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# Comprehensive research about the cooperative up-conversion luminescence of the ytterbium-doped oxyfluoride vitroceramics*

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The cooperative up-conversion blue luminescence of $Yb^{3+}$ ion-doped oxyfluoride vitroceramic material (Yb:FOV) and the influence of co-doped $Ho^{3+}$ ion, when excited by a 960 nm diode-laser, are studied in this paper. A strong blue 479.1 nm up-conversion luminescence of the Yb:FOV material is discovered. It is found that the 479.1 nm luminescence results from the cooperative up-conversion of the coupled states of the $Yb^{3+}$–$Yb^{3+}$ clusters formed by two adjacent $Yb^{3+}$ ions. The measured cooperative up-conversion luminescence main peak 479.1 nm of this paper is different from the characteristic fluorescence main peak of the $Tb^{3+}$ ion positioned at about 495–504 nm wave-range. Our result coincides with all the published correct papers, whose cooperative up-conversion luminescence main peaks of the direct $Yb^{3+}$–$Yb^{3+}$ clusters are all positioned at about 476–480 nm wave-range. All of these indicate that the large cooperative up-conversion blue luminescence of the direct $Yb^{3+}$–$Yb^{3+}$ clusters discovered in this paper is stable. It further proves that the cooperative up-conversion green luminescence may result from the $Yb^{3+}$-$Tb^{3+}$ cooperative effect. In particular, the original work of this paper improves considerably on the traditional concept by the experimental facts that the blue 479.1 nm cooperative up-conversion luminescence strength of Yb(5):FOV is 230 times greater than that of fluoride glass Yb(3):ZBLAN. This is a great development to meet the practical requirements for blue up-conversion luminescence strength. This result indicates that the large cooperative up-conversion blue luminescence could be achieved excellently by using a suitable material, such as oxyfluoride vitroceramic, which provides a better chance to form better $Yb^{3+}$–$Yb^{3+}$ clusters and has less relaxation to keep the more efficient up-conversion luminescence. It is also found that impurities seriously reduce the cooperative up-conversion luminescence intensity due to the cross-relaxation from the $Yb^{3+}$–$Yb^{3+}$ clusters, which means that the cooperative up-conversion blue luminescence could be further improved by pure $Yb^{3+}$ ion-doped materials that have as few impurities as possible to reduce the cross-relaxation. The large cooperative up-conversion blue luminescence of Yb(5):FOV also comes from its higher concentration (5 mol%) of activator $Yb^{3+}$ ion which acts well because the cooperative up-conversion blue luminescence intensity varies linearly against the square of the concentration of $Yb^{3+}$ ions in the range of 0.5–5 mol%. In summary, the great improvement of our work on cooperative up-conversion blue luminescence results from the comprehensive enhancement of the factors of better-coupled chance of the $Yb^{3+}$–$Yb^{3+}$ clusters, less cross-relaxation, better concentration contribution of $Yb^{3+}$ activator, non-saturation, and better up-conversion luminescence efficiency.

**Keywords:** up-conversion, cooperative, $Yb^{3+}$–$Yb^{3+}$ cluster, blue light
**PACC:** 7855, 4270, 7840

## 1. Introduction

Optical physics, especially of the multi-photon up-conversion, is the foundation of practical technologies in the modern world.[1–19] Better performance of integrated optoelectronics requires a more efficient up-conversion of photons from the energy of about 10,000 $cm^{-1}$ up to that of the blue–green wavelengths.[1–27] Up-conversion of photons can be realized through mechanisms such as sequential photon absorption, cooperative up-conversion,[1,2,4–7,9,12] energy transfer,[1,2,4–6,11,12] and avalanche. The introduction of $Yb^{3+}$ ions as a sensitizing centre could greatly enhance the up-conversion luminescence of rare-earth ion activators, which is used extensively in energy transfer and cooperative up-conversion. The concept of cooperative up-conversion was proposed several decades ago,[1,26] based on the excellent construction that two $Yb^{3+}$ ions transfer their energies simultaneously to a $Tm^{3+}$ or $Tb^{3+}$ ion whose en-

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ergy levels are as high as twice the $^2F_{5/2}$ level of the $Yb^{3+}$ ion. A number of $Yb^{3+}$-$Eu^{3+}$ or $Yb^{3+}$-$Tm^{3+}$ or $Yb^{3+}$-$Tb^{3+}$ cooperative up-conversion researches have been carried out to date.[1,2,6−8,11,14,22] However, it was thought in the past that the cooperative up-conversion was far less efficient than the energy transfer up-conversion because the near-resonant back energy-transfer from the $Tm^{3+}$ or $Tb^{3+}$ ion back to the $Yb^{3+}$ ion restricts the enhancement of this cooperative up-conversion luminescence, especially for a material with a huge phonon energy. The good direct $Yb^{3+}$–$Yb^{3+}$ cooperative up-conversion blue luminescence was correctly achieved only very recently.[7,9,12] The concept of cooperative up-conversion is further developed by the facts that the upper level of cooperative up-conversion luminescence is the coupled state $^2F_{5/2}{}^2F_{5/2}$ of the direct $Yb^{3+}$–$Yb^{3+}$ cluster positioned at the double-energy of the $^2F_{5/2}$ level of the $Yb^{3+}$ ion. It has also been proved that the cooperative up-conversion green luminescence results from the $Yb^{3+}$-$Tb^{3+}$ cooperative effect [9] and so on. The cooperative up-conversion blue luminescence of the direct $Yb^{3+}$–$Yb^{3+}$ clusters exhibits good attraction initially.[7,9,12] Meanwhile, further improvement is urgently needed because the luminescence intensity of the cooperative up-conversion in early experiments was small. It is well known also that the multiphoton up-conversion has extensive applications in lasers, three-dimensional (3D) volumetric display,[10] waveguide applications, biological applications, imaging, optical data storage, (temperature) sensors and so on.[1−27] In summary, cooperative up-conversion shows itself to be a good method to achieve integrated blue-light, which is of particular interest.[1,2,5−9,12]

