Journal of Alloys and Compounds 509 (2011) 8088–8092

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Spectroscopic properties of Yb^{3+} and Er^{3+} ions in heavy metal glasses

Wojciech A. Pisarski[a,*], Łukasz Grobelny[a], Joanna Pisarska[a], Radosław Lisiecki[b], Witold Ryba-Romanowski[b]

[a] University of Silesia, Institute of Chemistry, Szkolna 9, 40-007 Katowice, Poland
[b] Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna 2, 50-422 Wrocław, Poland

ARTICLE INFO

Article history:
Received 11 March 2011
Received in revised form 13 May 2011
Accepted 16 May 2011
Available online 23 May 2011

Keywords:
Heavy metal glasses
Rare earth ions
NIR Luminescence
Up-conversion

ABSTRACT

Selected heavy metal glasses containing Yb^{3+} and Er^{3+} ions have been studied. Near-infrared luminescence spectra at 1.53 μm and up-conversion spectra of Er^{3+} ions were registered under excitation of Yb^{3+} ions by 975 nm diode laser line. The luminescence bands correspond to $^4I_{13/2}$–$^4I_{15/2}$ (NIR), $^4S_{3/2}$–$^4I_{15/2}$ (green) and $^4F_{9/2}$–$^4I_{15/2}$ (red) transitions of Er^{3+}, respectively. The optical transitions of rare earth ions have been examined as a function of glass host. The unusual large spectral linewidth nearly close to 110 nm for $^4I_{13/2}$–$^4I_{15/2}$ transition of Er^{3+} ions in Yb–Er co-doped lead borate glass was obtained, whereas long-lived NIR luminescence at 1.53 μm was detected in lead germanate glass. The NIR luminescence and up-conversion phenomena strongly depend on stretching vibrations of glass host, which was confirmed by FT-IR spectroscopy.

1. Introduction

In recent years, many scientific works were devoted to optical properties of glass matrices containing Yb^{3+} and Er^{3+} ions [1–8]. The Yb^{3+} ions play the important role as an excellent sensitizer for Er^{3+}. When Yb^{3+} ions are pumped by 975 nm diode laser, the excitation energy is quickly transferred to Er^{3+}. The energy transfer process is usually very efficient due to small energy gap between $^2F_{5/2}$ (Yb^{3+}) and $^4I_{11/2}$ (Er^{3+}) excited states. There are two ways to depopulate the $^4I_{11/2}$ state of Er^{3+}. One of them is the most important radiative relaxation due to $^4I_{11/2}$–$^4I_{13/2}$ mid-infrared laser transition of Er^{3+} at about 2.8 μm, which is interesting in the domain of optical sources for sensors and applications in medicine. However, the quantum efficiency of this transition is rather low for several glass matrices. In most cases, the excitation energy relaxes nonradiatively to the upper $^4I_{13/2}$ laser state by multiphonon process. Next, we observe $^4I_{13/2}$–$^4I_{15/2}$ near-infrared laser transition of Er^{3+}, which is located in the eye-safe region and provides amplification near 1.5 μm in Erbium-Doped Fiber Amplifiers (EDFA). This is the most important NIR transition for application in the third optical communication window. On the other hand, the up-conversion process generating green and red luminescence is the second efficient way, which provide to depopulation of the $^4I_{11/2}$ state of Er^{3+}. Green and red lines are associated to $^4S_{3/2}$–$^4I_{15/2}$ and $^4F_{9/2}$–$^4I_{15/2}$ transitions of erbium ions, respectively. Glasses singly doped with Er^{3+} [9,10] or doubly doped with Er^{3+} and Yb^{3+} [11,12] were examined mainly for near-infrared (1.5 μm), mid-infrared (2.8 μm) and up-conversion luminescence applications. The up-conversion process in Yb–Er co-doped glass systems can also be applied for temperature sensing. Several glass matrices containing Yb^{3+} and Er^{3+} ions play a significant role in the sensitivity and accuracy of the up-conversion-based optical thermometer [13,14].

Heavy metal oxide, oxyfluoride and fluoride glasses referred as HMG systems singly doped with Er^{3+} [15–17] and doubly doped with Er^{3+} and Yb^{3+} [18] are very attractive and promising amorphous materials for near-infrared luminescence and up-conversion processes. An incorporation of lead oxide or bismuth oxide to traditional glasses containing rare earth ions significantly increases their radiative parameters. The radiative transitions start to dominate in the excited state relaxation and near-infrared luminescence bands of rare earth ions become more intense and long-lived. For that reason, we can also observe efficient conversion of near-infrared radiation into visible light for rare earth ions in heavy metal systems, in contrast to traditional high-phonon glasses. The experimental data obtained for heavy metal glasses doped with rare earth ions clearly indicate that the up-conversion processes play the important role for wide applications in the optoelectronics and medicine. For example, it is interesting to note that rare earth doped heavy metal glasses can be adopted for lighting in minimally invasive photodynamic therapy and minimally invasive surgery [19].

