



**You have downloaded a document from
RE-BUŚ
repository of the University of Silesia in Katowice**

Title: Rare earth doped lead-free germanate glasses for modern photonics

Author: Joanna Janek, Joanna Pisarska, Wojciech A. Pisarski

Citation style: Janek Joanna, Pisarska Joanna, Pisarski Wojciech A. (2014). Rare earth doped lead-free germanate glasses for modern photonics. "Photonics Letters of Poland" Vol. 6, no 2 (2014), s. 71-73, doi 10.4302/plp.2014.2.08



Uznanie autorstwa - Licencja ta pozwala na kopiowanie, zmienianie, rozprowadzanie, przedstawianie i wykonywanie utworu jedynie pod warunkiem oznaczenia autorstwa.



UNIwersYTET ŚLĄSKI
W KATOWICACH



Biblioteka
Uniwersytetu Śląskiego



Ministerstwo Nauki
i Szkolnictwa Wyższego

Luminescence decays from excited states of Pr^{3+} ions were also measured under 450nm excitation ($^3\text{P}_2$ state) while monitoring various emission wavelengths. Measured lifetimes are close to about 10 μs , when decay curves were monitored at 620 or 645nm emission wavelengths, respectively. They correspond to $^3\text{P}_0$ state of Pr^{3+} . Decay curve measurement under 450 nm excitation and 590nm emission wavelength gives quite different experimental results. In this case, the luminescence lifetime is close to 25 μs and its value is similar to that obtained from decay curve measurement under direct excitation of $^1\text{D}_2$ state by 590nm line and monitoring 620nm emission wavelength. It also confirmed that the broad band located in the reddish-orange spectral range overlaps two luminescence lines, which correspond to transitions originating from $^1\text{D}_2$ (orange band) and $^3\text{P}_0$ (red band) excited states of Pr^{3+} .

Figure 2 shows excitation and luminescence spectra of Eu^{3+} ions in lead-free germanate glasses. The excitation spectra were monitored at the 610nm emission wavelength. Several observed bands correspond to transitions originating from the $^7\text{F}_0$ ground state to the higher-lying $^5\text{G}_2$, $^5\text{L}_6$, $^5\text{D}_3$, $^5\text{D}_2$ and $^5\text{D}_1$ states of trivalent europium.

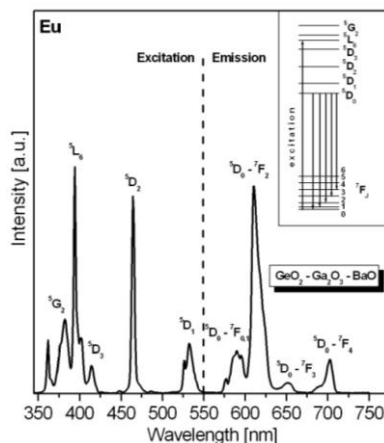


Fig. 2. Excitation and emission of Eu^{3+} in lead-free germanate glass.

The emission spectrum was measured under excitation by 393nm line ($^5\text{L}_6$ state). The excitation energy transfers nonradiatively very fast to the $^5\text{D}_0$ state due to small energy gaps between higher-lying excited states of Eu^{3+} . The energy gap between $^5\text{D}_0$ state and lower-lying $^7\text{F}_6$ state is quite large (Inset of Fig. 2). It suggests that radiative transitions from $^5\text{D}_0$ state are the dominant excited state relaxation. Several luminescence bands are observed, which correspond to $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J=0-4$) transitions of Eu^{3+} ions. Two of them, $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (red) and $^5\text{D}_0 \rightarrow ^7\text{F}_1$ (orange) transitions of Eu^{3+} are important from the spectroscopic point of view. The $^5\text{D}_0 \rightarrow ^7\text{F}_2$ red transition is an electric-dipole transition, which strongly depends on the environment surrounding Eu^{3+} ions. This

transition is also called hardly sensitive transition. The $^5\text{D}_0 \rightarrow ^7\text{F}_1$ orange transition has a magnetic-dipole character, which is less sensitive and independent of ligands around Eu^{3+} . The integrated luminescence intensity of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition to the integrated luminescence intensity of $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition is defined as red-to-orange luminescence intensity ratio R/O of Eu^{3+} . Based on the integrated luminescence intensities of each transition, the factor of R/O (Eu^{3+}) was calculated for lead-free germanate glass. The R/O factor of Eu^{3+} informs us about local asymmetry and covalence bonding between rare earths and nearest surroundings. Their values increase with increasing asymmetry and covalency. In our case, the factor of R/O (Eu^{3+}) is above 4, which suggests that the nearest surrounding Eu^{3+} ions is covalent in character. Luminescence decay from the $^5\text{D}_0$ state of Eu^{3+} ions was also measured. The luminescence decay curve is nearly exponential and the measured lifetime is close to 1.25ms.

