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BLUE COOPERATIVE UP-CONVERSION LUMINESCENCE OF Yb^{3+} IONS IN OXYFLUORIDE GLASS EXCITED BY 960 nm LASER*

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Investigates the up-conversion luminescence of Yb-doped oxyfluoride glass excited by a 960nm-diode laser. A new up-conversion cooperative radiation luminescence is found, which is rather strong and positioned at 476.1 nm. It comes from the coupled states of two-Yb^{3+}-ions cluster. It is significant because it is an effective and convenient method of producing blue light.

Keywords: cooperative up-conversion luminescence, oxyfluoride glass, Yb^{3+} ion cluster
PACC: 7855, 4255R, 7840

Frequency up-conversion research is a valuable front field in optical-physics science.[1] Its applications in laser,[2] optical data storage,[3] sensor,[4] biological diagnostics[5] and 3-d volumetric display[6−8] fields have good prospects. The blue light is one of most interesting topics.[9−15] This paper investigates the blue up-conversion luminescence phenomenon of Yb(5):FOG (FOG means oxyfluoride glass) and Yb(0.5):FOG oxyfluoride glass samples when excited by a 960nm diode laser. A new kind of up-conversion cooperative radiation fluorescence is found, which originates from the coupled state of clusters[12] consisting of two Yb^{3+} ions. It may lead to a new effective and convenient method to obtain strong blue up-conversion luminescence.

We selected Yb-doped oxyfluoride glass to study the cooperative up-conversion luminescence of the Yb^{3+} ion.[16] The samples used in our experiment were (a)Yb(5):FOG and (b) Yb(0.5):FOG oxyfluoride glass. Because the sample manufacture system is used to produce the Er-doped sample, the components of this system, such as the crucible, contain some Er^{3+} ions on its surface. So there is trace of Er^{3+} ions naturally in the Yb(5):FOG and Yb(0.5):FOG samples when Yb^{3+}:FOG samples are manufactured. The pump source was a 960nm CW diode laser manufactured by the Institute of Semiconductor of the Chinese Academy of Sciences. The laser beam was focused on the sample by a group of lenses, and the fluorescence emitted from the sample was collected and analysed by a Fluorolog-Tau-3 fluorescence photometer. The collection direction of the fluorescence was perpendicular to the laser excitation direction. The experimental conditions are kept the same, so as to ensure that the relative fluorescence intensities of all measured curves are comparable.[11]

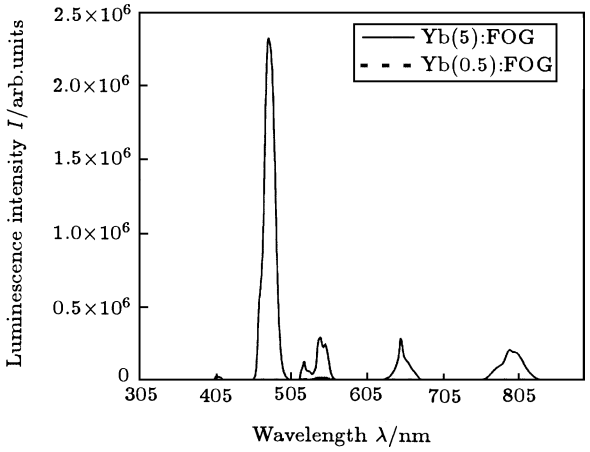


Fig.1. The 476.1 nm cooperative up-conversion luminescence of Yb-doped oxyfluoride glass excited by a 960 nm diode laser (other luminescence peaks are from trace Er ions up-conversion sensitized by Yb ions).

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The up-conversion luminous spectrum obtained is shown in Fig.1, in which we can find the strong 476.1 nm up-conversion fluorescence line. Meanwhile there are a series of characteristic luminescence peaks of Er^{3+} ions at 407.5, 522.5, 544.0, 650.0 and 793.5 nm, resulting from the trace of Er^{3+} ions present. Table 1 lists the relative peak intensity of the luminescence. By changing the laser power, the variation of the 476.1 nm up-conversion fluorescence intensity with laser power is also measured carefully, which is shown in Fig.2. Undoubtedly, the 476.1 nm luminescence is a two-photon up-conversion fluorescence.