The presented work deals with heavy metal glasses doubly doped with Yb^{3+} and Er^{3+} ions. The near-infrared luminescence at 1.5 μm due to $^4I_{13/2}$–$^4I_{15/2}$ transition as well as green and red

---

* Corresponding author.
E-mail address: Wojciech.Pisarski@us.edu.pl (W.A. Pisarski).

0925-8388/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2011.05.056

up-conversion corresponding to $^2H_{11/2}$, $^4S_{3/2}$–$^4I_{15/2}$ and $^4F_{9/2}$–$^4I_{15/2}$ transitions of Er^{3+} were examined under direct excitation of Yb^{3+} ions by 975 nm diode laser. Optical transitions of Yb^{3+} and Er^{3+} ions were analyzed in lead germanate glass and compared to the ones obtained for lead borate glass. Our experimental data clearly demonstrate that lead germanate glasses and lead borate glasses belong to the same heavy metal glass family, but their spectroscopic properties are quite different. The results with the singly Yb-doped lead borate glass are also presented to clarify the excitation energy transfer process.

The energy transfer mechanism was studied by use of several combinations of Yb^{3+} and Er^{3+} concentrations [20]. The relatively high Yb^{3+} content is required for optimal energy transfer efficiency. The results obtained previously for lead germanate glass [21,22] indicate that the optimized rare earth doping ratio of Er^{3+} and Yb^{3+} is 1:5 in order to enhance pumping efficiency.

2. Experimental

Heavy metal oxide glass systems (%mol) in $45PbO–45GeO_2–4Ga_2O_3–1Er_2O_3–5Yb_2O_3$ and $45PbO–45B_2O_3–4Ga_2O_3–1Er_2O_3–5Yb_2O_3$ chemical compositions were prepared by mixing and melting appropriate amounts of metal oxides of high purity (99.99%, Aldrich Chemical Co.). A homogeneous mixture was heated in a protective atmosphere of dried argon in glove box in order to minimize OH^- content. Mixed reagents were melted for 0.5 h at 1100 °C, and then quenched and annealed below T_g in order to eliminate internal stresses. The same procedure was applied for preparation of Yb singly doped sample in $45PbO–45B_2O_3–5Ga_2O_3–5Yb_2O_3$ chemical composition.

Thermal behavior of the glass samples was characterized by the PerkinElmer calorimeter. The heating curves were acquired with the rate of 10°/min. The glass transition temperatures T_g were determined with the accuracy of ±1 °C. The FT-IR spectra were performed by Bruker spectrometer using standard KBr disc techniques.

Luminescence has been excited with diode laser at 975 nm, then dispersed by a 1 m double grating monochromator and detected with a photomultiplier with S-20 spectral response or InGaAs detector, depending on spectral region. Luminescence spectra were recorded using a Stanford SRS 250 boxcar integrator controlled by a computer. Luminescence decay curves were recorded and stored by a Tektronix TDS 3052 oscilloscope. The resolution for spectral measurements was ±0.1 nm. Luminescence decay curves with accuracy ±1 μs were acquired. All measurements were carried out at room temperature.

3. Results and discussion

Ternary $PbO–GeO_2–Ga_2O_3$ and $PbO–B_2O_3–Ga_2O_3$ glass systems co-doped with Yb^{3+} and Er^{3+} ions were prepared by conventional melting and quenching method. The molar ratio $PbO:GeO_2 = PbO:B_2O_3 = 1:1$ is the same in the studied heavy metal glasses. The third Ga_2O_3 component plays the important role as a stabilizer of glass network. Additionally, the glass samples were prepared under the same experimental conditions (melting temperature and time), so the spectroscopic changes for rare earth ions are due to presence of GeO_2 or B_2O_3 component in lead-based heavy metal glasses, only. From the DSC curves, the glass transition temperatures T_g were determined for the studied glass systems. Our previously published results for lead borate glasses indicate that values of the glass transition temperature T_g varied from 310 °C to 475 °C, dependently on the B_2O_3/PbO ratio and the PbF_2 content [23]. For oxide glass, the glass transition temperature T_g is close to 440 °C and its value starts to decrease for oxyhalide glass samples with PbX_2 in $X = Br$ (390 °C) → $X = Cl$ (375 °C) → $X = F$ (340 °C) direction [24]. In this case, the glass transition temperature reduces from 440 °C to 397 °C when B_2O_3 component was replaced by GeO_2 in the studied PbO-based heavy metal glasses. The thermal data are in a good agreement with the previously obtained results for similar lead germanate glasses, for which glass transition temperatures T_g varies from 382 °C to 402 °C, depending on Er^{3+} concentration [25].

Two excited state relaxation processes can be observed after the nearly resonant energy transfer from $^2F_{5/2}$ state of Yb^{3+} to $^4I_{11/2}$ state of Er^{3+}. The first excited state relaxation is connected with near-infrared laser emission at about 1.5 μm, which is important for third optical telecommunication window.