The cooperative up-conversion blue luminescence of the $Yb^{3+}$-doped oxyfluoride vitroceramics (Yb:FOV) and the influence of the co-doped $Ho^{3+}$ ions, when excited by a 960 nm diode-laser, are studied comprehensively in this paper with various concentrations of $Yb^{3+}$ and $Ho^{3+}$ ions. A strong blue 479.1 nm up-conversion cooperative luminescence is observed and attributed to the coupled states of the $Yb^{3+}$–$Yb^{3+}$ clusters.[7,9,12] In order to know the cooperative up-conversion efficiency of the Yb:FOV material, a ZBLAN fluoride glass (Yb(3):ZBLAN) sample is studied comparatively also. The experimental conditions are kept the same so as to ensure that the relative fluorescence intensities of the measured curves are comparable. The original work of this paper improves on the traditional concept by the experimental facts that the 479.1 nm blue cooperative up-conversion luminescence strength of Yb(5):FOV is 230 times greater than that of Yb(3):ZBLAN. It is also found that the cooperative up-conversion luminescence of $Yb^{3+}Ho^{3+}$-codoped oxyfluoride vitroceramics (YbHo:FOV) is obviously smaller than that of $Yb^{3+}$ mono-doped FOV, indicating that the impurities will seriously reduce the cooperative up-conversion luminescence intensity of the $Yb^{3+}$–$Yb^{3+}$ cluster due to cross-relaxation. The results of this paper show that there is great prospect that a large cooperative up-conversion could be achieved excellently by using suitable materials, such as oxyfluoride vitroceramic which provides the opportunity to form better $Yb^{3+}$–$Yb^{3+}$ clusters and has less phonon-relaxation to keep the more efficient up-conversion luminescence. Moreover, cooperative up-conversion could be improved further by a material doped with pure $Yb^{3+}$ that has as little impurity as possible to reduce cross-relaxation. The physics basis is discussed comprehensively to understand the up-conversion better. The result of this paper may go some way toward satisfying the practical requirements on blue up-conversion luminescence strength.

## 2. Oxyfluoride vitroceramics

Five $Yb^{3+}$-doped or $Yb^{3+}Ho^{3+}$-codoped oxyfluoride vitroceramic samples are used in our experiments. They are made from powders of $SiO_2$, $PbF_2$, $ZnF_2$, $LuF_3$, $YbF_3$, and $HoF_3$. Two of them are doped singly with $Yb^{3+}$ ion at concentrations of 5 and 0.5 mol%, denoted as [a] Yb(5):FOV and [b] Yb(0.5):FOV respectively. The other three samples are $Yb^{3+}Ho^{3+}$-codoped oxyfluoride vitroceramics, denoted as [c] Yb(5) Ho(0.1):FOV, [d] Yb(5) Ho(0.5):FOV, and [e] Yb(1) Ho(0.5):FOV. The energy structures of $Yb^{3+}$ and $Ho^{3+}$ ions are shown in Fig.1. The composition of sample [c] Yb(5) Ho(0.1):FOV, as an example, is $SiO_2$ ($A$mol%), $PbF_2$ ($B$mol%), $ZnF_2$ ($C$mol%), $LuF_3$ ($D$mol%), $YbF_3$ (5%), and $HoF_3$ (0.1%), i.e. the sum of the concentrations of all the constituents must be equal to 100%, $A+B+C+D+5+0.1=100$. Each sample was prepared in a platinum crucible and annealed at the glass transition temperature $T_g$=389°C to obtain the glass state of the oxyfluoride material first. The transparent oxyfluoride vitroceramic is obtained by additional thermal treatment of the glass at 470°C to form microcrystallines within the glass matrix almost without loss of transparency. A Zr–

Ba–La–Al–Na system (ZBLAN) fluoride glass sample [f] Yb(3):ZBLAN is used in our experiments for comparison of the up-conversion luminescent abilities between oxyfluoride vitroceramic FOV and fluoride glass ZBLAN. The surfaces of all these samples are polished to optical quality, which reduces scattered light to allow a good spectroscopic measurement.

