JOURNAL OF RARE EARTHS
Vol.24, Spec. Issue, Dec. 2006, p.173

Research on Up-Conversion Mechanism in Er^{3+}/Yb^{3+}-Codoped Oxyfluoride Glass

Yang Kaisheng ([illegible])*, Xue Haili ([illegible]), Wu Kuang ([illegible]), Ran Haqiang ([illegible]),
Wang Weisheng ([illegible]), Zeng Bin ([illegible]), Zhang Xiyan ([illegible])
(*School of Material Science and Engineering, Changchun University of Science and Technology, Changchun 130022, China*)

Abstract: Er^{3+}/Yb^{3+}-codoped oxyfluoride crystallite glass was prepared with melting technique. The compositions and the melting temperature and the annealing temperature of the rare earth-doped crystallite glass were studied in detail. The emission spectra of samples were measured with the Hitachi F-4500 fluorescent photometer pumped by 980 nm wavelength laser. The up-conversion luminescence mechanism was illuminated on the view of the photophysics. By measuring the relationship between luminescent intensity and pump power, it is confirmed that the emission peaks at 550 nm belong to two-photon process, while that at 665 nm belongs to three-photon process. Moreover, the distributions of crystallite were determined by SEM.

Key words: Er^{3+}/Yb^{3+}; up-conversion; oxyfluoride glass; rare earths
CLC number: TN383 **Document code:** A **Article ID:** 1002-0721(2006)-0173-04

In recent years, the researches of rare earth doped energy up-conversion have been extensively studied owing to their potential application in optoelectronics, such as in lasers, three-dimensional display, wave guide and imaging. The meaning of the up-conversion luminescence is that the energy of luminescence centre photon radiation was higher than the energy of excitation photon when it was excited by a long wavelength laser. More effort has been devoted to preparing the new up-conversion materials and to studying their emission properties in these days. However, how to improve the up-conversion efficiency is the bottleneck for scientists to solve, because the up-conversion efficiency is strictly dependence on the phonon of the host materials and the higher phonon energy of the host always leads to lower up-conversion efficiency of rare-earth ions[1~4]. Due to its low phonon energy, chemical stability, strong mechanical intensity and simple fabrication, the oxyfluoride crystalline glass was studied widely. So the up-conversion luminescence properties of the Er^{3+}/Yb^{3+}-codoped oxyfluoride crystallite glass were studied deliberately. It was found that intensive green and red up-conversion emission occurred when excited by 980 nm semiconductor laser. At last, the up-conversion mechanism was elucidated on the point-view of spectrum.

1 Experimental

The component of $30BaB_2O_4$-$10AlF_3$-$22PbF_2$-$10CaF_2$-$5NaF$-$2YbF_3$-ErF_3 was selected as the investigated subject. The raw materials AlF_3, PbF_2, CaF_2 and NaF were analytically grade. BaB_2O_4, YbF_3 and ErF_3 were prepared in the laboratory. The homogeneously mixed raw materials were melt at 1000 ℃ in the muffle furnace. The liquid mass was casted on the iron plate. The samples were annealed at 380 ℃ for 2 h, and then at 420 ℃ for 1 h. Finally, the samples were cooled down to room temperature. The absorption spectra of samples were measured by UV-MINI-1240 spectrophotometer. The emission spectra were measured by Hitachi F-4500 fluorescence Spectrometer using the 980 nm semiconductor laser as the pump source. The measurement range was 400 ~ 700 nm. Raman spectra were measured by American AC-TO ~ 2758 Raman spectrometer. The scanning electron microscopy (SEM, EPI-3000H instrument) were used to characterize the morphology of the up-conversion luminescent materials.