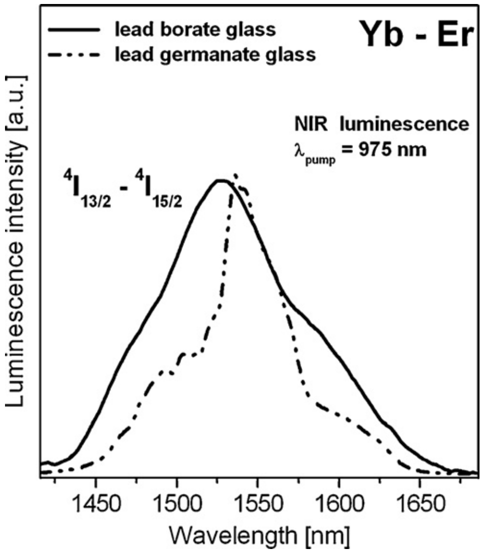

Fig. 1. Near-infrared luminescence of Er^{3+} ions in glass samples under excitation of Yb^{3+}.

Fig. 1 presents near-infrared luminescence of Er^{3+} ions in lead borate glass and lead germanate glass upon excitation of the $^2F_{5/2}$ state of Yb^{3+} with a diode laser at 975 nm. The excited Yb^{3+} ion resonantly transfers its energy to Er^{3+} ion, which nonradiatively decays from the $^4I_{11/2}$ state to the $^4I_{13/2}$ upper laser state. Then, we observe near-infrared emission lines centered at $\lambda_p = 1525$ nm for lead borate glass and $\lambda_p = 1535$ nm for lead germanate glass, which are associated to main $^4I_{13/2}$–$^4I_{15/2}$ laser transition of Er^{3+}. Luminescence lines were normalized in order to compare their spectral widths. The spectral linewidth for $^4I_{13/2}$–$^4I_{15/2}$ transition of Er^{3+} defined as full width in half maximum (FWHM) is twice higher for lead borate glass ($\Delta\lambda = 110$ nm) than lead germanate glass ($\Delta\lambda = 55$ nm). Our previously published results for lead borate glasses singly doped with Er^{3+} [10] indicate that the proper amount of B_2O_3 in heavy metal systems improved broadband property, which is very important for tunable NIR laser active media. The spectral linewidth $\Delta\lambda$ close to 100.5 nm was obtained for the oxide Er-doped lead borate glass and its value was reduced for the oxyhalide glass samples in Br → Cl → F direction [10]. Here, we observe the unusual large spectral linewidth for $^4I_{13/2}$–$^4I_{15/2}$ transition of Er^{3+} ions in Yb–Er co-doped lead borate glass. The $\Delta\lambda$ value is nearly close to 110 nm, which is required for tunable solid-state lasers and broadband optical amplifiers.

On the other hand, luminescence lifetime for the $^4I_{13/2}$ state of Er^{3+} is an important spectroscopic parameter for optical amplifiers. The relatively long lifetime of the metastable state required for the high population inversion is the critical factor in the success of Er-doped fiber amplifiers in the optical communications [16]. Lead borate glasses singly doped with Er^{3+} or doubly doped with Yb^{3+} and Er^{3+} exhibit very good broadband properties, but the luminescence decays from the upper $^4I_{13/2}$ laser state are relatively short compared to lead germanate glass. Luminescence decays from the $^4I_{13/2}$ state of Er^{3+} ions were analyzed in our previous works [10,26]. Luminescence decay analysis clearly indicates that the $^4I_{13/2}$ lifetime of Er^{3+} ions in lead borate glass is close to 400 μs and its value increases up to 820 μs, when PbO was totally replaced by PbF_2 [26]. Our values are not changed, when glass samples are co-doped with Yb^{3+} and Er^{3+}. It is in a good agreement with the results obtained earlier by Kassab et al. [27], where the same values of luminescence lifetimes for $^4I_{13/2}$ state of Er^{3+} in lead fluoroborate glasses singly