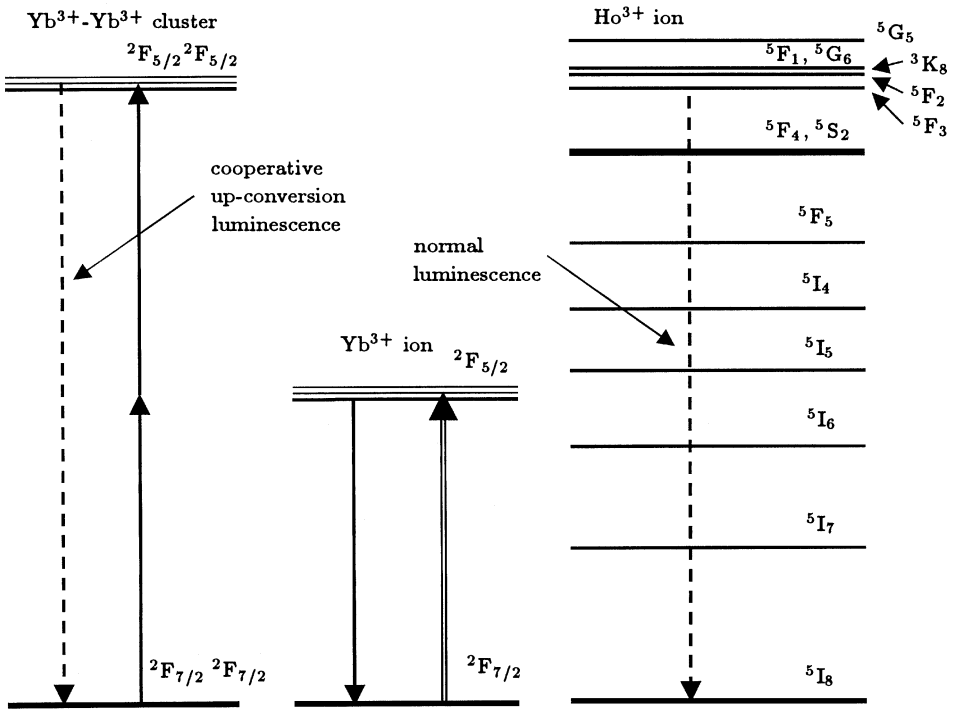



**Fig.1.** Schematic diagram of the up-conversion process and energy level structure of $Yb^{3+}$ and $Ho^{3+}$ ions.

## 3. Experimental devices

The up-conversion luminescence and common fluorescence spectra are measured using the experimental devices shown in Fig.2. The fluorescence-detecting instrument is a set of fluorescence spectrophotometer (JY-ISA, Fluorolog-Tau-3). Its sensitivity is good in the range of 197–870 nm. Its resolution is better than 0.5 nm, which could reach 0.1 nm when operated carefully. The linearity of the spectrophotometer is good within $6.0\times10^6$ counts, especially within $1.5\times10^6$ counts. The measuring wave-range is larger than 197–870 nm. When the up-conversion luminescent spectra are measured, the pump source selected is a 960 nm continuous diode-laser, manufactured by the Institute of Semiconductors of the Chinese Academy of Sciences. Its largest laser power is about 0.5W. The laser beam is focused onto a sample by a group of lenses, and the fluorescence emitted from the sample is collected by a set of concave mirrors and then analysed by the fluorescence spectrophotometer (JY-ISA, Fluorolog-Tau-3). The collection direction of the fluorescence is perpendicular to the propagation direction of the pumping laser. The experimental conditions are kept the same, so as to ensure that the relative fluorescence intensities of the measured curves are comparable. When common fluorescence spectra are measured, the traditional Xe lamp is used, which is the light source component of the fluorescence spectrophotometer (JY-ISA, Fluorolog-Tau-3). The precise repeatable experimental state can be changed alternately between up-conversion luminescence and common fluorescence spectra measurements.

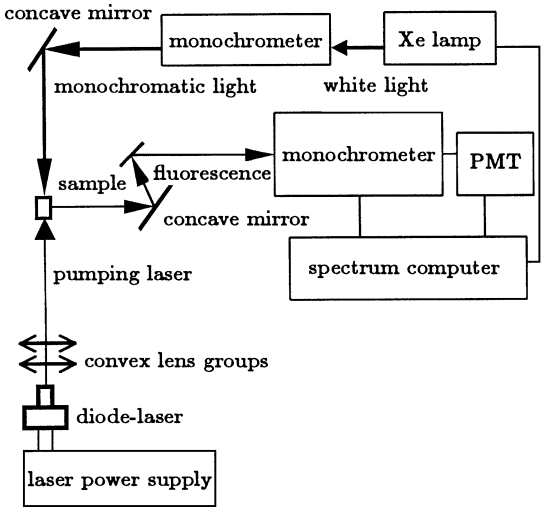



**Fig.2.** Schematic diagram of relative experimental devices.

## 4. Relative spectra of absorption and fluorescence

In order to fully study the up-conversion, the absorption and common fluorescence spectra are also measured in this paper. Optical absorption of a representative sample of Yb(0.5):FOV is measured using a spectrophotometer (UV-365) which exhibits a sharp peak at 975.3 nm ($10253\,cm^{-1}$) and a well-defined shoulder at 927.0 nm ($10787\,cm^{-1}$), as shown in Fig.3. An analysis of the absorption spectrum using a deconvolution method reveals another shoulder at 952.0 nm ($10504\,cm^{-1}$). Figure 4 shows the optical absorption of another sample Yb(5) Ho(0.5):FOV. The spectrum exhibits a number of additional absorption peaks in the visible and infrared wave-range. All these additional peaks come from the $Ho^{3+}$ ions in the sample. The absorption peak positions and their assignment are summarized in Table 1.[1]

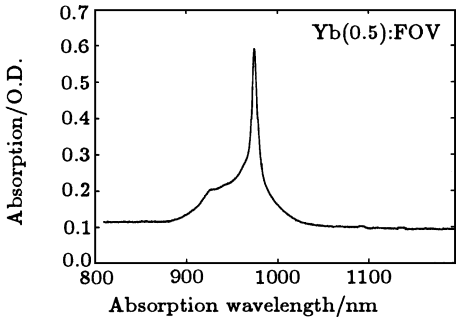



**Fig.3.** An absorption spectrum of Yb(0.5):FOV. The thickness of the sample is about 3.7mm. "O.D." is optical density.

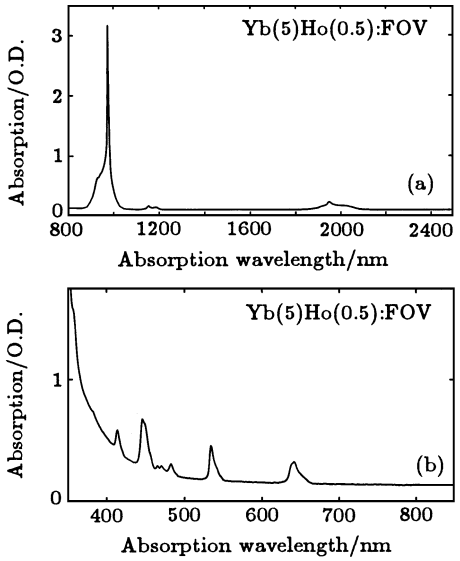



**Fig.4.** Absorption spectrum of Yb (5) Ho (0.5): FOV. The thickness of the sample is about 3.7mm. "O.D." is optical density.

