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Up-conversion spectrum properties of the oxy-fluoride glass co-doped with Er^{3+} and Yb^{3+}

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Abstract

Up-conversion of $45PbF_2$–$45GeO_2$–$10WO_3$ oxy-fluoride glasses co-doped with Yb^{3+} and Er^{3+} ions were prepared by fusion method through melting at 1223 K and then annealing at 653 K for 4 h. Transmittance of the undoped host glass was beyond 73% in a range of 0.6–2.5 μm and the co-doped glasses still provided good transmittance beyond 50%. Refractive indices of the host and co-doped glasses were 1.517 and 1.650, respectively. Blue, green and red fluorescence spectra were observed in a range of 400–700 nm under 980 nm diode laser excitation. Up-conversion spectra at about 410, 518, 530 and 650 nm were assigned to the 4f electron transitions of $^2H_{9/2} \rightarrow {}^4I_{15/2}$, $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ of Er^{3+} ion, respectively. The mechanism of energy transfer between Yb^{3+} and Er^{3+} ions in the glass was analyzed. Raman shift shows the non-radiative relaxation of the glass sample is low.

Keywords: Oxy-fluoride glasses; Co-doped phosphors; Fluorescence; Energy transfer

1. Introduction

Recently, the research interest on up-conversion luminescence materials has been growing in view of the short -wavelength blue LD system to improve the efficiency of CD players, laser printers and color displays [1,2]. Many works have been made to improve the up-conversion efficiency. However, the requirements of practical applications still have not been met with the present attainment. The main problem is to improve proper sensitizing combination, suitable pumping laser wavelength and conversion passage to enhance the up-conversion efficiency [3–6]. Synthetic studies for appropriate host materials are also very important. Among the dopants as the absorption and emission centers, Er^{3+} ion has been mostly widely studied for its opulent energy levels in the trivalent rare-earth ions [4–6]. Furthermore, Yb^{3+} ion that has unique advantages of high absorption cross-section and the efficient energy-transfer can perform to the other rare-earth acceptor ions as an efficient sensitizer [7–10].

In this paper, the up-conversion oxy-fluoride glasses co-doped with Yb^{3+} and Er^{3+} ions were prepared. The spectroscopic properties, the dependence of the emission intensity on the pumping power and the mechanism of energy transfer between Yb^{3+} and Er^{3+} in the glass were discussed.

2. Experimental

The $45PbF_2$–$45GeO_2$–$10WO_3$ host glasses were prepared by melting at 1223 K, quenching and annealing. The up-conversion glass samples were prepared from raw material mixtures of $[50-(x+y)]PbF_2$–$40GeO_2$–$10WO_3$–$xYbF_3$–$yErF_3$ ($x=y=10$). The precisely weighed batches were mixed homogeneously, melted in a platinum crucible at 1223 K for 20–25 min. The melts were poured in an iron

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mould followed by annealing at 653 K for 4 h in a furnace. Finally, the samples were cooled down to room temperature. The refractive indices of host glass and Yb^{3+}/Er^{3+} ions co-doped host glasses were measured by the conventional optical method with a sodium lamp as the light source at 589.3 nm. The transmittance patterns were recorded on an ultraviolet–visible-infrared spectrometer in a range of 0.35–2.5 μm. Fluorescence spectra of the samples were measured on a Hitachi F-4500 fluorescent spectrometer using the 980 nm semiconductor laser as the pump light source. Raman spectra of the co-doped glasses were obtained by using an OMARS89 Raman spectrometer.

3. Results and discussion

Figs. 1 and 2 show the transmittance curves of host glass and up-conversion glass sample, respectively. For the up-conversion glass co-doped with Yb^{3+} and Er^{3+} ions, the transmittance evidently decreased and characteristic absorption peaks of the rare-earth ions were observed. From the visible to near infrared region, the keen and feeble absorption peaks are attributed to the forbidden transition of 4f electron for rare-earth ions.

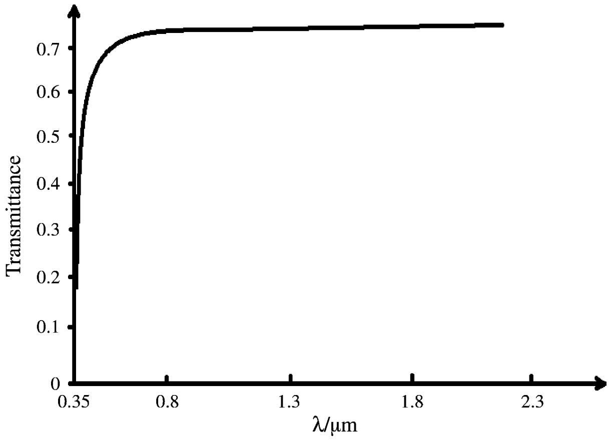

Fig. 1. The transmittance curve of host glass.