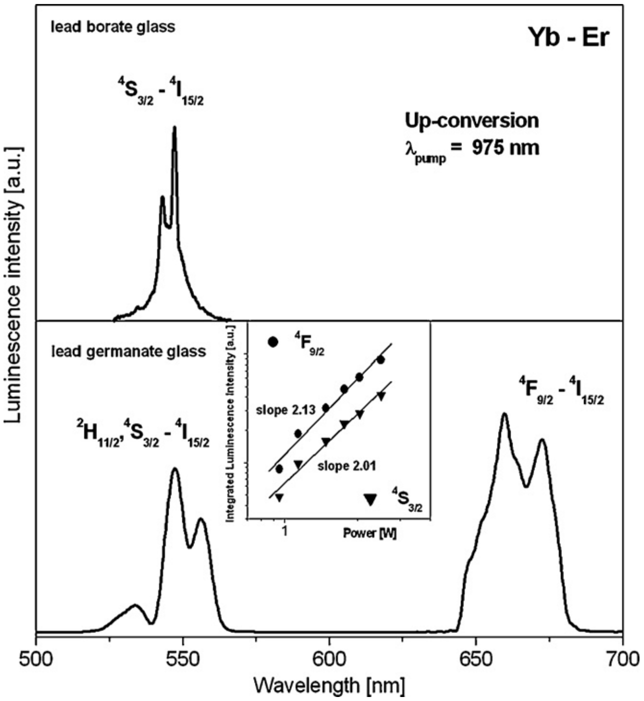

Fig. 2. Up-conversion luminescence of Er^{3+} ions in glass samples under excitation of Yb^{3+} Inset shows logarithmic dependence of integrated luminescence intensity on the excitation power.

doped with Er^{3+} and co-doped with Er^{3+} and Yb^{3+} were determined. However, these values are considerably lower than that obtained for lead germanate glass. The relatively long-lived near-infrared luminescence with the $^4I_{13/2}$ lifetime of 3.24 ms was detected for our lead germanate glass doubly doped with Yb^{3+} and Er^{3+}, which is about one magnitude of order higher in comparison to lead borate glass. The lifetime is consistent with the values (τ = 3.5–4.0 ms) measured for $PbO–GeO_2–Nb_2O_5$ glasses [28], but smaller than for the oxyfluoride lead germanate glass systems [16,29].

We can conclude that the spectroscopic parameters such as spectral linewidth and luminescence lifetime for rare earth ions in lead borate glass and lead germanate glass are quite different. Their values are strongly affected by glass hosts. From this point of view, the proper choice of glass host, which we would like to use for tunable and long-lived NIR luminescence is a compromise between spectral linewidth and luminescence lifetime for excited state of rare earth ions.

The second excited state relaxation is related to the up-conversion process, which usually generates green and red luminescence. Fig. 2 presents up-conversion luminescence spectra for lead borate glass (top) and lead germanate glass (bottom) co-doped with Yb^{3+} and Er^{3+}, which were excited by 975 nm line of diode laser. Inset shows the log–log dependence of the up-conversion integrated luminescence intensities on the excitation power.

Two successive energy transfer processes in Yb^{3+}–Er^{3+} co-doped glass samples are needed for the excitation of $^4F_{7/2}$ state of Er^{3+} ions. The excited Yb^{3+} ion transfers energy to Er^{3+} ion, which results in the excitation of $^4I_{11/2}$ state. The same or neighboring Yb^{3+} ion transfers energy to the Er^{3+} ion once again. Thus, two Er^{3+} ions excited in the $^4I_{11/2}$ state interact with each other. One of them is promoted to the $^4F_{7/2}$ state, whereas the other relaxes to the ground state. Then, the energy is nonradiatively transferred very fast from $^4F_{7/2}$ state to $^4S_{3/2}$ state by multiphonon relaxation. Finally, the excitation energy relaxes to the $^4I_{15/2}$ ground state emitting green light. When concentration of Er^{3+} is relatively high, the $^4F_{9/2}$ state was populated by well known cross-relaxation processes and red luminescence originating to transition from the $^4F_{9/2}$ state to the $^4I_{15/2}$ ground state occurs [30]. Fig. 3 presents the energy levels diagram, where all optical transitions are schematized in the case of the energy transfer process (ET) between Yb^{3+} and Er^{3+}.

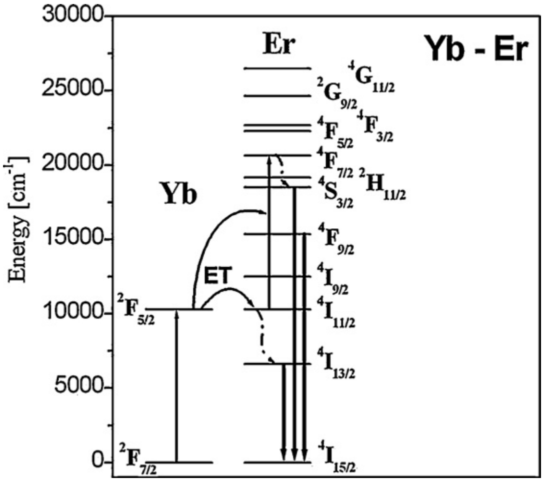

Fig. 3. Energy level diagram for Yb–Er systems. All radiative and nonradiative transitions are also schematized in the case of the energy transfer process (ET) between Yb^{3+} and Er^{3+}.