**Table 1.** Peak positions and barycentres of absorption of $Yb^{3+}$ $Ho^{3+}$ codoped oxyfluoride vitroceramics Yb(5) Ho(0.5):FOV. All the absorption peaks, except one, are due to the $Ho^{3+}$ ions.

| | Upper state | Peak wavelength/nm | Peak wavenumber/$cm^{-1}$ | Barycentre |
|---|---|---|---|---|
| 1 | $^5I_7$ | 2009.0(l) | 4978 | 1969.1 nm |
| | | 1948.0(h) | 5133 | $5078\,cm^{-1}$ |
| 2 | $^5I_6$ | 1187.0(l) | 8425 | 1167.1 nm |
| | | 1154.5(h) | 8662 | $8568\,cm^{-1}$ |
| 3 | $^2F_{5/2}(Yb^{3+})$ | 975.3(l)(h) | 10253 | |
| | | 952.0 | 10504 | |
| | | 927.0 | 10787 | |
| 4 | $^5I_5$ | 908.5(l) | 11007 | 897.1 nm |
| | | 891.0(h) | 11223 | $11147\,cm^{-1}$ |
| 5 | $^5I_4$ | Very small | 13219 (theory) | |
| 6 | $^5F_5$ | 643.0(l)(h) | 15552 | 643.0 nm |
| | | 639.5 | 15637 | $15552\,cm^{-1}$ |
| 7 | $^5S_2$ | 543.2 | 18409 | |
| $^5S_2 \rightarrow {}^5I_7$=543.2 nm $\rightarrow$ 1969.1 nm=13331 $cm^{-1}$=750.1 nm | | | | |
| 8 | $^5F_4$ | 535.9 | 18660 | |
| 9 | $^5F_3$ | 484.4 | 20644 | |
| 10 | $^5F_2$ | 472.0 | 21186 | |
| 11 | $^3K_8$ | 467.1 | 21408 | |
| 12 | $^5G_6$ | 451.0(l) | 22172 | 449.1 nm |
| | | 447.3(h) | 22356 | $22267\,cm^{-1}$ |
| 13 | $(^5G^3G)_5$ | 415.5 | 24067 | |
| 14 | $^5G_4$, $^3K_7$ | 384.5 | 26008 | |
| 15 | $(^5G^3H)_5$, $^3H_6$ | | | |

Note: "l" the peak whose wavelength is the longest, "h" the peak whose intensity is the highest.

The fluorescence spectra, in both excitation and emission formats, of Yb(5) Ho(0.5):FOV are measured using a fluorescence spectrophotometer. Two excitation spectra are shown in Fig.5, in which the upper curve corresponds to the excitation spectrum of 542.5 nm $^5S_2 \rightarrow ^5I_8$. It is clear that the excitation spectrum of 542.5 nm $^5S_2 \rightarrow ^5I_8$ fluorescence is near to that of 642.0 nm $^5F_5 \rightarrow ^5I_8$ because both their profiles and peaks are very similar. There are seven obvious excitation peaks. It is easy to see that these excitation peaks are 358.5 nm $^5I_8 \rightarrow (^5G^3H)_5$ and $^3H_6$, 415.0 nm $^5I_8 \rightarrow (^5G^3G)_5$, 448.5 nm $^5I_8 \rightarrow ^5G_6$, 466.5 nm $^5I_8 \rightarrow ^3K_8$, 472.0 nm $^5I_8 \rightarrow ^5F_2$, 483.5 nm $^5I_8 \rightarrow ^5F_3$ and 537.5 nm $^5I_8 \rightarrow ^5F_4$ absorption transitions. It is clear that $^5I_8 \rightarrow ^5G_6$ absorption transition is the most powerful to excite photo-fluorescences at both 542.5 and 652.0 nm. The hill-like peak at about

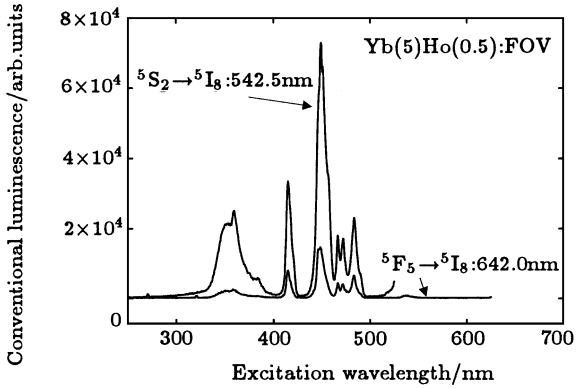



**Fig.5.** Excitation spectra of Yb(5) Ho(0.5):FOV. The fluorescence is detected at two wavelengths of 542.5 and 642.0 nm, which correspond to the $^5S_2 \rightarrow ^5I_8$ and $^5F_5 \rightarrow ^5I_8$ transitions, respectively.

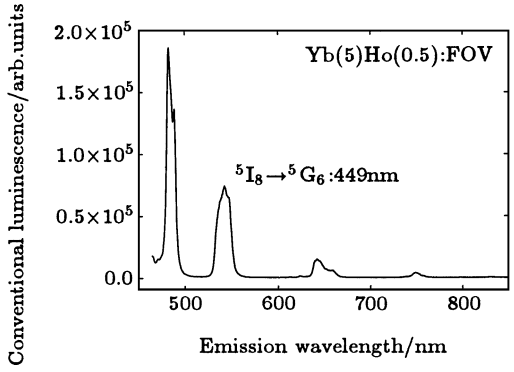



**Fig.6.** Photo-emission spectrum of Yb(5) Ho(0.5):FOV.

340 nm is the noise that comes from the metal impurity mixed in the manufacture procedure. When the light source is fixed at the $^5I_8 \rightarrow ^5G_6$ absorption wavelength 449 nm, the photo-emission spectrum of the $^5G_6$ energy level is obtained by measuring the radiation fluorescence along the long-wave side, as shown in Fig.6. It is easy to see that these photo-emission luminescences are (483.0, 489.0 nm) $^5F_3 \rightarrow ^5I_8$, 542.5 nm $^5S_2 \rightarrow ^5I_8$, (642.0, 658.0 nm) $^5F_5 \rightarrow ^5I_8$, and 749.5 nm $^5S_2 \rightarrow ^5I_7$ transitions respectively.

