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DIRECT UPCONVERSION SENSITIZATION LUMINESCENCE OF Ho(0.1)Yb(5):OXYFLUORIDE VITROCERAMICS*

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This paper studies the upconversion luminescence phenomenon of the Ho,Yb co-doped oxyfluoride vitroceramics. There is one group of strong upconversion luminescence lines positioned at 536.5nm, 18639cm^{-1}; 540.5nm, 18501cm^{-1}; 544.0nm, 18399cm^{-1}, which is easily identified as the transitions of $^5S_2 \rightarrow {}^5I_8$. There are other splendid upconversion luminescence lines, which are $^5S_2 \rightarrow {}^5I_7$, $^5F_5 \rightarrow {}^5I_8$, $^5G_6 \rightarrow {}^5I_8$, $(^5G^3G)_5 \rightarrow {}^5I_8$, $(^3F^3H^5G)_4 \rightarrow {}^5I_7$, $^5G_4 \rightarrow {}^5I_8$ and $(^5G^3H)_5 \rightarrow {}^5I_8$. It is also found that an interesting kind of upconversion cooperative radiation fluorescence comes from a kind of coupling state of clusters consisting of two Yb^{3+} ions.

Keywords: upconversion luminescence, oxyfluoride vitroceramics, Ho^{3+} ion
PACC: 7855, 4255R, 7840

I. INTRODUCTION

Upconversion research is a forward task of photophysics, which is one of the mainstay technologies in the future information society.[1−8]

Even though the upconversion efficiency of the ZBLAN material has reached a comparatively high level, it is still not large enough to use in practical applications. Therefore, it is necessary to find some proper sensitizing combination, suitable pumping passage, mechanism and material for this. It is particularly significant to enhance the upconversion luminescence brightness by increasing both the upconversion efficiency and the laser damage threshold.[8−19]

In this paper we study the upconversion luminescence phenomenon in the Ho(0.1)Yb(5) oxyfluoride vitroceramics. A splendid upconversion luminescence phenomenon of Ho^{3+} ion is found. All of the upconversion luminescence lines are identified. We also find that a new kind of upconversion cooperative radiation fluorescence comes from a kind of coupling state of clusters consisting of two Yb^{3+} ions.

II. STUDY OF CONVENTIONAL SPECTRA

The conventional photoemission and excitation spectra of Ho(0.1)Yb(5):FOV are measured by a Fluorolog-Tau-3 fluorescence photospectrometer. The photoemission spectrum of the 450nm $^5G_6$ energy level is given in Fig.1. Compared with the energy level structure of the Ho^{3+} ion[10] in Fig.2, it is easy to point out that these lines of photoemission luminescence are 483.0nm $^5F \rightarrow {}^5I_8$, 541.5nm $^5S_2 \rightarrow {}^5I_8$, 641.5nm $^5F_5 \rightarrow {}^5I_8$ transitions respectively. The detailed information is listed in Table 1, which coincides with the energy level structure of the Ho^{3+} ion.[10]

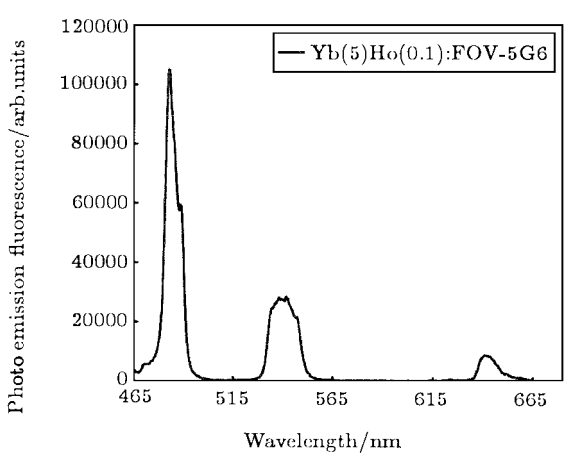


Fig.1. The conventional photoemission spectrum of Ho(0.1)Yb(5):FOV (00427h42).