Similarly to previous work [28], the intense and broad green and red up-conversion lines of Er^{3+} ions in lead germanate glass were detected upon excitation of Yb^{3+}. Luminescence bands correspond to the $^2H_{11/2}$–$^4I_{15/2}$ (green), $^4S_{3/2}$–$^4I_{15/2}$ (green) and $^4F_{9/2}$–$^4I_{15/2}$ (red) transitions of Er^{3+}. The up-conversion lines can be enhanced in the presence of Au nanoparticles [31,32] and lead halide PbX_2, where X denotes Cl [33,34] or F [35,36] in lead germanate glasses. The up-conversion luminescence intensity was increased drastically with GeO_2 content in mixed oxyfluoride $TeO_2–GeO_2–PbF_2–BaF_2$ glass systems co-doped with Yb^{3+} and Er^{3+} [37]. These effects are important for Yb–Er visible waveguide devices [38].

Here, we also observe quite intense red line due to $^4F_{9/2}$–$^4I_{15/2}$ transition of Er^{3+}, but concentration of Er^{3+} is relatively low. There exist two main possible pumping mechanisms for red luminescence. The first pumping mechanism is associated to fast nonradiative decay through multiphonon interaction from the $^4S_{3/2}$ state to the $^4F_{9/2}$ state. The energy gap between $^4S_{3/2}$ and $^4F_{9/2}$ states is about 3200 cm^{-1}, whereas phonon energy of the lead germanate glass is close to about 800 cm^{-1}. It indicates that at least four phonons would be required to bridge the energy gap between $^4S_{3/2}$ and $^4F_{9/2}$ excited states. Based on the second pumping mechanism, the $^4F_{9/2}$ state is populated using the following energy transfer processes:

$$^2F_{5/2}\,(Yb^{3+}) + {}^4I_{13/2}\,(Er^{3+}) \rightarrow {}^2F_{7/2}\,(Yb^{3+}) + {}^4F_{9/2}\,(Er^{3+})$$

$$^4I_{13/2}\,(Er^{3+}) + {}^4I_{11/2}\,(Er^{3+}) \rightarrow {}^4I_{15/2}\,(Er^{3+}) + {}^4F_{9/2}\,(Er^{3+})$$

Sun and et al. [34] deduced that the first pumping mechanism for the red luminescence is rather unlikely.

The log–log dependence of up-conversion luminescence intensities for the $^4S_{3/2}$–$^4I_{15/2}$ and $^4F_{9/2}$–$^4I_{15/2}$ transitions on the excitation power was determined. It can be obtained using the following relation: $I_{UPC} \sim P^n_{pump}$, where: I_{UPC} denotes the up-conversion integrated luminescence intensity, P—the laser power and n—photons. The slope of 2.01 and 2.13 for $^4S_{3/2}$–$^4I_{15/2}$ and $^4F_{9/2}$–$^4I_{15/2}$ transitions indicates that 2-photon mechanism was involved in the up-conversion process.

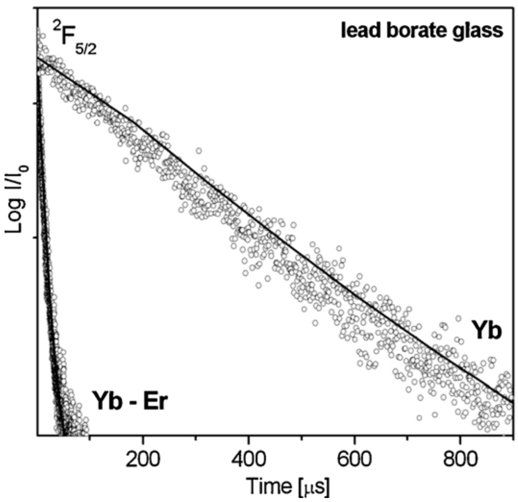

Fig. 4. Luminescence decay curves for $^2F_{5/2}$ state of Yb^{3+} in lead borate glass singly doped with Yb^{3+} ions and doubly doped with Yb^{3+} and Er^{3+} ions.

Quite different situation is observed for lead borate glass doubly doped with Yb^{3+} and Er^{3+}. Here, we detect very low intense and narrow green up-conversion luminescence due to the $^4S_{3/2}$–$^4I_{15/2}$ transition of Er^{3+} under excitation of Yb^{3+}. The relatively high power of the excitation source (3 W) was used to register the luminescence spectrum, due to low efficiency of the up-conversion process. This process is not observed for the studied system in the low power limit of the diode laser. For that reason, the log–log dependence of up-conversion luminescence intensity on the excitation power was not determined. It is consistent with the previously published results obtained for lead borate glasses singly doped with Er^{3+} ions. In contrast to Yb–Er glass systems, the conversion of near-infrared radiation into visible light does not occur for lead borate glass singly doped with Er^{3+} [1]. However, the up-conversion process is possible to detect for Er-doped lead borate glasses and transparent glass–ceramics under relatively high power of the excitation source [39].

