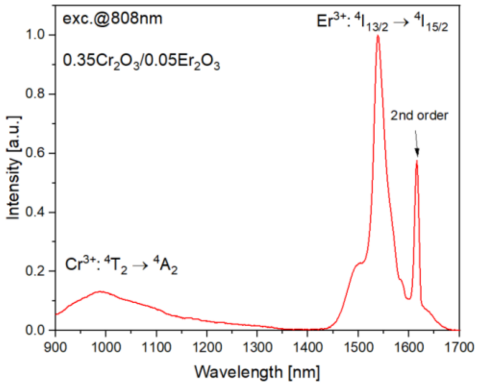

Fig. 5. The luminescence spectrum of BGG glass samples doped with Cr^{3+}/Er^{3+} ions.

To analyze the possibility of obtaining broadband luminescence spectra, we added a dopant in the form of 0.05 mol% Er_2O_3 to obtain broadband luminescence in the range of 1.0–1.6 µm. The luminescence spectrum is presented in Fig. 5 (λ_{exc}=808nm). We observed two emission bands at 1.1µm and 1.5µm, which can be attributed to the $^4T_2 \rightarrow {}^4A_2$ transition of Cr^{3+} ions and $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ions. Notably, we achieved a reduced luminescence intensity of Cr^{3+} ions against the erbium background compared to that observed with bismuth.

Based on the results of the luminescence spectra of bismuth-doped samples, it can be concluded that the condition for obtaining a 1.3µm luminescence band in the BGG glass is the presence of a bismuth ions separator. Moreover, it is attractive that Bi^+ glass sample covers O and E telecommunication bands. The presented BGG glass sample co-doped with Bi^+/Er^{3+} ions shows broad luminescence in the 1.0–1.6 µm band, and spectra cover O, E, S, and C telecommunication bands. However, it is worth mentioning that the luminescence intensity of Bi^+:$^3P_1 \rightarrow {}^3P_0$ transition is much lower than the luminescence band of Er^{3+} ions corresponding to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition. Glasses doped with Cr^{3+} show luminescence around 1100 nm, and compared to doping with Bi^+, their luminescence intensity on the background of Er^{3+} emission intensity is lower. To summarize, analyzed $Bi^+/Cr^{3+}/Er^{3+}$ doped BGG glasses show good properties for fiber drawing, and this type of glasses can find applications in broadband fiber amplifiers and ASE sources operating in the 1.0–1.6µm band.

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References

[1] T. Suzuki, G.S. Murugan, Y. Ohishi, Appl. Phys. Lett. **86**(13), 131903 (2005), doi: 10.1063/1.1891272
[2] N.V. Golubev *et al.*, J. Non-Cryst. Solids **515**, 42 (2019), doi: 10.1016/j.jnoncrysol.2019.04.006.
[3] Z. Xu, W. Feng, T. Chen, X. Liu, J. Qiu, Opt. Laser Technol. **158**, 108910 (2023), doi: 10.1016/j.optlastec.2022.108910.
[4] M.A. Hughes, T. Suzuki, Y. Ohishi, J. Non-Cryst. Solids **356**(44–49), 2302 (2010), doi: 10.1016/j.jnoncrysol.2010.03.043.
[5] J. Song, Z. Zhou, B. Zhong, M. Zhang, J. Huang, L. Han, J. Alloys Compd. **968**, 172126 (2023), doi: 10.1016/j.jallcom.2023.172126.
[6] M.A.U. Martines, M.R. Davolos, M.J. Júnior, D.F. de Souza, L.A.O. Nunes, J. Lumin. **128**(11), 1787 (2008), doi: 10.1016/j.jlumin.2008.04.011.
[7] S. Zhou, H. Dong, H. Zeng, J. Hao, J. Chen, J. Qiu, J. Appl. Phys. **103**(10), 103532, (2008), doi: 10.1063/1.2917303.
[8] T. Suzuki, Y. Ohishi, Appl. Phys. Lett. **88**(19), 191912 (2006), doi: 10.1063/1.2203214.
[9] T. Minh Hau *et al.*, Opt. Mater. **35**(3), 487 (2013), doi: 10.1016/j.optmat.2012.10.021.
[10] H.K. Dan *et al.*, J. Lumin. **219**, 116942 (2020), doi: 10.1016/j.jlumin.2019.116942.
[11] E.M. Dianov, Light Sci. Appl. **1**(5), 5 (2012), doi: 10.1038/lsa.2012.12.
[12] L. Wang, L. Tan, Y. Yue, M. Peng, J. Qiu, J. Am. Ceram. Soc. **99**(6), 2071 (2016), doi: 10.1111/jace.14197.
[13] Z. Jiang *et al.*, J. Non-Cryst. Solids **383**, 196 (2014), doi: 10.1016/j.jnoncrysol.2013.03.040.