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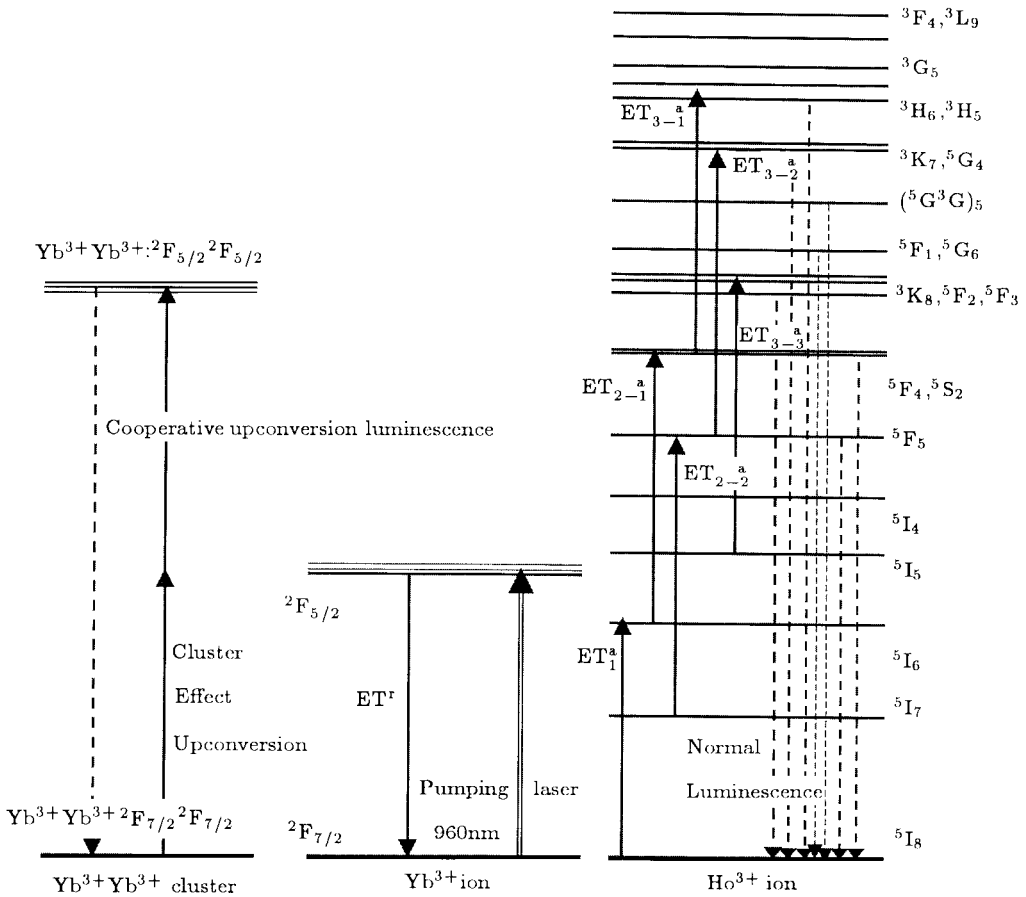


Fig.2. The energy level structure of Ho^{3+} and Yb^{3+} ions and the schematic diagram of the upconversion process (HoYb-els-Fig).

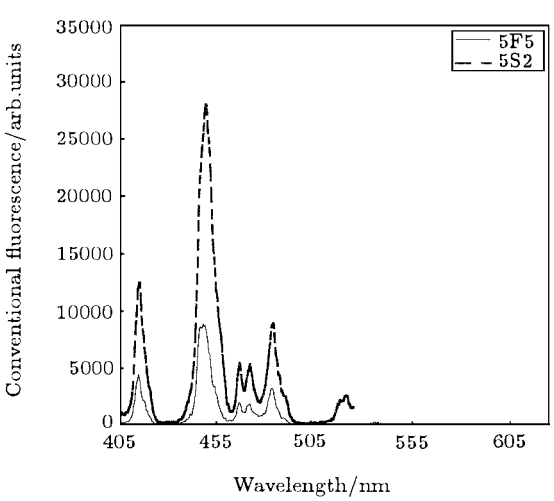


Fig.3. The conventional photoexcitation spectrum of Ho(0.1)Yb(5):FOV (00427h45).