## 5. Experimental results of cooperative up-conversion

Experimental results for the excellent cooperative up-conversion blue luminescence in the oxyfluoride vitroceramics are obtained in this paper. The up-conversion luminous spectra of samples Yb(5):FOV and Yb(0.5):FOV are measured first when excited by a 227mW 960 nm continuous diode-laser, which is measured just behind the focusing lens group and in the front of the sample. The results are shown in Fig.7. In order to compare the cooperative up-conversion luminescence abilities between the oxyfluoride vitroceramics and fluoride ZBLAN materials, the up-conversion luminous spectra of Yb(5):FOV and Yb(3):ZBLAN are measured comparably also, as shown in Fig.8. It is clear that the cooperative up-conversion luminescence of Yb(5):FOV is 230 times greater than that of Yb(3):ZBLAN. By changing the diode-laser power from 5.4 to 227mW, the variation of the 479.1 nm up-conversion luminescence intensity as a function of pump laser power is measured carefully also, as shown in Fig.9. Meanwhile, the up-conversion luminous spectra of Yb(5) Ho(0.1):FOV, Yb(5) Ho(0.5):FOV and Yb(1) Ho(0.5):FOV samples within 450–505 nm wave-range are measured, as shown in Fig.7 also. Their typical and obvious peak positions and peak intensities, that are comparable directly, are all summarized in Table 2. The waveform variation with laser power is measured also, as shown in Figs. 10–12. Figures 10–12 exhibit similar spectral features: there are no observable changes in either the positions or profiles when the laser power is changed. Thus, the strong blue 479.1 nm up-conversion luminescence of Yb(5):FOV shows itself extremely clearly.

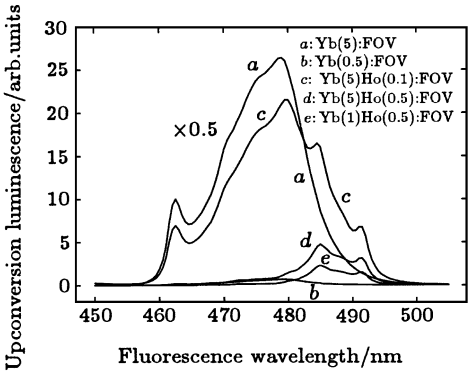



**Fig.7.** Cooperative up-conversion luminescence spectra of five Yb:FOV and YbHo:FOV samples, induced by a 960 nm laser. The intensities of all five curves are normalized and are directly comparable.

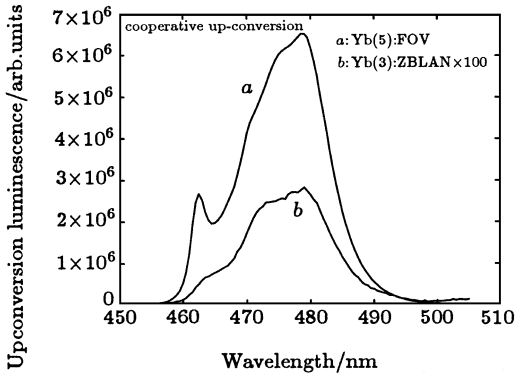



**Fig.8.** Cooperative up-conversion luminescence spectra of [a] Yb(5):FOV (line *a*) and [f] Yb(3):ZBLAN (line *b*), induced by a 960 nm laser. The data for [f] Yb(3):ZBLAN is enlarged by a factor of 100. The intensities of both curves are directly comparable.

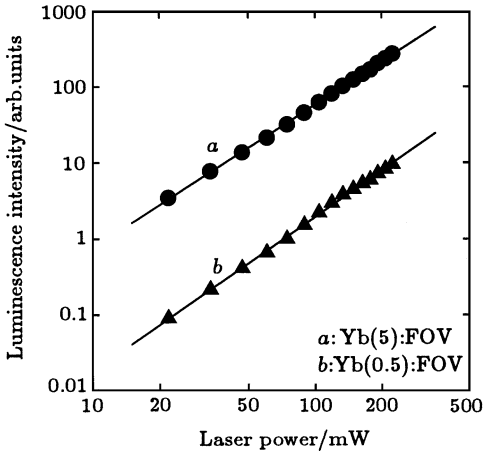



**Fig.9.** Cooperative up-conversion luminescence intensity as a function of 960 nm laser power for samples Yb(5):FOV and Yb(0.5):FOV. The curves *a* and *b* represent the results of [a] Yb(5):FOV and [b] Yb(0.5):FOV. The slopes of curve *a* and *b* are 1.885 and 2.029 respectively.

