Effect of GeO_2 content on upconversion luminescence of Er^{3+}-doped PbF_2-SiO_2-GeO_2 glasses

HONGPING MA
Department of Mechanical and Electrical, Zhejiang University of Science and Technology, Hangzhou 310012, People's Republic of China

SHIQING XU*
Institute of Optoelectronic Materials and Devices, College of Information Engineering, China Jiliang University, Hangzhou 310018, People's Republic of China
E-mail: shiqingxu75@hotmail.com

Solid-state blue and green light sources are desirable for high-density optical storage, color displays, optoelectronics, and medical diagnostics [1–4]. Many trivalent rare-earth ions such as Er^{3+}, Tm^{3+}, Ho^{3+}, Pr^{3+}, and Nd^{3+} were doped as absorption and emission centers in glass hosts. Among the rare-earth ions, Er^{3+} is one of the most studied rare-earth ions for green laser operation based upon upconversion [5, 6]. The host materials for Er^{3+}-doping are very important for obtaining highly efficient upconversion. This is because host materials with low phonon energy can reduce the nonradiative loss due to the mutiphonon relaxation and thus achieves strong upconversion luminescence. So far, much effort has been spent on fluoride glasses owing to their lower phonon energy than oxide glasses. However, chemical and thermal stability, corrosion resistance and fiberizability of these glasses as practical materials still remain problems [7]. Unlike for fluoride glasses, upconversion is seldom observed in oxide glasses with high phonon energies and can be limited to germanate [8], tellurite [9, 10], and gallate [9], glasses that have comparatively low phonon energies. Unfortunately silicate glasses, which are the most chemically and mechanically stable and also are more easily fabricated into various shapes such as a rod and optical fiber [7], have very faint upconversion fluorescence due to their large phonon energies [11]. Therefore, the design of a new silicate glass host for Er^{3+}-realizing intense upconversion fluorescence is a target at present.

As is known, glasses based on mixed oxide-halide systems combine the good optical properties of halide glasses (a broad range of optical transmittance and low optical losses) with the better chemical and thermal stability of oxide glasses [12], In our previous work [13], upconversion fluorescence spectroscopy of Er^{3+}/Yb^{3+}-codoped lead oxyfluorosilicate glass spectroscopic properties of Er^{3+}-doped oxyfluorosilicate glasses were investigated, and Er^{3+}/Yb^{3+}-codoped 50SiO_2-50PbF_2 glass showed intense upconversion luminescence and good thermal stability. In this letter, we report effect of GeO_2 content on upconversion luminescence of Er^{3+}-doped PbF_2-SiO_2-GeO_2 glasses.

Er^{3+}-doped 50PbF_2-(50-x)SiO_2-$x$$GeO_2-0.5Er_2O_3$ (PSGx, $x = 0, 10, 20, 30, 40$ mol%) glasses were prepared using the conventional melting and quenching method described in Ref. [13]. The upconversion luminescence spectra were obtained with a TRIAX550 spectrofluorimeter upon excitation of 975 nm LD with a maximum power of 2 W. In order to compare the luminescence intensity of Er^{3+} in different samples as accurate as we can, the position and power (100 mW) of the pumping beam and the width (1 mm) of the slit to collect the luminescence singnal were fixed under the same condition, and the samples were set at the same place in the experimental setup. In addition, the integrated intensities for the green and red emissions were also calculated to illustrate the variations of the luminescence intensity. The Raman spectrum was recorded on a FT Raman spectrophotometer Nicolet MODULE within the range of 100–1200 cm^{-1}. Nd:YAG operating at 1064 nm is used as the excitation source, and the laser power level was 500 mW. All measurements were taken at room temperature.

Fig. 1 shows the room temperature Raman spectrum of undoped PSGx glasses. In silicate glasses [14], the bands around 1060 and 950 cm^{-1} are assigned to stretching vibrations of Si–O–Si and $^{-}$O–Si–O^{-} groups, respectively. From Fig. 1. But only one scattering peak at 904 cm^{-1} in PSG0 glass was found, which only can be dissymmetry stretching vibration of $^{-}$O–Si–O^{-} bond in glass structure, and the scattering peak moves to long wavelength, which can be that the intensity of $^{-}$O–Si–O^{-} bond was weaken owing to polarization of Pb^{2+} and nonbridging

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* Author to whom all correspondence should be addressed.