It is interesting to see why both near-infrared luminescence and up-conversion lines of Er^{3+} ions in Yb–Er co-doped lead borate glass are less efficient and short-lived. Which mechanism is responsible for quenching of up-conversion process in lead borate glass. From literature data it is well known that the presence of OH^- groups successfully quench up-conversion luminescence spectra of Er^{3+} ions in glasses [40]. However, our glass samples were prepared in a special glass box in order to minimize hydroxyl content. Moreover, the intensity of FT-IR band at 3400 cm^{-1} was monitored in order to minimize OH^- content. Especially, it is very important factor for synthesis of mixed oxyhalide glass systems with low OH^- content, where PbX_2 (X = F, Cl, Br) component is strongly hygroscopic. Our previous studies indicate that the Er-doped oxide and oxyhalide lead borate glasses possess low-intensity FT-IR bands due to stretching vibrations of OH^- groups [10].

Another possible explanation is very low efficiency of energy transfer from Yb^{3+} to Er^{3+}. For that reason, luminescence decays from $^2F_{5/2}$ state of Yb^{3+} ions in Yb-singly doped and Yb–Er co-doped lead borate glass samples were registered. Fig. 4 shows luminescence decay curves for the $^2F_{5/2}$ state of Yb^{3+} ions in lead borate glasses singly doped with Yb^{3+} and doubly doped with Yb^{3+} and Er^{3+}. The $^2F_{5/2}$ luminescence lifetime is close to 710 μs, which is in a good agreement with the results obtained for similar glass doped with Yb^{3+} [41]. The value of τ decreases from 710 μs to 25 μs in the presence of Er^{3+} ions. Therefore, the energy transfer efficiency given by $\eta = 1 - \tau_1/\tau_2$ (where $\tau_1 = 25\,\mu s$; $\tau_2 = 710\,\mu s$) is close to 96.5%. The excitation energy transfer between Yb^{3+} and Er^{3+} ions in lead borate glass is very efficient, because the energy mismatch between interacting excited states $^2F_{5/2}$ (Yb^{3+}) and $^4I_{11/2}$ (Er^{3+}) is very small. At consequence, the nearly resonant Yb → Er energy transfer in lead borate glass occurs, in contrast to Yb → Tm system [42].

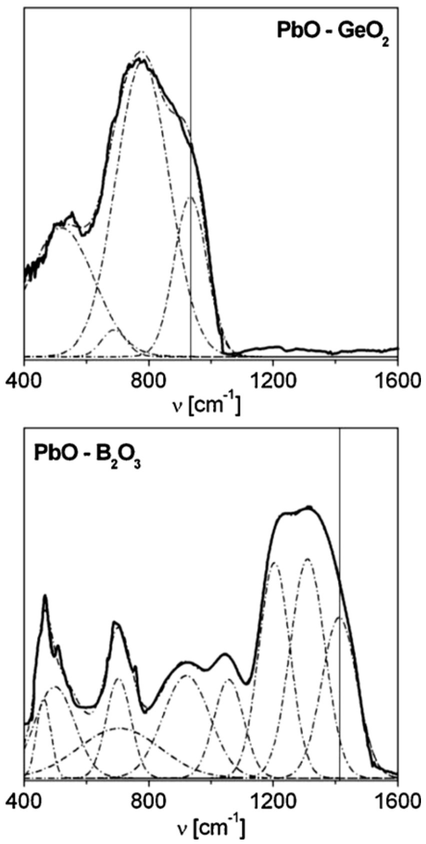

Fig. 5. FT-IR spectra for lead germanate glass and lead borate glass.

In aim to clarifying differences in the up-conversion luminescence, the FT-IR spectra for lead borate glass and lead germanate glass were carried out. Fig. 5 presents FT-IR spectra registered for the studied glass systems in the 400–1600 cm^{-1} frequency region, which were de-convoluted into Gaussian bands. In both cases, the FT-IR bands in the 460–520 cm^{-1} frequency region are observed, which correspond to Pb–O stretching vibrations of the $[PbO_4]$ structural units along with the deformation modes of the X–O glass network (X = Ge or B). The observed FT-IR bands in the 690–930 cm^{-1} frequency region are responsible for the vibrations of $[GeO_4]$, $[GeO_6]$ germanate units and interconnected through Ge–O–Ge bridges in $[GeO_4]$ structural units. The main FT-IR band located at about 775 cm^{-1} can be due to $[GeO_4]$ tetrahedral structural units attributable to the Ge–O–Ge asymmetric stretching modes [43]. Three characteristic groups of near-infrared bands are observed for lead borate glass. They correspond to BO_3 bending (650–700 cm^{-1}), B–O stretching vibrations of tetrahedral BO_4 units (850–1050 cm^{-1}) and trigonal BO_3 units (1200–1400 cm^{-1}), respectively [44]. The highest and most intense B–O and Ge–O stretching vibrations for both heavy metal glass systems are close to 1320 cm^{-1} and 775 cm^{-1}. It indicates that stretching vibrations of glass network are considerably higher for lead borate glass than lead germanate glass. At consequence, the up-conversion luminescence of Er^{3+} ions in lead borate glass was partially quenched by stronger vibrations of glass host. Our results clearly demonstrate that the vibration strengths of appropriate structural units surrounding around optically active ions are influenced strongly on the spectroscopic parameters for rare earth ions. This is also the main reason why we are not observed luminescence bands from the higher-lying $^4S_{3/2}$ and $^4F_{9/2}$ excited states of Er^{3+} in lead borate glass under 488 nm excitation in the $^4F_{7/2}$ state, in contrast to Er-doped lead germanate glass [28].