The conventional excitation spectra of $^5F_5$ and $^5S_2$ levels of Ho(0.1)Yb(5):FOV are also measured, as shown in Fig.3. There are six obvious excitation peaks. By comparing with the energy level structure of the Ho^{3+} ion in Fig.2, it is easy to point out that these excitation peaks are 415.3nm $^5I_8 \rightarrow (^5G^3G)_5$, 448.5nm $^5I_8 \rightarrow {}^5G_6$, 466.5nm $^5I_8 \rightarrow {}^3K_8$, 472.0nm $^5I_8 \rightarrow {}^5F_2$, 483.5nm $^5I_8 \rightarrow {}^5F_3$ and 536.0nm $^5I_8 \rightarrow {}^5F_4$ absorption transitions respectively. The detailed information is also listed in Table 1.

Table 1. The upconversion luminescence and the excitation or emission spectrum peaks of Ho(0.1)Yb(5):FOV.

Excitation spectrum peaks	Emission spectrum peaks	Upconversion luminescence peaks
		363.0nm, 27548 cm^{-1} $(^5G^3H)_5 \rightarrow {}^5I_8$
		389.5nm, 25674 cm^{-1} $^5G_4 \rightarrow {}^5I_8$
		407.0nm, 24570 cm^{-1} $(^3F^3H^5G)_4 \rightarrow {}^5I_7$
415.3nm, 24078 cm^{-1} $^5I_8 \rightarrow (^5G^3G)_5$		416.5nm, 24010 cm^{-1} $(^5G^3G)_5 \rightarrow {}^5I_8$
448.5nm, 22297 cm^{-1} $^5I_8 \rightarrow {}^5G_6$		444.0 nm, 22523 cm^{-1} $^5G_6 \rightarrow {}^5I_8$
466.5nm, 21436 cm^{-1} $^5I_8 \rightarrow {}^3K_8$		
472.0nm, 21186 cm^{-1} $^5I_8 \rightarrow {}^5F_2$		
		479.5nm, 20855 cm^{-1}(L)
		475.5nm, 21030cm^{-1}
		462.5nm, 21622cm^{-1}
		$^2F_{5/2}$ $^2F_{5/2}$(YbYb)$\rightarrow$ $^2F_{7/2}$ $^2F_{7/2}$(YbYb)
483.5nm, 20683 cm^{-1} $^5I_8 \rightarrow {}^5F_3$	483.2nm, 20695 cm^{-1}(L)	484.3nm, 20648 cm^{-1}(L)
	489.0nm, 20450 cm^{-1} $^5F_3 \rightarrow {}^5I_8$	491.1nm, 20362 cm^{-1} $^5F_3 \rightarrow {}^5I_8$
536.0nm, 18657 cm^{-1} $^5I_8 \rightarrow {}^5F_4$	541.5nm, 18467 cm^{-1} $^5S_2 \rightarrow {}^5I_8$	536.5nm, 18639 cm^{-1}(L)
		540.5nm, 18501 cm^{-1}
		544.0nm, 18399 cm^{-1} $^5S_2 \rightarrow {}^5I_8$
	641.5nm, 15588 cm^{-1} $^5F_5 \rightarrow {}^5I_8$	643.5nm, 15540 cm^{-1}(L)
		652.5nm, 15326 cm^{-1} $^5F_5 \rightarrow {}^5I_8$
	750.0nm, 13333 cm^{-1} $^5S_2 \rightarrow {}^5I_7$	750.5nm, 13324 cm^{-1} $^5S_2 \rightarrow {}^5I_7$
	799.9nm, 12502 cm^{-1} $^5I_4 \rightarrow {}^5I_8$	

"L" represents the largest signal.