The most interesting phenomenon concerns the up-conversion fluorescence of 476.1 nm (21005 cm^{-1}). From Figs.1, 2 and table 1, we can find that the 476.1 nm up-conversion luminescence intensity of Yb(5):FOG is about 1000 times greater than that of Yb(0.5):FOG. It shows that the 476.1 nm up-conversion luminescence is closely related to the concentration of Yb^{3+} ions. In fact, the Yb^{3+} ion concentration of a:Yb(5):FOG is only ten times greater than that of b:Yb(0.5):FOG. Thus the 476.1 nm up-conversion luminescence cannot be oriented by any linear process involving single Yb^{3+} ion system, because the luminescence intensity of a single ion system should be linearly proportional to the Yb^{3+} ion concentration. In fact, it is reasonably believed to be rather a kind of cooperative up-conversion radiation fluorescence originating from the coupled state of two-Yb^{3+}-ion cluster.[12]

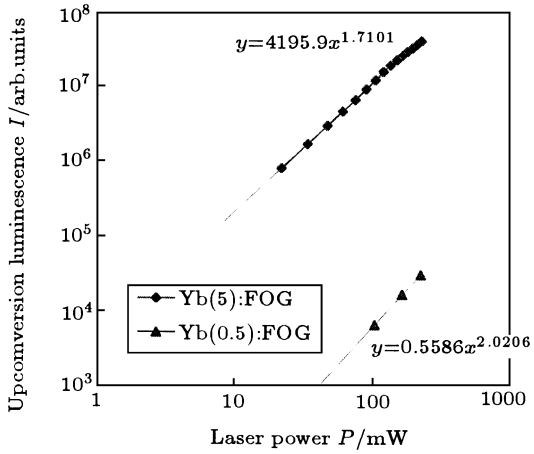


Fig.2. The log–log plot of Yb ion 476.1 nm cooperative up-conversion luminescence intensity of Yb:FOG upon laser power.

Table 1. The up-conversion luminescence peak intensity of (a) Yb(5):FOG and (b) Yb(0.5):FOG samples when excited by 960 nm-diode laser. (The up-conversion luminescence of Er^{3+} ions comes from trace of Er^{3+} ions in Yb:FOG samples).

Ion	Wavelength λ/nm	Transition	Yb(5):FOG	Yb(0.5):FOG
Yb^{3+}	476.1	$^2F_{5/2}{}^2F_{5/2}(Yb^{3+}Yb^{3+})$	2.32×10^6	2.00×10^3
		$\rightarrow{}^2F_{7/2}{}^2F_{7/2}(Yb^{3+}Yb^{3+})$		
Er^{3+}	407.5	$(^2G^4F^2H)_{9/2}(Er^{3+})\rightarrow{}^4I_{15/2}(Er^{3+})$	3.72×10^4	5.00×10^1
	522.5	$^2H_{11/2}(Er^{3+})\rightarrow{}^4I_{15/2}(Er^{3+})$	1.30×10^5	4.59×10^3
	544.0	$^4S_{3/2}(Er^{3+})\rightarrow{}^4I_{15/2}(Er^{3+})$	2.92×10^5	1.56×10^4
	650.0	$^4F_{9/2}(Er^{3+})\rightarrow{}^4I_{15/2}(Er^{3+})$	2.84×10^5	1.38×10^3
	793.5	$^4I_{9/2}(Er^{3+})\rightarrow{}^4I_{15/2}(Er^{3+})$	2.09×10^5	1.13×10^3

The main peak of this cooperative radiation luminescence is positioned at 476.1 nm, with photon energy 21005 cm^{-1}, while that of the 960nm laser light is 10417cm^{-1}. As we know,[11,16] the absorption peak positions of the Yb^{3+} ion $^2F_{5/2}$ level in oxyfluoride glass are 10267, 10438 and 10799 cm^{-1}. Thus from energy considerations it is also reasonable to believe that the 476.1 nm fluorescence comes from a cooperative radiation process. It is easy to excite a Yb^{3+} ion to its $^2F_{5/2}$ level by a pump laser (10417cm^{-1}, 960 nm). Therefore if two Yb^{3+} ions happen to form a cluster, the coupled state may be made up by either 10267 and 10799 cm^{-1} sub-states and then positioned at 21066, or 10438 and 10438 cm^{-1} sub-states then positioned at 20876 cm^{-1}, and so on. It is both very close to the 476.1 nm fluorescence photon energy 21005 cm^{-1}. Thus it is firmly believed that the 476.1 nm fluorescence is a kind of cooperative radiation up-conversion fluorescence.