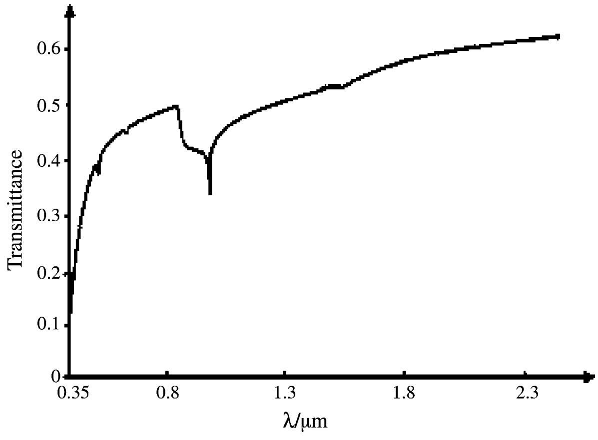

Fig. 2. The transmittance curve of up-conversion glass co-doped with Yb^{3+} and Er^{3+} ions.

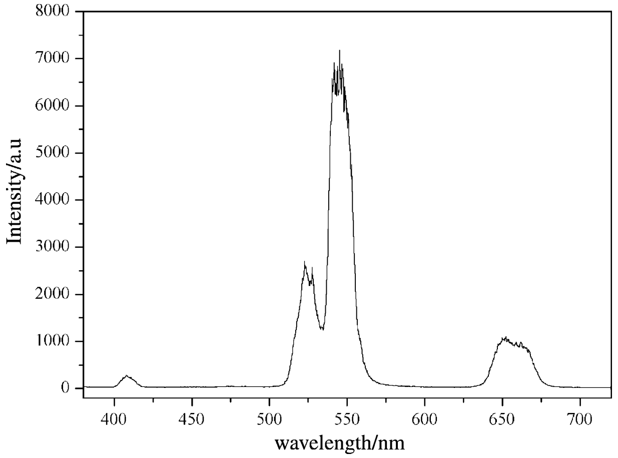

Fig. 3. The emission spectrum of up-conversion glass co-doped with Yb^{3+} and Er^{3+} ions.

The refractive indices of host and co-doped up-conversion glasses were 1.517 and 1.650, respectively. The refractive indices of constituents mostly depend on the value of their polarizability. When the Yb^{3+} and Er^{3+} ions are doped to the host glasses, these rare-earth ions have high polarizability and increase the density values of the host glasses. Consequently, the refractive indices of the co-doped up-conversion glasses were higher than those of the host glasses.

Fig. 3 shows the emission spectrum recorded under the excitation by 980 nm semiconductor laser. Four peaks at 410, 518, 530 and 650 nm were observed on the profile. The up-conversion luminescence mechanism of co-doped Yb^{3+}/Er^{3+} glass is schematically illustrated in Fig. 4 [6–8]. Based on the energy level configuration graph of Er^{3+} ion, the four peaks correspond to the transition of $^2H_{9/2} \rightarrow {}^4I_{15/2}$, $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$, respectively. The Yb^{3+} ion has the larger absorption cross-section

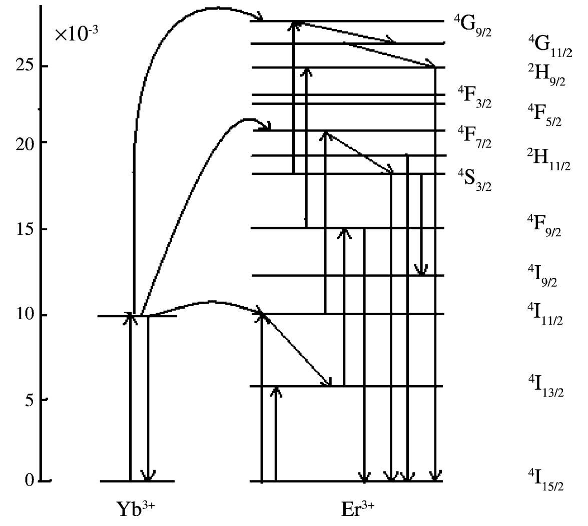

Fig. 4. The up-conversion mechanism doped with co-Yb^{3+} and Er^{3+}.