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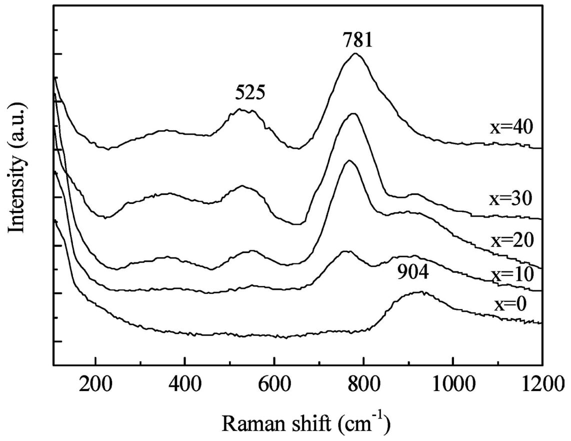

Figure 1 The Raman spectrum of undoped PSG*x* glasses.

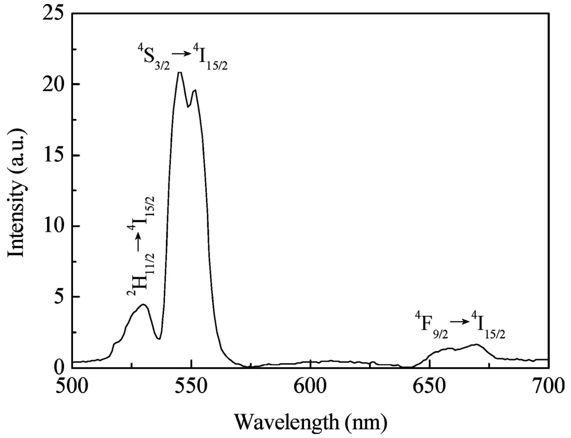

Figure 2 The temperature upconversion luminescence spectra of Er^{3+}-doped PSG40 glass under 975 nm excitation.

oxygen. With increasing GeO_2 content, the band intensity at 904 cm^{-1} was gradually weaken, and the new bands around 525 and 781 cm^{-1} were found, are assigned to bending vibrations of O–Ge–O group and dissymmetry stretching vibration of Ge–O–Ge [14]. From Fig. 1, it can be concluded that the maximum phonon energy of PSG*x* glasses decrease with increasing GeO_2 content.

The room temperature upconversion luminescence spectrum in the range of 500–700 nm for Er^{3+}-doped PSG40 glass under 975 nm excitation are shown in Fig. 2. The intense green bands at 529 and 545 nm correspond to the $^2H_{11/2} \rightarrow ^4 I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition, respectively. Besides the two green bands above, a weak red emission is observed at 657 nm, and associated with the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition. It is also important to point out that the green emission is bright enough to be observed by naked eye at excitation power as low as 70 mW for Er^{3+}-doped PSG40 glass sample.

Fig. 3 illustrates the dependence of upconversion luminescence intensity on GeO_2 content. With increasing GeO_2 content, the intensities of green (529 nm) and red (657 nm) emissions increase slightly, while the green emission (545 nm) increases significantly. These results suggest that GeO_2 has more influence on the green (545 nm) emission than the green (529 nm) and red (657 nm) emissions.

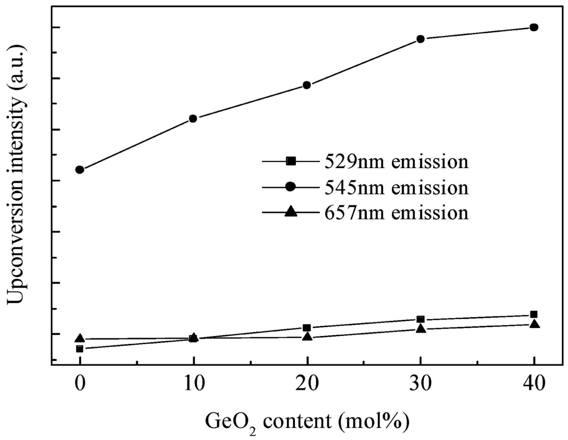

Figure 3 The dependence of upconversion luminescence intensity of Er^{3+}-doped PSG*x* glasses on GeO_2 content.

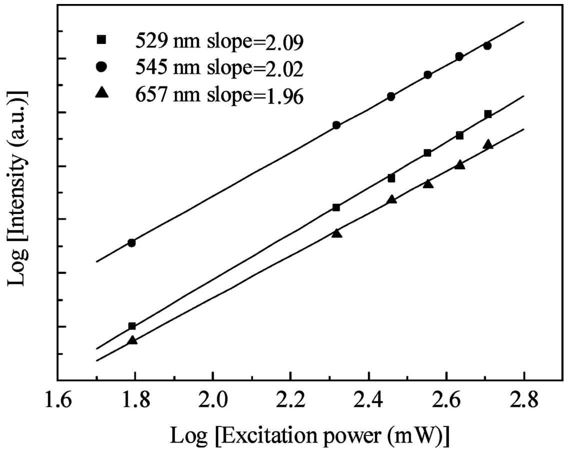

Figure 4 Dependence of upconversion fluorescence intensity on excitation power under 975 nm excitation for Er^{3+}-doped PSG40 glass.

