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Frequency upconversion properties of Yb^{3+}-Er^{3+} co-doped oxyfluoride germanate glass

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Short wavelength output compact solid state lasers have become one of the most active areas of lasers research and development today [1]. Compared with other techniques, upconversion is of interest because it does not need either stringent constraint of phase matching or of high excitation wavelength stability and the output wavelength is not restricted to a given harmonic. In the past decades, the host materials widely studied for upconversion were fluoride crystals and glasses because fluorides have low nonradiative relaxation rates [2]. However, the mechanical strength, chemical durability and thermal stability of fluoride glasses are generally less than those of oxide glasses. These properties are important for developing rare-earth doped optical fibers. Recently, heavy metal oxide (HMO) glasses, which contain high content of PbO or Bi_2O_3, have considerable potential as lasing materials such as upconversion and planar optical waveguides [3, 4]. The HMO glasses mainly includes tellurite based glasses, bismuth based materials and germanate based glasses, which are desirable hosts for optically active ions. Of these HMO materials, lead germanate glasses are of growing interest, because they combine higher mechanical strength, chemical durability and better thermal stability even though the maximum phonon energy ($810\ cm^{-1}$) is slightly larger than that of tellurite glasses (750–780 cm^{-1}) [5–8]. In addition, the recent study of glasses containing more than one anion has revealed the possibility of the creation of glasses where the properties are varied by replacing the traditional oxygen by another anion, particularly by halides [9]. The substitution of a fluoride for an oxygen can improve the glass forming behavior of melts and the thermal stability of glasses [10, 11]. However, only a few reports have concentrated on the oxyfluoride germanate glasses and, few investigations have been carried out on the spectroscopic properties of rare-earth doped oxyfluoride germanate glasses. The present paper investigated the upconversion spectroscopic properties of Yb^{3+}-Er^{3+} co-doped $5.5NaF_2$-$8Na_2O$-$11.3PbO$-$14.5BaF_2$-$3.6Al_2O_3$-$4.1AlF_3$-$51.2GeO_2$ (mol%; GPAB, hereafter) glass. The doping concentrations of Yb^{3+} and Er^{3+} ions were 7.8×10^{20} and 0.78×10^{20} ions/cm^3, respectively.

The glass sample was synthesized by a conventional melting and quenching method [12]. Reagent grade NaF_2, Na_2CO_3, Pb_3O_4, BaF_2, Al_2O_3, AlF_3, and high purity GeO_2 (>99.999%) were used as starting materials. Yb^{3+} and Er^{3+} ions were introduced as Yb_2O_3 and Er_2O_3 with 99.99% purity, respectively. Batches of 20 g were carefully weighted and mixed homogeneously and then melted in a closed alumina crucible in an electric furnace at 1050 °C. During the melting, it was noted that acrid clouds of white vapor were released from the melts containing fluoride compounds. Therefore, it is necessary to shorten the melt time as short as possible. 10 min was considered suitable to obtain transparent and homogeneous samples. The 10-min period used here essentially represents the time required to heat the crucible and batches to a temperature above the melting point of the mixture. All melts were poured onto the stainless plate mold and annealed in a muffle oven at glass transformation temperature.

The obtained glass was cut and polished carefully to meet the requirements for optical measurements. Absorption spectra of the glass samples were recorded with a Perkin-Elmer-LANBDA 900UV/VIS/NIR spectrophotometer in the range of 380–1700 nm. Upconversion luminescence measurement was performed with a 976 nm laser diode (2W) excitation and detected by a TRIAX550 spectrophotometer controlled by a computer. All the measurements were taken at room temperature.

The absorption spectrum of the GPAB glass is presented in Fig. 1 where the absorption bands are assigned to transitions from the ground states $^4I_{15/2}$ of Er^{3+} and $^2F_{7/2}$ of Yb^{3+} to excited states. The absorption band of Yb^{3+} for the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition overlaps that of Er^{3+} for the $^4I_{15/2} \rightarrow {}^4I_{11/2}$ transition. When the excitation was performed at the $^2F_{5/2}$ level with a diode laser of 976 nm, the emission from the $^2F_{5/2}$ state of Yb^{3+} overlaps the absorption band for the $^4I_{15/2} \rightarrow {}^4I_{11/2}$ transition of Er^{3+} due to only one electronic excited state for Yb^{3+} ions [13]. This results in an efficient resonant-energy transfer (ET) from Yb^{3+} to Er^{3+} in the Yb^{3+}-Er^{3+} co-doped system.