The up-conversion processes are supposed to be as follows. Firstly, each isolated Yb^{3+} ion absorbs a pump photon and is excited to the $^2F_{5/2}$ state from the $^2F_{7/2}$ ground state. Then the two Yb^{3+} ions, both in the $^2F_{5/2}$ excited state, form a coupled cluster state $^2F^2_{5/2}F_{5/2}(Yb^{3+}Yb^{3+})$ under strong laser pumping. The 476.1 nm fluorescence is then radiated from this excited coupled state to the ground state $^2F^2_{7/2}F_{7/2}(Yb^{3+}Yb^{3+})$. The energy level struc-

ture and the schematic diagram of up-conversion process are shown in Fig.3. Furthermore, this cooperative up-conversion radiation luminescence of Yb(5):FOG found in our experiment is rather strong. It may provide an effective and convenient method to produce blue light.[17−18]

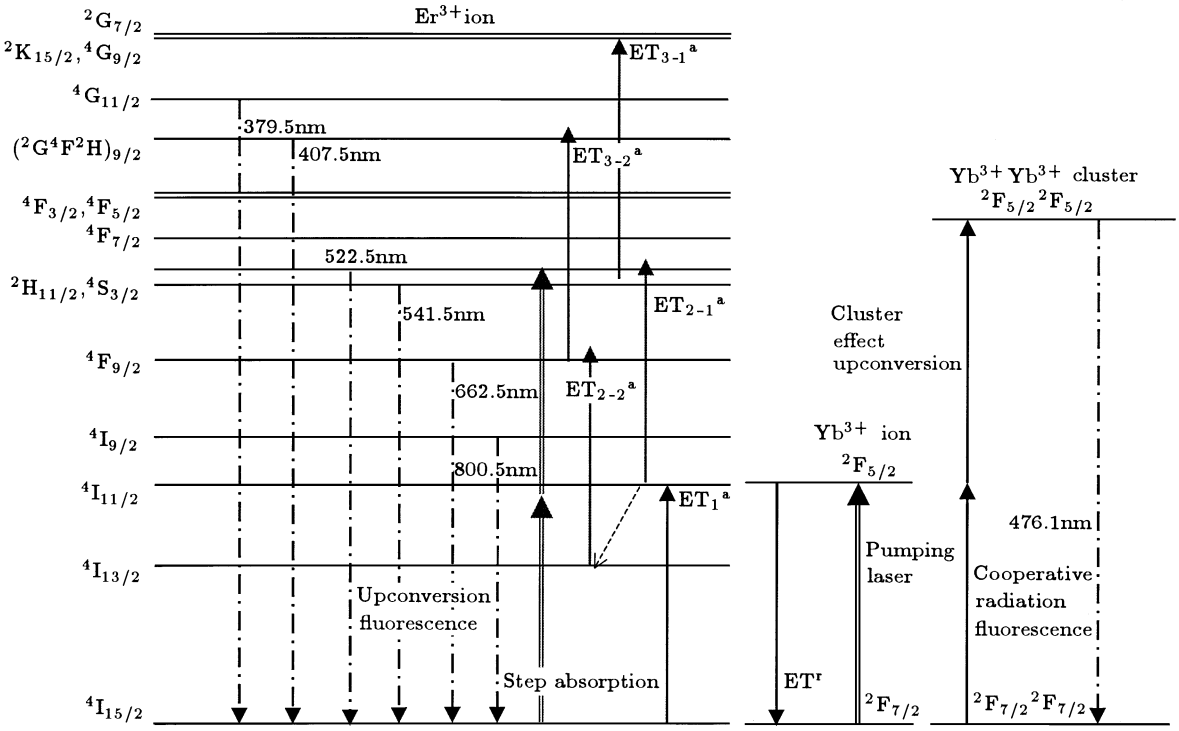


Fig.3. The energy level structure of Yb^{3+}, Er^{3+} ions and the schematic diagram of up-conversion process. (Er luminescence comes from traces of Er ions.)