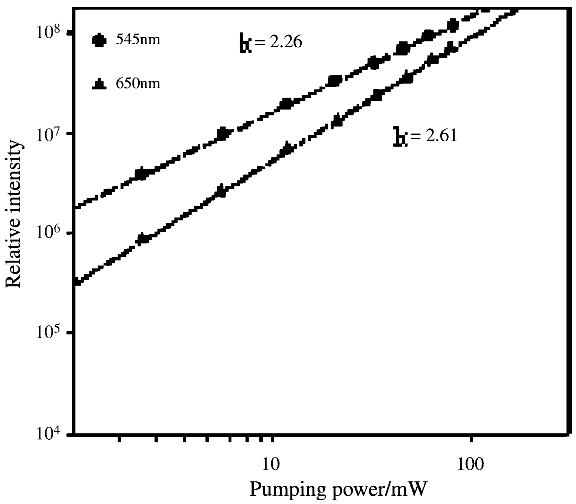

Fig. 5. Up-conversion intensity vs. pumping power.

for the 980 nm infrared light and the $^2F_{5/2}$ energy level of Yb^{3+} ion is extraordinarily adjacent to the $^4I_{11/2}$ one of Er^{3+} ion. Furthermore, the $^4F_{5/2}$ energy level of Yb^{3+} ion is almost twice as large as the $^4I_{13/2}$ one of Er^{3+} ion. As a result, the energy transfer from the Yb^{3+} to Er^{3+} ion should take place. At the same time, the energy transfer between Er^{3+} ions is also performed. Moreover, the ions in the excitation state of $^4I_{13/2}$ energy level absorb the pumping photon of 980 nm and realize the up-conversion of the absorption course in the excitation state. All three courses finally make the transit of Er^{3+} ion to the excitation state of $^4F_{7/2}$ and $^4G_{9/2}$ energy level, and then the non-radiative transitions to $^2H_{11/2}$ and $^4S_{3/2}$ for $^4F_{7/2}$ and to $^2H_{9/2}$ for $^4G_{9/2}$ take place. The transition produces green light from $^2H_{11/2}$ and $^4S_{3/2}$ to the ground state and blue light from $^2H_{9/2} \rightarrow {}^4I_{15/2}$. The red up-conversion luminescence rooting in $^4F_{9/2}$ results from the excitation state absorption of $^4I_{13/2}$ and the cross relaxation between $^4S_{3/2}$ and $^4I_{15/2}$.

The up-conversion integral intensity dependences on the pumping power are shown in Fig. 5. The relationship between them can be approximately expressed as a proportional equation: $I_{vis} \propto (I_{in})^n$, where n is the infrared absorbing number when one visible photon is emitted. I_{vis} is the up-conversion luminescence intensity and I_{in} is the infrared excitation intensity. From the slopes of the log–log plots, we can conclude that the two-photon absorption process is required for the green emission and the up-conversions involve two-photon and three-photon absorption processes for the red emission bands.

The Raman spectra of the up-conversion glass co-doped with Yb^{3+} and Er^{3+} ions in a range from 100 to 2000 cm^{-1} are shown in Fig. 6. The maximum phonon cut-off energy at 1500 cm^{-1} indicates that the non-radiative relaxation of the up-conversion glass sample is low. The peak at 350 cm^{-1} is attributed to the bond stretching of Pb–F and the peaks at 806 and 920 cm^{-1} are due to the vibrations modes of Ge–O.

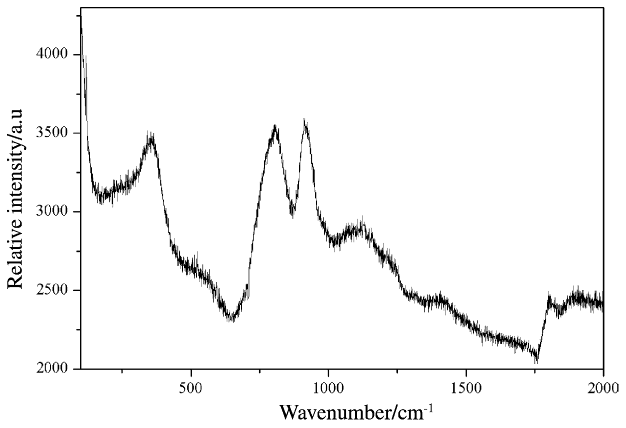

Fig. 6. Raman spectrum of the up-conversion glass sample co-doped with Yb^{3+} and Er^{3+} in the range of 100–2000 cm^{-1}.

4. Conclusions

The up-conversion glasses based on the $45PbF_2$–$45GeO_2$–$10WO_3$ host glass co-doped with Yb^{3+} and Er^{3+} ions have the refractive index of 1.650 and give strong green and red emission peaks at 530 and 650 nm. The green emission is due to two-photon absorption process while the up-conversions involving two-photon and three-photon absorption processes correspond to the red emission bands. The Raman shift curve analysis indicates that the non-radiative relaxation of oxyfluoride glass is low. Consequently, new up-conversion fluorescence glasses as the base materials of novel up-conversion blue-green wavelength laser is possibly prepared by adjusting the contents of the composition of host glass and doping proper rare-earth ions.

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