2 Results and Discussion

Fig.1 shows the absorption spectrum of the Er^{3+}/Yb^{3+}-codoped oxyfluoride crystallite glass. Four peaks

Received date: 2006-06-20; revised date: 2006-09-09
Biography: Yang Kaisheng (1958-), Professor, Majoring in phase chemistry functional materials
* Corresponding author (E-mail: [illegible]@126.com)

around 487, 520, 540 and 650 nm were diagnosed from the figure. This four peaks corresponding to the energy level $^4F_{7/2}$, $^2H_{11/2}$, $^4S_{3/2}$ and $^4F_{9/2}$ of Er^{3+} ion, respectively. In addition, the intense absorption corresponding to the excited level of Yb^{3+} ion is also observed at the 980 nm, whereas the absorption of the $^4I_{11/2}$ level of Er^{3+} ion is hidden in this band and intense level.

The emission spectrum of the sample was shown in Fig. 2, in which the 980 nm semiconductor laser was used as pump source. There are three peaks around 520, 540 and 650 nm corresponding to the transition of $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$, respectively. In this work, the intensity of green emission was much stronger than that of the red emission. This phenomenon could be elucidated that the rare earth ions were enclosed by fluoride with the increasing chemical stability and mechanical robustness due to the cross linkage effects of the oxides.

Fig. 3 shows the up-conversion mechanisms of green and red emission. In the figure, the solid line, dotted line and hollow arrow indicate the radiation process, ET energy conversion process and multi-phonon relaxation process, respectively. The Yb^{3+} ion had