As is well known, if the up-conversion luminescence originates from a two Yb^{3+} ion system, such as an energy transfer process between Yb^{3+} ions or a cluster coupled state made up of two Yb^{3+} ions, the up-conversion luminescence intensity would be proportion to the square of the Yb^{3+} ion concentration. Usually the up-conversion luminescence intensity increases less than the square of the Yb^{3+} ion concentration due to the energy cross-relaxation. However, it is interesting that the up-conversion luminescence intensity of Yb(5):FOG is 1000 times greater than that of Yb(0.5):FOG. This means that the coupling probability of two Yb^{3+} ions into a Yb^{3+}–Yb^{3+} cluster under the pumping of laser decreases when the concentration of Yb^{3+} ions is reduced too much. The coupling probability and up-conversion luminescence intensity is dependent upon not only the concentration of Yb^{3+} ions but also the basic material property. It could be seen by our experiment that the oxyfluoride glass is a kind of good material for cooperative up-conversion radiative luminescence of Yb^{3+} ion clusters.

The fluorescence lines of 407.5, 522.5, 541.5, 652.0 and 800.5 nm are the luminescence of Er^{3+} ions. The concentration of Er^{3+} ions in both Yb(5):FOG and Yb(0.5):FOG would be the same, because they are introduced naturally by the manufacture procedure. However, the luminescence intensity of Er^{3+} ions in Yb(5):FOG and Yb(0.5):FOG is quite different. There are only weak 522.5 and 541.5 nm luminescence of Yb(0.5):FOG resulting from the step-by-step absorption of Er^{3+} ions. For the Yb(5):FOG sample, the luminescence of Er^{3+} ions, especially the 407.5, 652.0 and 800.5 nm luminescence, is very much enhanced. It obviously results from the energy transfer from Yb^{3+} ions to Er^{3+} ions.

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References

[1] Chen J E *et al* 1994 *Opt. Phys. Sci.* (Beijing: Science Press) (in Chinese)
[2] Allain J Y, Monerie M and Poignant H 1992 *Electron. Lett.* **28** 111
[3] Lande D *et al* 1997 *Opt. Lett.* **22** 1722
[4] Collins S F *et al* 1998 *J. Appl. Phys.* **84** 4649
[5] Faris G W and Dyer M J 1999 *"Demonstration of Molecular Upconvertors",* in *Quantum Electronics and Laser Science Conference,* Paper QFB3 (Baltimore, MD: Optical Society of America)
[6] Chen X B *et al* 1998 *Proc. SPIE* **3560** 122
[7] Chen X B *et al* 1995 *OPTRON. · Laser.* **6** 344
[8] Chen X B and Nie Y X 2000 *Proc. SPIE* **4221** 73
[9] Chen X B *et al* 1993 *Acta Phys. Sin.* (*Overseas Edition*) **2** 695
[10] Chen X B *et al* 1993 *Acta Phys. Sin.* (*Overseas Edition*) **2** 771
[11] Chen X B and Nie Y X *et al* 1999 *Acta Phys. Sin.* **48** 948 (in Chinese)
[12] Chen X B and Nie Y X *et al* 1999 *Acta Phys. Sin.* (*Overseas Edition*) **8** 216
[13] Chen X B *et al* 1993 *Chin. Phys. Lett.* **10** 692
[14] Zhang X X, Hong P, Bass M and Chai B H T 1995 *Phys. Rev.* B **51** 9298
[15] Chen X B *et al* 1993 *Chin. Phys. Lett.* **10** 242
[16] Carnall W T, Fieldd R and Rajnank K T 1968 *J. Chem. Phys.* **49** 4424
[17] Chen X B *et al* 1996 *Development of Optics Property Research of Condensed Matter* (Shanghai: Fudan University Press) p 87 (in Chinese)
[18] Chen X B *et al* 1996 *Acta Phys. Sin.* **45** 698 (in Chinese)