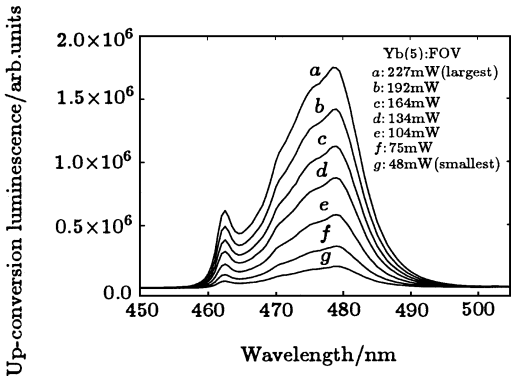



**Fig.10.** Up-conversion luminescence spectra of Yb(5): FOV at different values of excitation laser power.

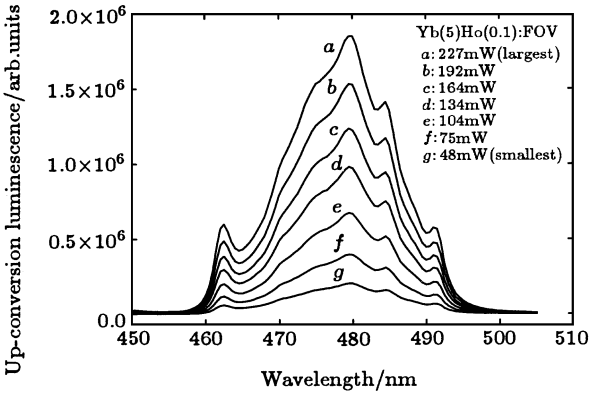



**Fig.11.** Up-conversion luminescence spectra of Yb(5) Ho(0.1):FOV at different values of excitation laser power.

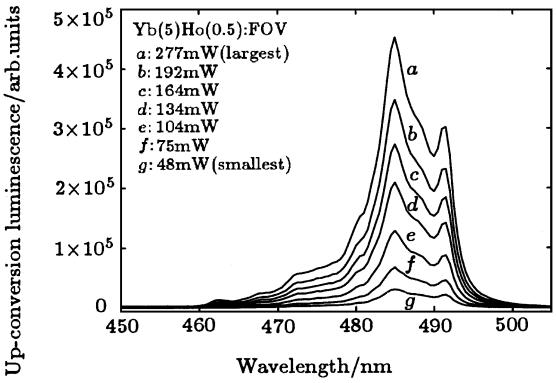



**Fig.12.** Up-conversion luminescence spectra of Yb(5) Ho(0.5):FOV at different values of excitation laser power.

**Table 2.** The peak positions and relative peak intensities of the up-conversion luminescence of Yb:FOV, YbHo:FOV and Yb:ZBLAN.

| | $Yb^{3+}$–$Yb^{3+}$ cluster character peak | | | $Ho^{3+}$ character peak | |
|---|---|---|---|---|---|
| | $Yb^{3+}Yb^{3+}$-$C^{sub}$ | $Yb^{3+}Yb^{3+}$-$B^{sub}$ | $Yb^{3+}Yb^{3+}$-$A^{main}$ | $^5F_3 \rightarrow {}^5I_8$ | |
| [a] Yb(5):FOV | 462.5 nm | 475.5 nm | 479.1 nm | No peak | No peak |
| | $21622\,cm^{-1}$ | $21030\,cm^{-1}$ | $20872\,cm^{-1}$ | | |
| | $2.00\times10^6$ | $4.81\times10^6$ | $5.27\times10^6$ | | |
| [b] Yb(0.5):FOV | 462.8 nm | 475.6 nm | 479.5 nm | No peak | No peak |
| | $21608\,cm^{-1}$ | $21026\,cm^{-1}$ | $20855\,cm^{-1}$ | | |
| | $1.92\times10^4$ | $5.67\times10^4$ | $6.80\times10^4$ | | |
| [c] Yb(5) Ho(0.1):FOV | 462.5 nm | 475.3 nm | 479.8 nm | 484.6 nm | 491.2 nm |
| | $21622\,cm^{-1}$ | $21039\,cm^{-1}$ | $20842\,cm^{-1}$ | $20637\,cm^{-1}$ | $20357\,cm^{-1}$ |
| | $6.93\times10^5$ | $1.80\times10^6$ | $2.15\times10^6$ | $1.65\times10^6$ | $6.74\times10^5$ |
| [d] Yb(5) Ho(0.5):FOV | 462.5 nm | Very small | 480.5 nm | 485.0 nm | 491.3 nm |
| | $21622\,cm^{-1}$ | | $20812\,cm^{-1}$ | $20619\,cm^{-1}$ | $20354\,cm^{-1}$ |
| | $1.40\times10^4$ | | $1.59\times10^5$ | $4.73\times10^5$ | $3.10\times10^5$ |
| [e] Yb(1) Ho(0.5):FOV | 463.0 nm | 475.0 nm | 480.1 nm | 485.0 nm | 491.3 nm |
| | $21598\,cm^{-1}$ | $21053\,cm^{-1}$ | $20829\,cm^{-1}$ | $20619\,cm^{-1}$ | $20619\,cm^{-1}$ |
| | $9.70\times10^2$ | $1.52\times10^4$ | $4.88\times10^4$ | $2.27\times10^5$ | $1.48\times10^5$ |
| [f] Yb(3):ZBLAN | 464.0 nm | 473.5 nm | 479.0 nm | No peak | No peak |
| | $21552\,cm^{-1}$ | $21119\,cm^{-1}$ | $20877\,cm^{-1}$ | | |
| | $5.79\times10^3$ | $2.05\times10^4$ | $2.34\times10^4$ | | |

## 6. Analysis and discussion about cooperative up-conversion luminescence

Very interesting phenomena concerning the 479.1 nm cooperative up-conversion blue luminescence of the Yb:FOV are shown in this paper. First, the 479.1 nm up-conversion luminescence is a two-photon up-conversion luminescence, as shown clearly in Fig.9. For both samples [a] Yb(5):FOV and [b] Yb(0.5):FOV, the integrated luminescence intensity as a function of the excitation laser power is shown in Fig.9 in a double-logarithmic plot. These data in double-logarithmic plots log $F$–log $P$ clearly follow two straight lines; the slopes of curves $a$ and $b$, obtained through least-square fitting, are $1.885\pm0.011$ and $2.029\pm0.018$ respectively. It is clear that both slopes are close to 2. Experimental results indicate that the observed blue luminescence excited by a 960 nm laser results from the two-photon up-conversion process.[1–7] The schematic diagram of up-conversion and the energy level structure of $Yb^{3+}$ and $Ho^{3+}$ ions is shown in Fig.1.