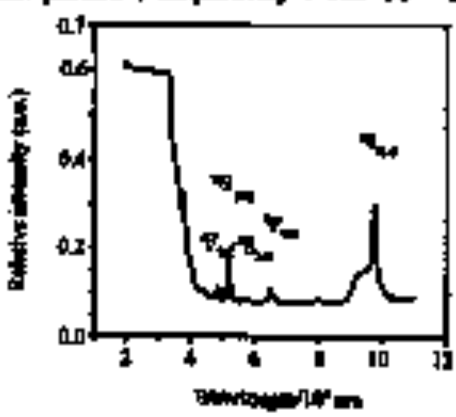

Fig.1 Absorption spectrum of Yb^{3+}/Er^{3+} co-doped oxyfluoride glass

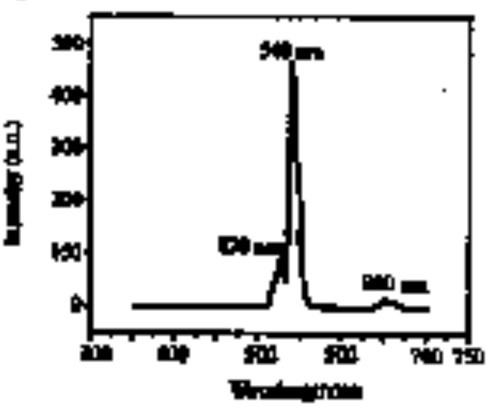

Fig.2 Emission spectrum of Yb^{3+}/Er^{3+} co-doped oxyfluoride glass

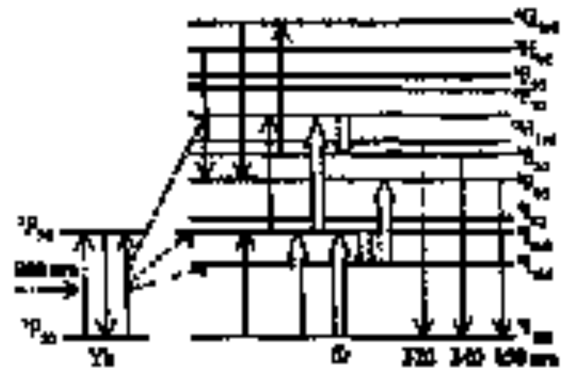

Fig.3 Up-conversion mechanism of Yb^{3+}/Er^{3+} codoped oxyfluoride glass

huge absorption cross section around 980 nm wavelength, and the $^2F_{5/2}$ energy level of Yb^{3+} ion was extraordinarily approach to the $^4I_{11/2}$ energy level of Er^{3+} ion. Furthermore, the $^2F_{5/2}$ energy level of Yb^{3+} ion was almost twice as large as its $^4I_{11/2}$ energy level. Thus, the energy transfer from the Yb^{3+} to Er^{3+} ion should take place combined with the energy transfer between Er^{3+} ion. All the photophysical processes could be described as follows: the transition from the $^2F_{7/2}$ ground-state to the $^2F_{5/2}$ excited-state of the Yb^{3+}-sensitizer occurred as the sample was excited by 980 nm semiconductor laser; the excited-state Yb^{3+} ion transferred its energy to the luminous center Er^{3+} ion, making it transit from $^4I_{15/2}$ ground-state to $^4I_{11/2}$ state; the subsequent energy-transfer process promoted the Er^{3+} ion transiting from the $^4I_{11/2}$ level to the upper $^4F_{7/2}$ level, and then the multi-phonon relaxation to the $^2H_{11/2}$, $^4S_{3/2}$ level[3-5]. As a result, the green emission was obtained by the transition from $^2H_{11/2}$ and $^4S_{3/2}$ excited-state to $^4I_{15/2}$ ground-state. Whereas, the red emission was obtained by the transition from $^4F_{9/2}$ excited-state to $^4I_{15/2}$ ground-state. And the specific process is as follows:

(1) Two-photon process:

$$^2F_{7/2}(Yb^{3+}) + {}^4I_{15/2}(Er^{3+}) \xrightarrow[\text{1 photon}]{980\ nm} {}^2F_{5/2}(Yb^{3+}) + {}^4I_{15/2}(Er^{3+})$$

$$^4I_{15/2}(Er^{3+}) + {}^4I_{11/2}(Er^{3+}) \xrightarrow{ESA} {}^4I_{11/2}(Er^{3+}) + {}^4I_{15/2}(Er^{3+})$$

$$^4I_{11/2}(Er^{3+}) \xrightarrow[\text{1 photon}]{980\ nm} {}^4F_{7/2}(Yb^{3+})$$

$$^4I_{11/2}(Er^{3+}) + {}^2F_{5/2}(Yb^{3+}) \xrightarrow{ET} {}^2F_{7/2}(Yb^{3+}) + {}^4F_{7/2}(Er^{3+})$$

$$^4F_{7/2}(Er^{3+}) \xrightarrow{ESA} {}^2H_{11/2}(Er^{3+}) + {}^4S_{3/2}(Er^{3+})$$

(2) Three-photon process:

$$^4I_{15/2}(Er^{3+}) + {}^2F_{5/2}(Yb^{3+}) \xrightarrow[\text{n photon}]{980\ nm} {}^4I_{11/2}(Er^{3+}) +$$

$$^2F_{5/2}(Yb^{3+}) \xrightarrow{\text{relaxation}} {}^4I_{13/2}(Er^{3+}) + {}^2F_{7/2}(Yb^{3+}) \longrightarrow$$

$$^4I_{13/2}(Er^{3+}) + {}^4I_{13/2}(Er^{3+}) \xrightarrow[\text{n photon}]{980\ nm} {}^4F_{9/2}(Er^{3+}) + {}^2F_{7/2}$$

$$(Yb^{3+}) \xrightarrow{\text{relaxation}} {}^4S_{3/2}(Er^{3+}) + {}^2F_{5/2}(Yb^{3+}) \xrightarrow[\text{+ phonon}]{980\ \text{nm}} {}^4G_{11/2}$$

$$(Er^{3+}) + {}^2F_{5/2}(Yb^{3+}) \xrightarrow{\text{absorption}} {}^4F_{7/2}(Er^{3+}) + {}^2F_{7/2}(Yb^{3+})$$

In order to further illuminate this physical process, the relationship between up-conversion luminescence intensity and the pumping power was studied in Fig. 4. The relationship can be approximately expressed as a proportional equation: $I_{up} \propto (I_{in})^n$, where n is the infrared absorbing number when one visible photon is emitted. I_{up} is the up-conversion luminescence intensity and I_{in} is the infrared excitation intensity. Based on the slopes of the log-log plots, it is concluded that the green and red emission were belong to two-photon and three-photon absorption processes, respectively[5].