4. Conclusions

Two excited state relaxation processes originating from Er^{3+} ions in selected heavy metal glass systems have been observed, when $^2F_{5/2}$ state of Yb^{3+} ions was excited with diode laser at 975 nm. The first one is related to the near-infrared $^4I_{13/2}$–$^4I_{15/2}$ laser transition of Er^{3+} ions, which is useful for third optical telecommunication window. The second one is connected with green and red up-converted luminescence, which corresponds to the $^2H_{11/2}$,$^4S_{3/2}$–$^4I_{15/2}$ and $^4F_{9/2}$–$^4I_{15/2}$ transitions of Er^{3+} ions. The NIR luminescence spectra and up-conversion processes were examined as a function of glass host. Especially, some spectroscopic parameters like spectral linewidth for the $^4I_{13/2}$–$^4I_{15/2}$ transition and $^4I_{13/2}$ luminescence lifetime of Er^{3+} ions in Yb–Er co-doped lead borate glass and lead germanate glass were determined and compared. The unusual large spectral linewidth nearly close to 110 nm for $^4I_{13/2}$–$^4I_{15/2}$ transition of Er^{3+} ions in Yb–Er co-doped lead borate glass was obtained, which is required for tunable solid-state lasers and broadband optical amplifiers. On the other hand, the long luminescence lifetime of the $^4I_{13/2}$ metastable level is required for the high population inversion. The relatively long-lived NIR luminescence with $\tau(^4I_{13/2}) = 3.24$ ms was detected for lead germanate glass doubly doped with Yb^{3+} and Er^{3+}, which is about one magnitude of order higher in comparison to lead borate glass. Our investigations clearly demonstrate that the near-infrared and up-conversion luminescence phenomena strongly depend on stretching vibrations of glass host, which was confirmed by FT-IR spectroscopy.

Acknowledgement

The Ministry of Science and Higher Education supported this work under research project no N N204 313937.