The power dependence of the aforementioned upconversion signals was analyzed and the results are depicted in log–log plots of Fig. 4. As can be seen, all the three emissions present quadratic dependence on the excitation power, which indicates that two photon steps are involved for the upconversion process [3].

According to the energy matching conditions and the quadratic dependence on excitation power, the possible upconversion mechanisms for the emission bands are discussed based on the simplified energy levels of Er^{3+} presented in Fig. 5 [15–17]. For the green emissions, in the first step, the $^4I_{11/2}$ level is directly excited with 975 nm light. The second step involves the excitation processes based on the long-lived $^4I_{11/2}$ level as follows: Energy transfer (ET) $^4I_{11/2}$ (Er^{3+}) + $^4I_{11/2}(Er^{3+}) \rightarrow {}^4F_{7/2}(Er^{3+}) + {}^4I_{15/2}(Er^{3+})$, and excited state absorption (ESA) $^4I_{11/2}$ (Er^{3+}) + a photon $\rightarrow {}^4F_{7/2}$ (Er^{3+}). The populated $\rightarrow^4 F_{7/2}$ level of Er^{3+} then relaxes rapidly and nonradiatively to the next lower levels $^2H_{11/2}$ and $^4S_{3/2}$ resulting from the small energy gap

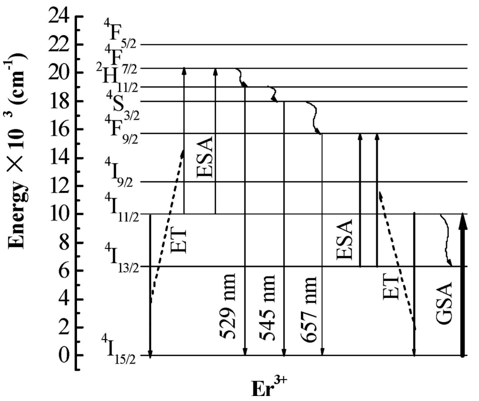

Figure 5 Energy level of Er^{3+} and possible transition pathways in Er^{3+}-doped PbF_2-SiO_2-GeO_2 glasses.

between them. The above processes then produces the two ${}^2H_{11/2} \rightarrow {}^4I_{15/2}$ and ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ green emissions centered at 529 and 545 nm, respectively. Since the energy gap below the ${}^4S_{3/2}$ level is larger over 3100 cm^{-1}, and the nonradiative transition through mutiphonon relaxation from ${}^4S_{3/2}$ level becomes smaller. Therefore, the bright green upconversion luminescence was emitted through the ${}^4S_{3/2} + {}^2H_{11/2} \rightarrow {}^4I_{15/2}$ transition. The relatively weak red emission entered at 657 nm is originated from the ${}^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition. The population of ${}^4F_{9/2}$ are based on the processes as follows: ESA: ${}^4I_{13/2}(Er^{3+})$ + a photon → ${}^4F_{9/2}$ (Er^{3+}), and ET between Er^{3+} ions: ${}^4I_{13/2}(Er^{3+}) + {}^4I_{11/2}(Er^{3+}) \rightarrow {}^4I_{15/2}(Er^{3+}) + {}^4I_{9/2}(Er^{3+})$. The ${}^4I_{13/2}$ level is populated owing to the nonradiative relaxation from the upper ${}^4I_{11/2}$ level. Besides, the nonradiative process from ${}^4S_{3/2}$ level, which is populated by means of the process described previously, to ${}^4F_{9/2}$ level also contributes to the red emission.

In conclusion, effect of GeO_2 content on upconversion lminescence of Er^{3+}-doped PbF_2–SiO_2–GeO_2 glasses under 975 nm excitation was investigated. Under 975 nm excitation, the intense green (529 and 545 nm) and relatively weak red (657 nm) emissions are observed at room temperature. The upconversion processes involved a sequential two-photon absorption for the green and red emissions. With increasing GeO_2 content, the intensities of green (529 nm) and red (657 nm) emissions increase slightly, while the green (545 nm) emission increases significantly. The intense green upconversion luminescence of Er^{3+}-doped PSG40 glass can be act as potential materials for developing upconversion optical devices.

Acknowledgments

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