Ⅲ. UPCONVERSION EXPERIMENTS AND RESULTS

We select the Ho,Yb-codoped SiO_2-$AlO_{1.5}$-PbF_2-CdF_2 oxyfluoride vitroceramics (HoYb:FOV) samples to proceed the direct upconversion sensitization luminescence research of the Ho^{3+} ion. The laser device used in our experiment is a 960nm continuous-wave (CW) diode laser manufactured by the Institute of Semiconductor Physics of the Chinese Academy of Sciences. The largest pumping laser power is 224mW, and the smallest is 5.4mW. By using a group of lenses the laser is focused on to the sample. The laser facula on the sample is adjusted at about 0.8mm×2.5mm. Thus the largest pumping laser power density is about 1.12×10^4mW/cm^2, and the smallest is about 2.70×10^2mW/cm^2. We collect and handle the luminescence emitted from the sample with a Fluorolog-Tau-3 luminescence photometer of JY INC. The collection direction of luminescence is perpendicular to the laser excitation direction. As for the doping concentration in the HoYb:FOV samples, it is about 5 mol% Yb^{3+} ions and 0.1 mol% Ho^{3+} ions. The thickness of the samples used is about 1.5mm.

We use a 960nm-diode laser to excite the samples. The upconversion luminescence at the large laser facula position is measured, as shown in Fig.4. It is found that there are plenty of upconversion luminescence lines. It is easy to recognize the reversion of the luminescence by comparison with Table 1 and Fig.2. Detailed results are as follows: there is a group of strong upconversion luminescence lines at (536.5nm, 18639cm^{-1}; 540.5nm, 18501cm^{-1}; 544.0nm, 18399cm^{-1}), which are attributed to the transitions of $^5S_2 \rightarrow {}^5I_8$. There are other upconversion luminescence lines of middle intensities, which can be classified as (643.5nm, 15540cm^{-1}; 652.5nm, 15326cm^{-1}) fluorescence of $^5F_5 \rightarrow {}^5I_8$ transition; (479.5nm, 20855cm^{-1}) fluorescence group, and (750.5nm, 13324cm^{-1}) fluorescence of $^5S_2 \rightarrow {}^5I_7$ transition. Besides, there are some weak upconversion luminescence (363.0nm, 27548 cm^{-1}), (389.5nm, 25674 cm^{-1}), (407.0nm, 24570cm^{-1}), (416.5nm, 24010 cm^{-1}) and (444.0nm, 22523 cm^{-1}) lines, which are also easy to be recognized as the transitions of $(^5G^3H)_5 \rightarrow {}^5I_8$, $^5G_4 \rightarrow {}^5I_8$, $(^3F^3H^5G)_4 \rightarrow {}^5I_7$, $(^5G^3G)_5 \rightarrow {}^5I_8$ and $^5G_6 \rightarrow {}^5I_8$. The detailed information is given in Table 1.

Changing the laser power, we have carefully measured the dependence of upconversion luminescence intensity upon pumping laser power at the large laser facula position, as shown in Fig.5 and listed in Table 2. The integral area of every luminescence lines represents luminescence signal intensity.

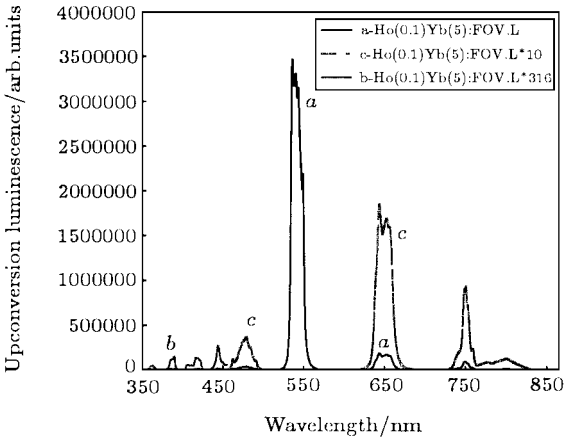


Fig.4. Upconversion luminescence of Ho(0.1)Yb (5):FOV induced by 960nm laser in large laser facula (10506h17).