References

[1] Z. Shang, G. Ren, Q. Yang, Ch. Xu, Y. Liu, Y. Zhang, Q. Wu, J. Alloys Compd. 460 (2008) 539.
[2] Y. Fang, L. Hu, M. Liao, L. Wen, J. Alloys Compd. 457 (2008) 19.
[3] K. Liu, E.Y.B. Pun, J. Alloys Compd. 470 (2009) 340.
[4] J. Zhou, F. Moshary, B.M. Gross, M.F. Arend, S.A. Ahmed, J. Appl. Phys. 96 (2004) 237.
[5] S.F. Li, Q.Y. Zhang, Y.P. Lee, J. Appl. Phys. 96 (2004) 4746.
[6] X.P. Jiang, Z.M. Yang, T. Liu, S.H. Xu, J. Appl. Phys. 105 (2009) 103113.
[7] G. Qin, W. Qin, Ch. Wu, D. Zhao, J. Zhang, S. Lu, S. Huang, W. Xu, J. Non Cryst. Solids 347 (2004) 52.
[8] S.W. Yung, S.M. Hsu, C.C. Chang, K.L. Hsu, T.S. Chin, H.I. Hsiang, Y.S. Lai, J. Non Cryst. Solids 357 (2011) 1328.
[9] H. Lin, S. Jiang, J. Wu, F. Song, N. Peyghambariam, E.Y.B. Pun, J. Phys. D: Appl. Phys. 36 (2003) 812.
[10] W.A. Pisarski, J. Pisarska, R. Lisiecki, Ł. Grobelny, G. Dominiak-Dzik, W. Ryba-Romanowski, Chem. Phys. Lett. 472 (2009) 217.
[11] D.F. de Sousa, L.F.C. Zonetti, M.J.V. Bell, R. Lebullenger, A.C. Hernandes, L.A.O. Nunes, J. Appl. Phys. 85 (1999) 2502.
[12] M. Ajroud, M. Haouari, H. Ben Ouada, H. Maaref, A. Brenier, B. Champagnon, Mater. Sci. Eng. C 26 (2006) 523.
[13] P.V. dos Santos, M.T. de Araujo, A.S. Gouveia-Neto, J.A. Medeiros Neto, A.S.B. Sombra, IEEE J. Quant. Electron. 35 (1999) 395.
[14] L. Feng, B. Lai, J. Wang, G. Du, Q. Su, J. Lumin. 130 (2010) 2418.
[15] L.C. Courrol, L.R.P. Kassab, M.E. Fukumoto, N.U. Wetter, S.H. Tatumi, N.I. Morimoto, J. Lumin. 102–103 (2003) 91.
[16] S. Xu, Z. Yang, G. Wang, S. Dai, J. Zhang, L. Hu, Z. Jiang, J. Alloys Compd. 377 (2004) 253.
[17] W.A. Pisarski, J. Mol. Struct. 744–747 (2005) 473.
[18] A.S. Oliveira, M.T. de Araujo, A.S. Gouveia-Neto, A.S.B. Sombra, J.A. Medeiros Neto, N. Aranha, J. Appl. Phys. 83 (1998) 604.
[19] D.L. Yang, H. Gong, E.Y. Pun, X. Zhao, H. Lin, Opt. Express 18 (2010) 18997.
[20] L.R.P. Kassab, M.E. Fukumoto, L. Gomes, J. Opt. Soc. Am. B 22 (2005) 1255.
[21] Z. Yang, S. Xu, L. Hu, Z. Jiang, J. Alloys Compd. 370 (2004) 94.
[22] Q. Nie, Ch. Jiang, X. Wang, T. Xu, H. Li, Mater. Res. Bull. 41 (2006) 1496.
[23] W.A. Pisarski, J. Pisarska, Glass Technol.: Eur. J. Glass Sci. Technol. A 47 (2006) 159.
[24] J. Pisarska, R. Lisiecki, W. Ryba-Romanowski, G. Dominiak-Dzik, T. Goryczka, Ł. Grobelny, W.A. Pisarski, J. Non Cryst. Solids 357 (2011) 1228.
[25] H. Yamauchi, Y. Ohishi, Opt. Mater. 27 (2005) 679.
[26] W.A. Pisarski, G. Dominiak-Dzik, W. Ryba-Romanowski, J. Pisarska, J. Alloys Compd. 451 (2008) 220.
[27] L.R.P. Kassab, L.C. Courrol, A.S. Morais, S.H. Tatumi, N.U. Wetter, L. Gomes, J. Opt. Soc. Am. B 19 (2002) 2921.
[28] R. Balda, J. Fernandez, M.A. Arriandiaga, J.M. Fdez-Navarro, Opt. Mater. 25 (2004) 157.
[29] Z. Yang, Z. Jiang, J. Lumin. 121 (2006) 149.
[30] Ch. Xu, Q. Yang, G. Ren, Y. Liu, J. Alloys Compd. 503 (2010) 82.
[31] L.R.P. Kassab, F.A. Bomfim, J.R. Martinelli, N.U. Wetter, J.J. Neto, C.B. de Araujo, Appl. Phys. B 94 (2009) 239.
[32] F.A. Bomfim, J.R. Martinelli, L.R.P. Kassab, T.A. Assumpcao, C.B. de Araujo, J. Non Cryst. Solids 356 (2010) 2598.
[33] H. Sun, L. Zhang, L. Wen, M. Liao, J. Zhang, L. Hu, S. Dai, Z. Jiang, Appl. Phys. B 80 (2005) 881.
[34] H. Sun, L. Wen, Z. Duan, L. Hu, J. Zhang, Z. Jiang, J. Alloys Compd. 414 (2006) 142.
[35] Z. Yang, S. Xu, L. Hu, Z. Jiang, J. Opt. Soc. Am. B 21 (2004) 951.
[36] H. Sun, L. Hu, Ch. Yu, G. Zhou, Z. Duan, J. Zhang, Z. Jiang, Chem. Phys. Lett. 408 (2005) 179.
[37] Y. Zhang, Ch. Lu, Y. Feng, L. Sun, Y. Ni, Z. Xu, Mater. Chem. Phys. 126 (2011) 786.
[38] H. Gong, L. Lin, X. Zhao, E.Y.B. Pun, D.Z. Yang, H. Lin, J. Alloys Compd. 503 (2010) 133.
[39] W.A. Pisarski, J. Pisarska, R. Lisiecki, Ł. Grobelny, G. Dominiak-Dzik, W. Ryba-Romanowski, Opt. Mater. 31 (2009) 1781.
[40] S. Xu, D. Fang, Z. Zhang, Z. Jiang, J. Solid State Chem. 178 (2005) 2159.
[41] L.R.P. Kassab, L.C. Courrol, N.U. Wetter, L. Gomes, V.L.R. Salvador, A.S. Morais, J. Alloys Compd. 344 (2002) 264.
[42] J. Pisarska, R. Lisiecki, W. Ryba-Romanowski, G. Dominiak-Dzik, W.A. Pisarski, J. Alloys Compd. 451 (2008) 226.
[43] S. Rada, E. Culea, M. Rada, J. Non Cryst. Solids 356 (2010) 1277.
[44] W.A. Pisarski, T. Goryczka, B. Wodecka-Duś, M. Płońska, J. Pisarska, Mater. Sci. Eng. B 122 (2005) 94.