Also, the 479.1 nm up-conversion blue luminescence is closely related to the concentration of $Yb^{3+}$ ions. From Fig.7 and Table 2, it is obvious that the 479.1 nm up-conversion luminescence intensity of Yb(5):FOV is about 100 times greater than that of Yb(0.5):FOV. However, the $Yb^{3+}$ ion concentration in Yb(5):FOV is only ten times greater than that of Yb(0.5):FOV. Similarly, the 462.5 nm up-conversion blue luminescence intensity of Yb(5) Ho(0.5):FOV is nearly 25 times greater than that of Yb(1)Ho(0.5):FOV although there is an obvious influence of $Ho^{3+}$ ion. This illustrates that the 479.1 nm up-conversion luminescence is proportional to the square of the $Yb^{3+}$ ion concentration. It could be deduced that the 479.1 nm up-conversion luminescence does not come from any linear process involving the single $Yb^{3+}$ ion system, because the up-conversion luminescence intensity of a single $Yb^{3+}$ ion system must be linearly proportional to the $Yb^{3+}$ ion concentration. As is well known, if the two-photon up-conversion luminescence originated from a two-$Yb^{3+}$ ion system, such as either 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 usually proportional to the square of the $Yb^{3+}$ ion concentration due to the dipole-dipole interaction. Therefore, this 479.1 nm blue up-conversion luminescence should only come from either energy transfer between $Yb^{3+}$ ions or a cluster-coupled state made up of two $Yb^{3+}$ ions.

Furthermore, it is reasonable to believe that

the 479.1 nm up-conversion luminescence is a kind of cooperative up-conversion luminescence originating from the coupled states of the $Yb^{3+}$–$Yb^{3+}$ cluster.[1,2,5–9,11,12] The main peak of this cooperative up-conversion luminescence lies at about 479.1 nm with two sub-peaks at about 462.5 and 475.5 nm. According to the absorption of the Yb(0.5):FOV sample shown in Fig.3 and Table 1, the absorption Stark peak positions of the $Yb^{3+}$ ion $^2F_{5/2}$ level of oxyfluoride vitroceramics are ($Yb^{3+}$-$I^{main}$: 975.3 nm, 10253 $cm^{-1}$), ($Yb^{3+}$-$II^{sub}$:952.0 nm, 10504 $cm^{-1}$) and ($Yb^{3+}$-$III^{sub}$:927.0 nm, 10787 $cm^{-1}$). The $Yb^{3+}$ ion is easily excited to its $^2F_{5/2}$ level from ground $^2F_{7/2}$ level by absorbing the 10417 $cm^{-1}$ photon energy of a 960 nm laser light. Therefore, if two $Yb^{3+}$ ions happen to form a cluster, the coupled state may be located at 20757 $cm^{-1}$ that is made up by the $Yb^{3+}$ ion sub-states ($Yb^{3+}$-$I^{main}$:975.3 nm, 10253 $cm^{-1}$) and ($Yb^{3+}$-$II^{sub}$:952.0 nm, 10504 $cm^{-1}$), which is very close to the measured main peak ($Yb^{3+}Yb^{3+}$-$A^{main}$: 479.1 nm, 20872 $cm^{-1}$) of the cooperative up-conversion luminescence. In a similar manner, the coupled state may be made up by the sub-states ($Yb^{3+}$-$III^{sub}$:927.0 nm, 10787 $cm^{-1}$) and ($Yb^{3+}$-$III^{sub}$:927.0 nm, 10787 $cm^{-1}$), located at 21574 $cm^{-1}$ also, which is quite close to the measured sub-peak ($Yb^{3+}Yb^{3+}$-$C^{sub}$:462.5 nm, 21622 $cm^{-1}$). Then, the coupled state may be made up by the $Yb^{3+}$ ion sub-states ($Yb^{3+}$-$II^{sub}$:952.0 nm, 10504 $cm^{-1}$) and ($Yb^{3+}$-$II^{sub}$:952.0 nm, 10504 $cm^{-1}$) located at 21008 $cm^{-1}$, or made up by the sub-states ($Yb^{3+}$-$I^{main}$:975.3 nm, 10253 $cm^{-1}$) and ($Yb^{3+}$-$III^{sub}$: 927.0 nm, 10787 $cm^{-1}$) positioned at 21040 $cm^{-1}$, both of which are quite close to the measured sub-peak ($Yb^{3+}Yb^{3+}$-$B^{sub}$:475.5 nm, 21030 $cm^{-1}$). So it is believed from an energy-match consideration that the 479.1 nm fluorescence is a kind of cooperative up-conversion luminescence.[7,9,12] The up-conversion processes are as follows. First, 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 at the $^2F_{5/2}$ excited state form a coupled cluster state $^2F_{5/2}{}^2F_{5/2}(Yb^{3+}Yb^{3+})$ under the laser pumping. The 479.1 nm cooperative up-conversion luminescence is then radiated from this excited coupled state to the ground coupled state $^2F_{7/2}{}^2F_{7/2}(Yb^{3+}Yb^{3+})$. Moreover, the measured up-conversion luminescence main peak 479.1 nm in this paper coincides with all the published correct papers, Refs.[7], [9], [12], etc., whose up-conversion luminescence main peaks of the direct $Yb^{3+}$–$Yb^{3+}$ cluster are all located at about the 476–480 nm wave-range.[1,2,7–9,26] The main peak we have observed is different from the characteristic fluorescence main peak of $Tb^{3+}$ ion located at about 495–504 nm wave-range.[1,2,24] It has also been proved that the cooperative up-conversion green luminescences result from the $Yb^{3+}$-$Tb^{3+}$ cooperative effect [9] and so on. All of these indicate that the large cooperative up-conversion blue luminescence of the direct $Yb^{3+}$–$Yb^{3+}$ cluster discovered in this paper is clearly seen and stable.