Fig. 5 is the Raman spectra of Yb^{3+}/Er^{3+} co-doped oxyfluoride crystallite glass. It shows that the maximum phonon energy of sample at 870 cm^{-1} was smaller than that of borate (1400 cm^{-1}), phosphate (1100 cm^{-1}), silicate (1000 cm^{-1}) and germinate (900 cm^{-1}). Considering its low phonon energy, we deduced that our oxyfluoride glass may be a good candidate for up-conversion luminescence materials of rare-earth ions[9-11].

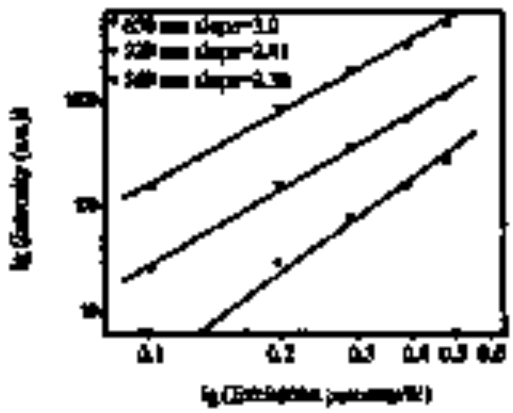

Fig.4 Dependence of fluorescence intensity on pump power

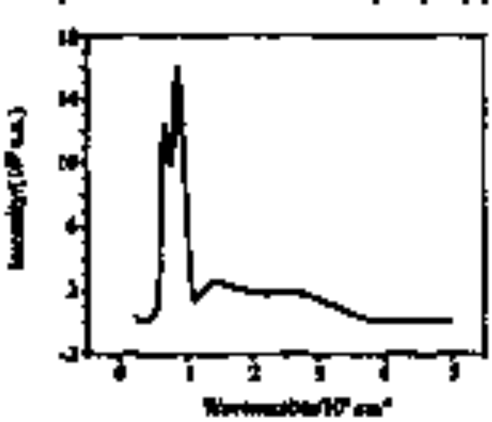

Fig.5 Raman spectrum of up-conversion glass

Fig.6 shows the SEM of oxyfluoride glass with and without stallization treatment. Very few and non-uniform crystallite was observed in Fig.5(a). Compared with the untreated sample, more and uniform crystallites were observed in the stallization sample. The particle diameter was discovered about 100 – 150 nm through the calculation. So Yb^{3+}/Er^{3+} co-doped oxyfluoride crystallite can be regarded as the crystallite glass[20]. Thus, it could be concluded that stallization treatment had an important effect on the formation of crystallite, and that optimal stallization temperature was the key factor controlling the stallization. In this work, the temperature of stallization treating was obtained by the analyzing of Differential Thermal Curve.

