Replacement of glass-former B_2O_3 by GeO_2 in an amorphous host evidenced by optical methods

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Abstract—Two completely different glass-host matrices containing lead, i.e. borate and germanate glasses doped with erbium were studied. The replacement of glass-former B_2O_3 by GeO_2 in an amorphous host was evidenced by optical methods. The luminescence decay from the $^4I_{13/2}$ upper laser state of Er^{3+} ions is relatively short, whereas the up-converted emission signal is reduced definitely in borate glass containing lead due to its high B-O stretching vibrations. The results indicate that germanate glasses containing lead are promising for near-infrared luminescence and up-conversion applications.

Heavy metal oxide glasses referred as HMOG systems belonging to a family of non-crystalline host materials have received great attention in the last years. This glass family has high chemical durability and thermal stability against crystallization, heat capacity and thermal conductivity, wide range of light transmission, quite large glass-forming region easy to incorporate rare earths as optically active ions, and relatively high values of refractive indices. In particular, the last parameter, i.e. a large refractive index of the HMOG system improves radiative transitions for rare earth ions. Among inorganic HMOG systems, radiative properties of rare earth ions in germanate [1–3] and borate [4–6] glasses containing lead are excellent. They were characterized by using various spectroscopic techniques. These phenomena are important in relation to practical applications in photonic devices and such glass systems can be successfully used, among others, for up-conversion luminescence systems [7] or optical fibers [8–10]. Further investigations indicate that the replacement of glass-modifier PbO by PbF_2 in germanate [11] and borate [12] glasses modify the glass-host structure and influence significantly the optical properties of rare earths. Optical changes are evidently stronger, where glass-former B_2O_3 is replaced by GeO_2 in an amorphous host. These optical aspects are examined here. Optically active ions were limited to trivalent Er^{3+}, the most popular and important rare earth ion in photonics.

Heavy metal oxide glasses in %mol: $45Me_xO_y$-45PbO-$9Ga_2O_3$-$1Er_2O_3$ (where Me_xO_y denotes B_2O_3 or GeO_2) have been synthesized in a traditional way, where reagents were melted at 1100°C for 0.5h. Before this procedure, all reagents were mixed together in an agate ball mill in order to obtain a homogeneous composition. Emission spectra were recorded under diode-laser excitation at 980nm. For measurements of emission spectra and their decays, a PTI QuantaMaster QM40 was also used, coupled with a tunable pulsed optical parametric oscillator (OPO), pumped by a third harmonic of a Nd:YAG laser (Opotek Opolette 355 LD). The emission was dispersed by double 200mm monochromators and recorded using a multimode UVVIS PMT (R928) and Hamamatsu H10330B-75 detectors. The measurements were carried out with a resolution of 0.1nm. The lifetimes were measured with an accuracy of 1μs.

Two excited state relaxation processes are observed in the studied glass systems under excitation of the $^4I_{11/2}$ state of Er^{3+} ions with a diode laser at 980nm. The first excited state relaxation is related to near-infrared luminescence of trivalent Er^{3+}, which is important for a telecommunication window and broadband optical amplifiers. The second excited state relaxation is due to the conversion of infrared radiation (λ_{exc}=980nm) into visible light. It results in generation of green and red luminescence lines of Er^{3+}.

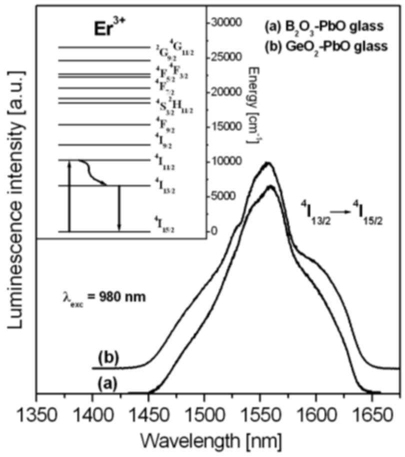

Fig. 1. NIR luminescence spectra of Er^{3+} ions in glass-hosts.

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Figure 1 shows near-infrared luminescence of Er^{3+} ions in germanate and borate glasses containing lead. Luminescence spectra centered at about 1530 nm correspond to main $^4I_{13/2} \rightarrow {}^4I_{15/2}$ laser transition of Er^{3+}. It was schematized on the Inset of Fig. 1.

Excitation energy transfers nonradiatively very fast from $^4I_{11/2}$ state to lower-lying $^4I_{13/2}$ state of Er^{3+} ions. Next, near-infrared luminescence corresponding to the electronic transition between the $^4I_{13/2}$ state and the $^4I_{15/2}$ ground state takes place. The spectral linewidth defined as full width at half maximum (FWHM) was determined and compared. In both cases, the spectral linewidths for the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} are relatively large and their values are close to 87 nm (GeO_2-PbO based glass) and 90 nm (B_2O_3-PbO based glass), respectively. Our previous investigations indicate that glass-modifiers M_2O_3 (where M = Ga or Al) in phosphate glass containing lead influenced strongly the luminescence linewidth for the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ions [13]. Quite an opposite situation is observed here. Independently of glass-former GeO_2 or B_2O_3, the spectral linewidth for the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} is quite large and both glass systems are promising for near-infrared tunable solid-state laser active media and broadband optical amplifiers. However, these glass-host systems are completely different, when we compare luminescence lifetimes for excited states of Er^{3+}.