The upconversion luminescence spectrum of the studied glass is shown in Fig. 2. The figure shows that the green and red emissions have similar intensity. Based on the absorption spectroscopic data the green emission bands centered at 531 and 546 nm are assigned to the $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$

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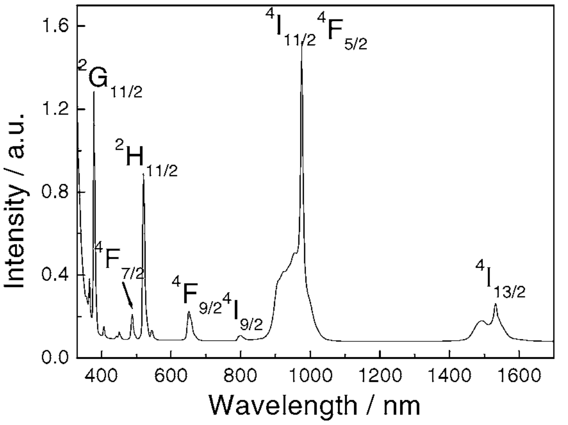

Figure 1 Absorption spectrum of Yb^{3+}-Er^{3+} co-doped GPAB glass.

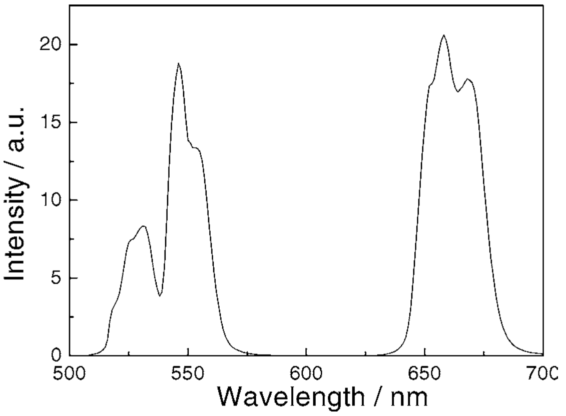

Figure 2 Upconversion spectrum of Yb^{3+}-Er^{3+} co-doped GPAB glass excited by 976 nm diode laser.

transitions of Er^{3+}, respectively. The 658-nm red emission band is associated with the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition.

In an upconversion mechanism the upconversion emission intensity $I_{\rm up}$ is proportional to the mth power of the infrared (IR) excitation intensity $I_{\rm IR}$; i.e., $I_{\rm up} \propto I_{\rm IR}^{\rm m}$ [14], where m is the number of the IR photons absorbed per upconversion photon emitted. Plotting log $I_{\rm UP}$ versus log $I_{\rm IR}$ yields a straight line with slope m, as shown in Fig. 3 for the green and red emissions. The values of m obtained were 1.89 and 1.54, respectively. These results indicate that a two-photon absorption contributes to the green upconversion and the red emission is not attributed to a biphotonic mechanism.

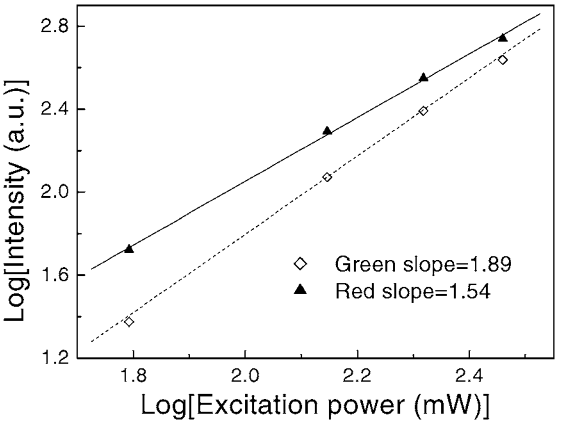

Figure 3 Dependence of the integrated intensity of upconversion emissions on excitation power.

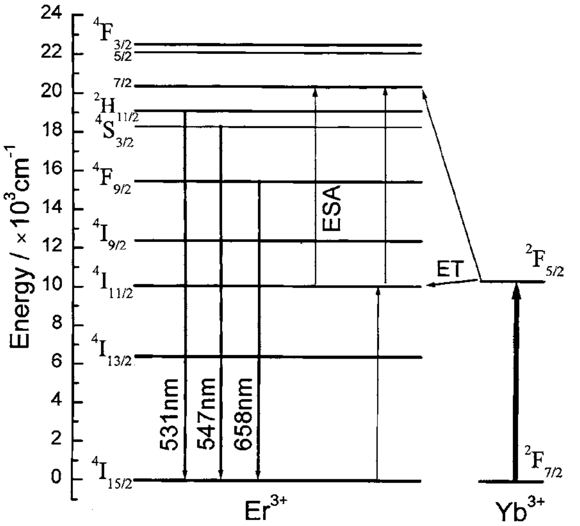

Figure 4 Simplified energy-level diagram of the Yb^{3+} and Er^{3+} ions. Upward arrows indicate excitation photons and downwards stand for fluorescence emission.