Finally, the luminescence properties of Er-doped lead-free germanate glass in the visible and near-infrared spectral ranges have been studied. Figure 3 presents excitation and luminescence spectra of Er^{3+} in lead-free germanate glass. The spectra were measured in the UV-visible region. The excitation spectrum was monitored at the 545nm emission wavelength. The observed bands in the 350-500nm correspond to transitions originating from the $^4\text{I}_{15/2}$ ground state to the higher-lying $^4\text{G}_{9/2}$, $^4\text{G}_{11/2}$, $^2\text{G}_{9/2}$, $^2\text{F}_{3/2}$, $^4\text{F}_{5/2}$ and $^4\text{F}_{7/2}$ states of trivalent erbium. The emission spectrum was measured under excitation by the 488nm line ($^4\text{F}_{7/2}$ state). Generally, two emission lines in the green and red spectral region were successfully observed. The most intense green line corresponds to $^2\text{H}_{11/2}$, $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ transition, whereas the less intense red line is due to $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transition of erbium, respectively. All transitions are indicated on the energy level scheme (Inset of Fig. 3).

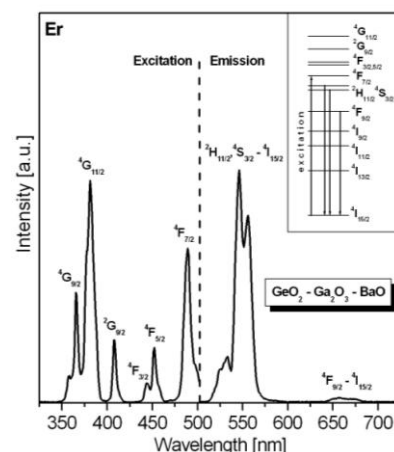


Fig. 3. Excitation and emission of Er^{3+} in lead-free germanate glass.

The near-infrared luminescence spectrum of Er^{3+} ions in lead-free germanate glass is presented in Fig. 4. The glass sample was excited by the 488nm line. The observed NIR luminescence at about 1530nm corresponds to the main ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ laser transition of Er^{3+} , which is demanded for broadband optical amplifiers operating in the third telecommunication window.

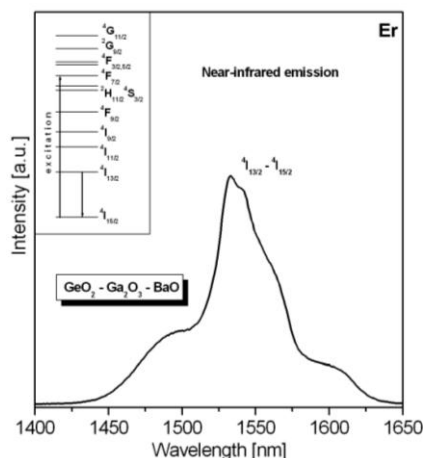


Fig. 4. Near-infrared emission of Er^{3+} in lead-free germanate glass.

One of the most important spectroscopic parameters is the measured luminescence lifetime for the excited level of rare earth ions. The relatively long luminescence lifetime of the metastable level required for the high population inversion is a critical factor in the success of Er-doped fiber amplifiers (EDFA) in the optical communications. The luminescence decay curve for the ${}^4\text{I}_{13/2}$ state of Er^{3+} was well fitted to a single exponential function because of the low activator concentration and the lack of energy transfer processes between erbium ions. The measured lifetime for ${}^4\text{I}_{13/2}$ state of Er^{3+} ions in lead-free germanate glass is close to 5.35ms and its value is higher in comparison to similar germanate glasses containing lead [14-16].