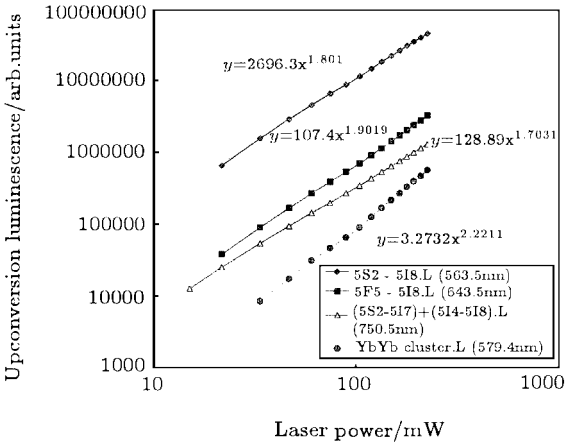


Fig.5. The upconversion luminescence intensity variation of Ho(0.1)Yb(5) with the laser power in large facula "L" (f-HoYb1v).

Table 2. Slope of log–log plot of F–P curve of Ho(0.1)Yb(5):oxyfluoride vitroceramics.

Peak position	643.5nm	536.5nm	479.5nm	750.5nm
Transition	$^5F_5 \rightarrow {}^5I_8$	$^5S_2 \rightarrow {}^5I_8$	YbYb cluster	$^5S_2 \rightarrow {}^5I_7 + {}^5I_4 \rightarrow {}^5I_8$
Slope γ at large facula	1.90	1.80	2.22	1.70

IV. ANALYSIS

Carefully observing and comparing the experimental results, we can find that the slope of the F–P log–log plot of $^5F_5$ and $^5S_2$ level upconversion luminescence intensity versus 960nm pumping laser power is about γ=1.7∼1.9, which is close to the normal two-photon variation relation γ=2. This illustrates that the upconversion luminescence of $^5F_5$ and $^5S_2$ energy level is two-photon upconversion luminescence.

From Fig.2 we can find the mechanism of the upconversion in this HoYb:FOV system. The photon energy of the 960nm-pumping laser is 10417cm^{-1}, which is not resonant with the ground-state energy of Ho^{3+} ion. This would not be a step-by-step multi-photon absorption upconversion. However, the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ absorption of Yb^{3+} ion is resonant with the photon energy of the 960nm-pumping laser. Thus the upconversion mechanism in this HoYb:FOV system is sure to be the energy transfer from Yb^{3+} to Ho^{3+} ion.