It is generally accepted that luminescence lifetime for the $^4I_{13/2}$ upper laser state of Er^{3+} ions is an important spectroscopic parameter for broadband optical amplifiers. Based on numerous experimental studies it is well known that a relatively long $^4I_{13/2}$ luminescence lifetime is necessary for high population inversion. This is a crucial parameter in the successful way for erbium-doped fiber amplifiers working in a third telecommunication window.

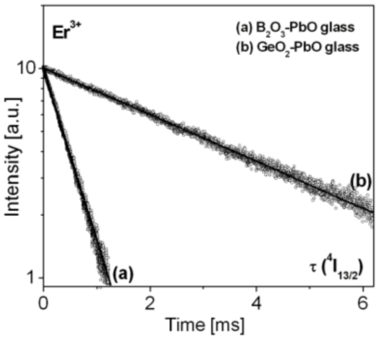

Fig. 2. Luminescence decays from the $^4I_{13/2}$ state of Er^{3+}.

Figure 2 presents luminescence decays from the $^4I_{13/2}$ upper laser state of Er^{3+} ions in germanate and borate glasses containing lead. The $^4I_{13/2}$ luminescence lifetimes of Er^{3+} ions are close to 3.9ms (GeO_2-PbO based glass) and 0.5ms (B_2O_3-PbO based glass), respectively. One can see that the replacement of glass-former B_2O_3 by GeO_2 in the studied glass-host results in an almost 8-fold enhancement in the luminescence lifetime. Based on luminescence decays and our previous investigations [14] it was suggested that germanate glass-host doped with erbium is evidently more preferred in relation to practical application for broadband optical amplifiers.

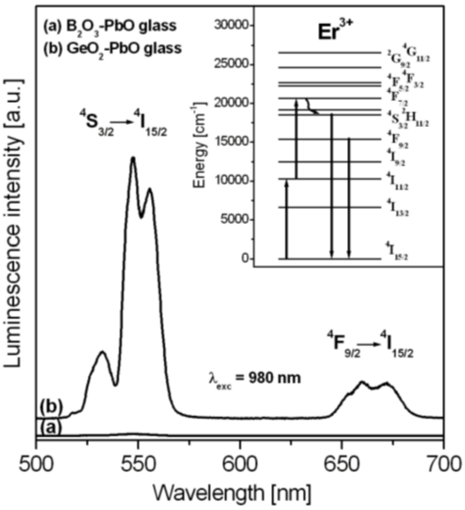

Fig. 3. Up-conversion luminescence of Er^{3+} ions in glass-hosts.

Figure 3 presents up-conversion luminescence spectra of Er^{3+} in germanate and borate glasses containing lead. The inset shows all transitions on the energy level scheme. Firstly, the $^4I_{11/2}$ state of Er^{3+} is populated after 980nm excitation by a diode laser. In the next step, the neighboring Er^{3+} ion transfers its energy to the same $^4I_{11/2}$ state. Thus, two Er^{3+} ions excited in the $^4I_{11/2}$ state interact with each other. As a consequence of this interaction, one of them is relaxes to the higher-lying $^4F_{7/2}$ state, whereas the other is transferred to the $^4I_{15/2}$ ground state. Finally, the excitation energy nonradiatively relaxes very fast from $^4F_{7/2}$ state to $^4S_{3/2}$ state and then luminescence lines corresponding to $^4S_{3/2} \rightarrow {}^4I_{15/2}$ (green) and $^4I_{9/2} \rightarrow {}^4I_{15/2}$ (red) transitions of Er^{3+} ions in germanate glass-host are well observed. Our further investigations clearly indicate that the replacement of glass-former GeO_2 by B_2O_3 in an amorphous host reduced definitively the up-converted emission signal. Green and red luminescence lines of Er^{3+} are practically absent for borate glass due to its high B-O stretching vibrations. However, the conversion of near-infrared radiation into visible light can be observed for Er^{3+} ions in borate glass containing lead and glass-ceramic under high-power of the excitation source [15]. These phenomena are strongly dependent on the phonon energy of the glass-host. The phonon energy is higher for borate glass than germanate glass [16–18]. The nonradiative multiphonon relaxation rates of rare earth ions increase exponentially with increasing phonon energy of the glass-host [19]. Thus, the up-converted luminescence signal in borate glass is usually reduced. It is due to higher multiphonon relaxation rates and lower radiative quantum efficiencies. The same situation was also well observed for luminescence decays from $^4I_{13/2}$ state of Er^{3+} presented in Fig. 2. The $^4I_{13/2}$ luminescence lifetime of Er^{3+} ions was shortened significantly due to high phonon energy and dominant multiphonon relaxation present in borate glass containing lead.

The log-log dependence of up-conversion emission intensities for the $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition on the excitation power was also determined using the following relation: $I_{UPC} \sim P^n$ where: I_{UPC} – the up-conversion integrated emission intensity, P – the laser power and n – the number of photons. The slope for the $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ions in germanate glass containing lead is equal to 1.8, suggesting a two-photon mechanism of the up-conversion luminescence process.

In summary, germanate and borate glasses containing lead were studied using optical methods. Optically active ions were limited to trivalent Er^{3+}. Up-conversion luminescence spectra and near-infrared luminescence spectra of Er^{3+} ions located at 1530nm were examined as a function of the glass-host. The replacement of glass-former GeO_2 by B_2O_3 results in the absence of the up-converted luminescence signal and the shortening of luminescence decay from the $^4I_{13/2}$ upper laser state of Er^{3+}. It is due to relatively high phonon energy of borate based glass. The experimental results clearly suggest that germanate glasses containing lead are promising materials for near-infrared luminescence and up-conversion applications.

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