In conclusion, lead-free germanate glass systems in $60\text{GeO}_2\text{-}30\text{BaO}\text{-}9.5\text{Ga}_2\text{O}_3\text{-}0.5\text{Ln}_2\text{O}_3$ molar composition were prepared and next studied using excitation and luminescence spectroscopy. The rare earths as optically active ions were limited to Pr^{3+} , Eu^{3+} and Er^{3+} ions. Here, the experimental results are presented and discussed in relation to practical applications in modern visible and near-infrared photonics.

Several luminescence bands are successfully observed, corresponding to characteristic electronic transitions of trivalent rare earth ions. For Pr^{3+} -doped glass sample, the ${}^3\text{P}_0 \rightarrow {}^3\text{H}_4$ (blue) and ${}^3\text{P}_0 \rightarrow {}^3\text{F}_2$ (red) transitions located at about 490nm and 645nm are the most intense emission lines. The observed luminescence bands of Eu^{3+} are due to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ ($J=0\div 4$) transitions. Two of them, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ (red)

and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ (orange) transitions of Eu^{3+} ions are important from the spectroscopic point of view. The integrated emission intensities of both transitions defined as red-to-orange luminescence intensity ratio R/O (Eu^{3+}) inform us about local asymmetry and covalence bonding between rare earths and the nearest surroundings. Quite a high value of the R/O factor suggests that the nearest surrounding Eu^{3+} ions are covalent in character. Luminescence spectra for an Er^{3+} -doped glass sample were registered in the visible and near-infrared spectral ranges. The visible luminescence spectrum consists of two green and red bands, which are due to the ${}^2\text{H}_{11/2}$, ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$ and ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$ transitions of erbium, respectively. The observed NIR luminescence at about 1530nm corresponds to the main ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ laser transition of Er^{3+} . The relatively long luminescence lifetime for the upper ${}^4\text{I}_{13/2}$ laser state of Er^{3+} suggest that lead-free germanate glasses are promising materials for near-infrared broadband optical amplifiers operating in the third telecommunication window.

Acknowledgements: The National Science Centre (Poland) supported this work under research project 2011/03/B/ST7/01743.

References

- [1] M. Yamane, Y. Asahara, *Glasses for photonics* (Cambridge University Press 2000).
- [2] A. Jha *et al.*, *Prog. Mater. Sci.* **57**, 1426 (2012).
- [3] J.S. Wang, E.M. Vogel, E. Snitzer, *Opt. Mater.* **3**, 187 (1994).
- [4] J. Dorosz, *Ceramics* **86** (2005).
- [5] J. Dorosz, R.S. Romaniuk, *INTL J. Electron. Telecom.* **57**, 191 (2011).
- [6] M. Kochanowicz, W. Mazerski, J. Żmojda, K. Czajkowski, D. Dorosz, *Phot. Lett. Poland* **5**, 35 (2013).
- [7] J. Żmojda, D. Dorosz, M. Kochanowicz, J. Dorosz, *Phot. Lett. Poland* **2**, 76 (2010).
- [8] H. Lin, E.Y.B. Pun, B.J. Chen, Y.Y. Zhang, *J. Appl. Phys.* **103**, 056103 (2008).
- [9] S.S. Bayya, G.D. Chin, J.S. Sanghera, I.D. Aggarwal, *Opt. Expr.* **14**, 11687 (2006).
- [10] J.M. Jewell, P.L. Higby, I.D. Aggarwal, *J. Am. Ceram. Soc.* **77**, 697 (1994).
- [11] R.R. Xu, Y. Tian, M. Wang, L.L. Hu, J.J. Zhang, *Appl. Phys. B* **102**, 109 (2011).
- [12] R. Xu, Y. Tian, L. Hu, J. Zhang, *Appl. Phys. B* **104**, 839 (2011).
- [13] V.K. Tikhomirov, S.A. Tikhomirova, *J. Non-Cryst. Solids* **274**, 50 (2000).
- [14] R. Balda, A. Oleaga, J. Fernandez, J.M. Fdez-Navarro, *Opt. Mater.* **24**, 83 (2003).
- [15] H. Yamauchi, Y. Ohishi, *Opt. Mater.* **27**, 679 (2005).
- [16] W.A. Pisarski, Ł. Grobelny, J. Pisarska, R. Lisiecki, W. Ryba-Romanowski, *J. Alloys Compd.* **509**, 8088 (2011).