It is easy to describe the passage of the upconversion processes, as shown in Fig.2. The symbol ET^r represents releasing energy transfer, ET^a represents absorbing energy transfer. The energy transfer passages from Yb^{3+} ion to Ho^{3+} ions are as follows. The first-step energy transfer ET_1 from Yb^{3+} ion to Ho^{3+} ion is $\{^2F_{5/2}(Yb^{3+}) \rightarrow {}^2F_{7/2}(Yb^{3+}), {}^5I_8(Ho^{3+}) \rightarrow {}^5I_6(Ho^{3+})\}$. The second-step energy trans fers have two passages:ET_{2-1} is $\{^2F_{5/2}(Yb^{3+}) \rightarrow {}^2F_{7/2}(Yb^{3+}), {}^5I_6(Ho^{3+}) \rightarrow {}^5F_4\ {}^5S_2(Ho^{3+})\}$;$ET_{2-2}$ is $\{^2F_{5/2}(Yb^{3+}) \rightarrow {}^2F_{7/2}(Yb^{3+}), {}^5I_7(Ho^{3+}) \rightarrow {}^5F_5(Ho^{3+})\}$. The third-step energy transfers have three passages: ET_{3-1} is $\{^2F_{5/2}(Yb^{3+}) \rightarrow {}^2F_{7/2}(Yb^{3+}), {}^5S_2(Ho^{3+}) \rightarrow {}^3H_6(Ho^{3+})\}$; ET_{3-2} is $\{^2F_{5/2}(Yb^{3+}) \rightarrow {}^2F_{7/2}(Yb^{3+}), {}^5F_5(Ho^{3+}) \rightarrow {}^5G_4(Ho^{3+})\}$; and ET_{3-3} is $\{^2F_{5/2}(Yb^{3+}) \rightarrow {}^2F_{7/2}(Yb^{3+}), {}^5I_5(Ho^{3+}) \rightarrow {}^3K_8\ {}^5F_2(Ho^{3+})\}$. The reason why these upconversion energy transfer passages are quite effective is that they have proper energy matching and the energy levels $^5I_6$, $^5I_7$, $^5F_5$ and $^5S_2$ are all better metastable states.

A very interesting phenomenon concerns the 479.5nm (20855cm^{-1}) group upconversion luminescence of HoYb:FOV.

The upconversion luminescence of Ho(0.1)Yb(5): FOV and Yb(5):FOV is measured, as shown in Fig.6. The results indicate that the upconversion luminescence of $Ho^{3+}Yb^{3+}$: FOV has been varied obviously from that of Yb:FOV. The main upconversion luminescence peak 479.5nm of Ho(0.1)Yb(5):FOV is the same as that of Yb(5):FOV. In fact, it is reasonable to believe that the 479.5nm upconversion luminescence of HoYb:FOV is a kind of cooperative upconversion radiation fluorescence originating from a coupling state consisting of Yb^{3+}-Yb^{3+} clusters as that of Yb:FOV.[5,11] However, the up-

conversion luminescence of $Yb^{3+}Ho^{3+}$:FOV obviously has two additional peaks, which are not present in that of Yb:FOV. The additional peaks of upconversion luminescence of HoYb:FOV are at (484.3nm, 20648cm^{-1}) and (491.1nm, 20362cm^{-1}), which are very near the $^5I_8 \rightarrow {}^5F_3$ absorption peak (484.4nm, 20644 cm^{-1}) and the photoemission fluorescence peak (483.2nm) and (489.0nm) of HoYb:FOV.[10] Thus it may be believed confidently that the upconversion luminescence peaks (484.3nm, 20648cm^{-1}) and (491.1nm, 20362cm^{-1}) of Ho(0.1)Yb(5):FOV can be attributed to $^5F_3 \rightarrow {}^5I_8$ fluorescence transition of Ho^{3+} ion. In brief, the upconversion luminescence of $Yb^{3+}Ho^{3+}$:FOV located at about 479nm is of two types. One type is the cooperative upconversion luminescence lines (479.5nm, 20855 cm^{-1}(L); 475.5nm, 21030cm^{-1}; 462.5nm, 21622cm^{-1}) of the coupling state of Yb^{3+}-Yb^{3+} cluster. The other type is the normal $^5F_3 \rightarrow {}^5I_8$ upconversion luminescence (484.3nm,20648cm^{-1} and 491.1nm, 20362cm^{-1}) of single Ho^{3+} ion.