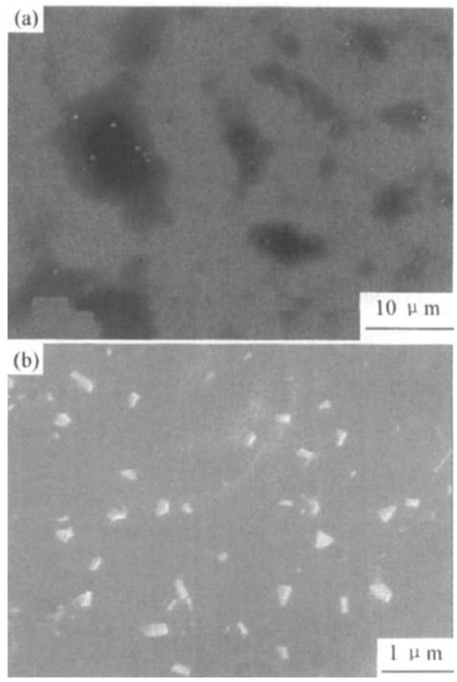

Fig.5 SEM of up-conversion glass
(a) Untreated sample; (b) Stallization sample

3 Conclusion

In this article, Yb^{3+}/Er^{3+} co-doped oxyfluoride crystallite glass was prepared by fusion method. The samples were analyzed using spectral methods and SEM. The relationship between luminescence intensity and pumping power was also studied. Through previous analysis, the conclusions were drawn as follows: Firstly, there are five peaks around 487, 520, 540, 650 and 980 nm on the absorption spectrum and the maximum absorption peak was central at 980 nm wavelength; secondly, intensive green emission and weak red emission have been obtained pumped by 980 nm laser which belongs to two-photon and three-photon process, respectively. Finally, the sample has low phonon energy through Raman analysis and uniform crystallite distribution were observed by SEM. These experiment data confirm such hypothesis that our oxyfluoride glass may be better candidates for up-conversion luminescence materials of rare earth ions.

References:

[1] [illegible] Hongpan, [illegible], Xu Shiqing et al. Upconversion emission in Er^{3+}-doped novel bismuthate glass [J]. Journal of the Chinese Rare Earth Society (in Chin.), 2004, 22(6): 837.

[2] Xiao Siguo, Yang Xiaoliang, Liu Zhengwei. Experimental study on up-conversion luminescence of Ho^{3+} doping fluoride materials [J]. Chinese Rare Earths (in Chin.), 2001, 22(5): 9.

[3] Zhao Suling, Hou Yanbing. Upconversion luminescence of rare earth ions [J]. Semiconductor Optoelectronics, 2000, 21(4): 241.

[4] Liu [illegible], Zhao Suling, Hou Yanbing, et al. Upconversion luminescence of fluoro-oxide glass-ceramics codoped with Er^{3+} and Yb^{3+} [J]. Journal of Optoelectronics Laser, 2001, 12(5): 449.

[5] Zhao Suling, Xu Zheng, Hou Yanbing, et al. Dependence of temperature on upconversion emission of $YLiF_4$: Er^{3+} [J]. Journal of Rare Earths, 2003, 21(4): 409.

[6] Yang Zhongmin, Xu Shiqing, Hu Lili, et al. Frequency upconversion properties of Yb^{3+}-Er^{3+} co-doped oxyfluoride germanate glass [J]. Journal of Materials Science, 2004, 39: 2223.

[7] [illegible], Zhang [illegible], et al. Preparation and optical properties of Er^{3+} doped gadolinium borosilicate glasses [J]. Journal of Rare Earths, 2005, 23(2): 157.

[8] Silva C J da, Araujo M T de, Gouveia E A, et al. Thermal effect on multiphonon-assisted anti-Stokes excited upconversion fluorescence emission in Yb^{3+}-sensitized Er^{3+}-doped optical fiber [J]. Appl. Phys. B, 2000, 70: 185.

[9] [illegible], Xu Wei, [illegible], et al. Interactions between [illegible] in glass [illegible] and light upconversion and [illegible] [J]. Acta Physica Sinica, 2000, 49(1): 110.

[10] Xu Shiqing, Wang Guonian, Zhang Junjie, et al. The upconversion luminescence research of Er^{3+}-doped heavy metal oxyfluoride silicate glasses [J]. Acta Physica Sinica, 2004, 53(6): 1840.

[11] Liu [illegible], [illegible], [illegible], et al. Upconversion luminescence of [illegible] doped [illegible] [J]. Journal of the Chinese Rare Earth Society (in Chin.), 2002, 20: [illegible].

[12] Wang [illegible], Zhang [illegible], [illegible], et al. Study of [illegible] nano-crystalline glass-ceramics [illegible] as [illegible] storage device [J]. Journal of Functional Materials, 2004, 35(3): 341.