According to the energy matching conditions and the dependence of upconversion emission intensity on excitation power, the possible upconversion mechanism is analyzed on the basis of the simplified energy level diagrams of Yb^{3+} and Er^{3+} ions as illustrated in Fig. 4. Two steps are involved in the visible upconversion emission process. First, a 976 nm photon is absorbed by an Yb^{3+}, which provokes the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition. In a rapid way the excited Yb^{3+} ion transfer the energy to the nearest Er^{3+} ion, exciting it from the ground state to the $^4I_{11/2}$ level. Then another excited Yb^{3+} ion transfer its energy to this excited $^4I_{11/2}$ Er^{3+} ion, resulting in the population inversion of the $^4F_{7/2}$ level. This process can be described as Yb^{3+} $(^2F_{5/2})$ + $Er^{3+}(^4I_{15/2}) + Yb^{3+}$ $(^2F_{5/2}) \rightarrow Yb^{3+}(^2F_{7/2}) + Er^{3+}(^4F_{7/2})$ + $Yb^{3+}(^2F_{7/2})$. In addition, the excited-state absorption (ESA) from the $^4I_{11/2}$ is also a main contribution to the green emission. This process can be described as Er^{3+} $(^4I_{11/2})$ + a photon $\rightarrow$ $Er^{3+}(^4F_{7/2})$. The excited energy that stored in the $^4F_{7/2}$ level relaxes nonradiatively to the $^2H_{11/2}$ level because of the low energy gap, for example, about 1200 cm^{-1} in our experiment. Then a fast thermal equilibrium is established between the $^2H_{11/2}$ and $^4S_{3/2}$ levels [15]. Since the energy gap below the $^4S_{3/2}$ level is larger, for example, over 3100 cm^{-1} from the absorption spectrum data, the nonradiative decay through multiphonon relaxation from the $^4S_{3/2}$ level becomes smaller. Therefore, the bright green fluorescence was emitted through the $^2H_{11/2} + {}^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition. For the red emission, F. Goutaland *et al.* [16] attributed this phenomenon to the Er^{3+}-Er^{3+} quenching deexcitation. One excited Er^{3+} ion deexcites from $^4F_{7/2}$ to $^4F_{9/2}$ and raises the other from $^4I_{11/2}$ to $^4F_{9/2}$. The two Er^{3+} ions can emit two 658 nm photons at the cost of three incoming photons. However, in our case, the concentration of Er^{3+} is relatively low and the interaction between Er^{3+} ions cannot be a predominant factor for red emission [17]. Due to the relative large doping concentration of Yb^{3+} ions, Yb^{3+} pairs [18] may be formed in our glass and interact with the neighboring one or two Er^{3+} ions. These processes can be described as follows:

$$2\mathrm{Yb}^{3+}\left({}^2F_{5/2}\right) + \mathrm{Er}^{3+}\left({}^4I_{15/2}\right) \rightarrow 2\mathrm{Yb}^{3+}\left({}^2F_{7/2}\right) + \mathrm{Er}^{3+}\left({}^4F_{7/2}\right) \quad (1)$$

$$2\mathrm{Yb}^{3+}\left({}^2F_{5/2}\right) + \mathrm{Er}^{3+}\left({}^4I_{15/2}\right) + \mathrm{Er}^{3+}\left({}^4I_{11/2}\right) \rightarrow 2\mathrm{Yb}^{3+}\left({}^2F_{7/2}\right) + \mathrm{Er}^{3+}\left({}^4F_{9/2}\right) + \mathrm{Er}^{3+}\left({}^4F_{9/2}\right) \quad (2)$$

Process (1) plays an important role in the green upconversion while process (2) predominantly contributes to the increase of the populations in the ${}^4F_{9/2}$ level.

In conclusion, the green and red upconversion fluorescence was easily observed with the naked eye under the 976-nm excitation. Based on the absorption spectroscopic data, the observed intense green emission is assigned to the ${}^2H_{11/2} + {}^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition while the red emission at 658 nm originates from the ${}^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition. According to the energy matching conditions and the dependence of upconversion emission intensity on excitation power, a two-photon absorption process contributes to the green upconversion, while the red emission is possibly attributed to the interaction of the Yb^{3+} pairs with their nearest Er^{3+} ions.

Acknowledgments

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