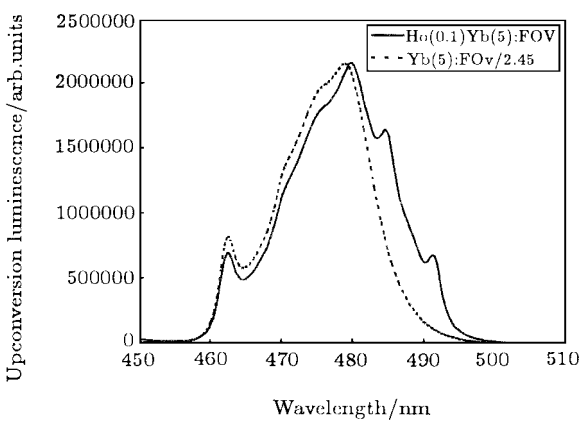


Fig.6. Comparison of the cooperative upconversion luminescence lines of Ho(0.1)Yb(5):FOV and Yb(5):FOV (10220h1B).

From Table 1 and Fig.5, an interesting phenomenon can be seen. The slope of the F–P log–log plot of 479nm-group upconversion luminescence intensity versus laser power is about γ=2.22 at the large facula position, which is obviously larger than that of the two-photon variation relation such as the $^5F_5$ and $^5S_2$ upconversion luminescence. Thus the 479nm-group upconversion luminescence is surely contributed partly by three-photon fluorescence. As is known, the cooperative upconversion luminescence of the coupling state of Yb^{3+}-Yb^{3+} cluster is a two-photon upconversion luminescence. Thus the normal $^5F_3 \rightarrow {}^5I_8$ upconversion luminescence of Ho^{3+} ion should be mainly a three-photon upconversion luminescence.

The passage of cluster effect upconversion induced by the coupling state of Yb^{3+}-Yb^{3+} cluster is also shown in Fig.2, in which CEU represents cluster effect upconversion. It could be described as: $\{^2F_{7/2}(Yb^{3+})+{}^2F_{7/2}(Yb^{3+})\} \rightarrow \{^2F_{5/2}(Yb^{3+})+{}^2F_{5/2}(Yb^{3+})\} \rightarrow \{^2F_{5/2}\ {}^2F_{5/2}\ (Yb^{3+}Yb^{3+})\} \rightarrow \{^2F_{7/2}\ {}^2F_{7/2}(Yb^{3+}Yb^{3+})\}$.

V. CONCLUSION

There are plenty of upconversion luminescence lines when Ho(0.1)Yb(5):FOV is excited by a 960nm laser. There is a group of strong upconversion luminescence lines located at (536.5nm, 18639cm^{-1}; 540.5nm, 18501cm^{-1}; 544.0nm, 18399cm^{-1}), which is easily identified as the transitions of $^5S_2 \rightarrow {}^5I_8$. Other upconversion luminescence lines are positioned at (363.0nm, 27548 cm^{-1}), (389.5nm, 25674 cm^{-1}), (407.0nm, 24570cm^{-1}), (416.5nm, 24010 cm^{-1}), (444.0nm, 22523 cm^{-1}), (643.5nm, 15540cm^{-1}; 652.5nm, 15326cm^{-1}) and (750.5nm, 13324cm^{-1}), which are also easy to recognize as the transitions of $(^5G^3H)_5 \rightarrow {}^5I_8$, $^5G_4 \rightarrow {}^5I_8$, $(^3F^3H^5G)_4 \rightarrow {}^5I_7$, $(^5G^3G)_5 \rightarrow {}^5I_8$ $^5G_6 \rightarrow {}^5I_8$, $^5F_5 \rightarrow {}^5I_8$ and $^5S_2 \rightarrow {}^5I_7$.

An interesting phenomenon concerns the 479.5nm (20855cm^{-1}) group of upconversion luminescence lines of HoYb:FOV, which is of two types of lines. One type is the cooperative upconversion luminescence lines (479.5nm, 20855 cm^{-1}(L); 475.5nm, 21030cm^{-1}; 462.5nm, 21622cm^{-1}) of the coupling state of Yb^{3+}-Yb^{3+} cluster. The other type is the normal $^5F_3 \rightarrow {}^5I_8$ upconversion luminescence lines (484.3nm,20648cm^{-1} and 491.1nm, 20362cm^{-1}) of single Ho^{3+} ion.

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