Finally, it is important to note that the cooperative up-conversion blue luminescence ability is much enhanced by our oxyfluoride vitroceramics. As we know, the fluoride ZBLAN glass is one of the materials for up-conversion luminescence with best efficiency. The up-conversion efficiency has been studied widely.[27] The up-conversion luminescence efficiency of Yb:FOV can be known easily by comparing the up-conversion luminescence abilities between the FOV and ZBLAN materials. It is clear that the 479.1 nm cooperative up-conversion blue luminescence strength of Yb(5):FOV is 230 times greater than that of Yb(3):ZBLAN according to the results of Fig.8 and Table 2 of this paper. This is a significant development toward satisfying the practical requirements on blue up-conversion luminescence strength, in view of that the cooperative up-conversion mechanism was before considered far less efficient than the energy transfer up-conversion. The reason for the improvement is that the FOV material provides much more opportunities for $Yb^{3+}$ ions to directly form better $Yb^{3+}$–$Yb^{3+}$ clusters than the ZBLAN glass so that it can radiate much stronger cooperative up-conversion blue luminescence.

The co-doped $Ho^{3+}$ ion has an obvious influence on the cooperative up-conversion luminescence of $Yb^{3+}$–$Yb^{3+}$ clusters. In the cooperative up-conversion luminescence of YbHo:FOV two obvious additional peaks emerge that are not present in that of Yb:FOV, which can be easily seen from Fig.7 and Table 2. The main additional peak of up-conversion luminescence of the YbHo:FOV is positioned at (484.6 nm, 20637 $cm^{-1}$), which is very near to the $^5I_8 \rightarrow {}^5F_3$ absorption peak (484.2 nm, 20646 $cm^{-1}$) of $Ho^{3+}$ ion shown in Fig.4 and Table 1. Another additional sub-peak (491.2 nm, 20357 $cm^{-1}$) of the YbHo:FOV up-conversion luminescence is quite near to the small (490.8 nm, 20377 $cm^{-1}$) sub-peak of the $Ho^{3+}$ ion $^5I_8 \rightarrow {}^5F_3$ absorption. This can be seen clearly in Tables 1 and 2. Thus it is believed that the

up-conversion luminescences (484.6 nm, 20637 $cm^{-1}$) and (491.2 nm, 20357 $cm^{-1}$) are $^5F_3 \rightarrow ^5I_8$ fluorescence transition of $Ho^{3+}$ ion. The former is a transition to the lower Stark state of $^5I_8$ level, while the latter is a transition to the higher Stark state of $^5I_8$ level. Thus, the group of 479 nm up-conversion luminescence of the YbHo:FOV is made up of two kinds of up-conversion. One is the cooperative up-conversion luminescence of the coupled states of the $Yb^{3+}$–$Yb^{3+}$ clusters at (463, 475, 479 nm), the other is the normal $^5F_3 \rightarrow ^5I_8$ up-conversion luminescence of $Ho^{3+}$ ion at (485, 491 nm). This phenomenon is similar to that in the related papers concerning the $Yb^{3+}$–$Yb^{3+}$ cooperative up-conversion.[9,24]

It is clear that the co-doped $Ho^{3+}$ ion causes the obvious reduction in the cooperative blue up-conversion luminescence of the coupled states of the $Yb^{3+}$–$Yb^{3+}$ cluster. It can be seen from Fig.7 and Table 2 that the 479 nm up-conversion luminescence of Yb(5) Ho(0.1):FOV is about 40.8% that of Yb(5):FOV. Also we can see that the 479 nm up-conversion luminescence of Yb(5) Ho(0.5):FOV is only about 3.01% that of Yb(5):FOV. This illustrates that the co-doped $Ho^{3+}$ ion obviously decreases the cooperative up-conversion luminescence of the $Yb^{3+}$–$Yb^{3+}$ cluster. In fact, there is a resonant energy transfer from the $^2F_{5/2}{}^2F_{5/2}$ coupled state of the $Yb^{3+}$–$Yb^{3+}$ clusters to the $^3K_8$, $^5F_2$ and $^5F_3$ levels of the $Ho^{3+}$ ions because their energy levels match very well. The energy of the $^3K_8$, $^5F_2$ and $^5F_3$ levels would relax to that of the $^5F_4$ and $^5S_2$ levels at a fast rate since the $^5F_4$ and $^5S_2$ levels are a little lower than the $^3K_8$, $^5F_2$ and $^5F_3$ levels. Thus the energy of the $Yb^{3+}$–$Yb^{3+}$ clusters will transfer unidirectionally to that of the $Ho^{3+}$ ions if there are $Ho^{3+}$ ions in the material. Because the samples used before were $Yb^{3+}$ samples doped with $Er^{3+}$ or $Ho^{3+}$ or $Tm^{3+}$ ions, the energy of the $^2F_{5/2}{}^2F_{5/2}$ coupled state might be moved out very fast, which may be a reason why the $Yb^{3+}$–$Yb^{3+}$ cooperative up-conversion luminescence was regarded as a kind of small up-conversion fluorescence before. This implies that the impurities mixed during the manufacturing procedure would seriously reduce the cooperative up-conversion luminescence intensity of the $Yb^{3+}$–$Yb^{3+}$ clusters due to cross-relaxation also. It is also significant that the pure $Yb^{3+}$ ion-doped sample, which has extremely little impurity to reduce the cross-relaxation of the $Yb^{3+}$–$Yb^{3+}$ clusters, could achieve the higher cooperative up-conversion luminescence of the $Yb^{3+}$–$Yb^{3+}$ clusters.

As is well known, the interesting concept of cooperative up-conversion of $Yb^{3+}$-$Tm^{3+}$ or $Yb^{3+}$-$Tb^{3+}$ has been proposed for many years.[1,26] However, the near-resonant back energy-transfer from $Tm^{3+}$ or $Tb^{3+}$ ions back to the $Yb^{3+}$ ions restricts the enhancement of this cooperative up-conversion luminescence, particularly for huge phonon energy materials.[22] It has also been proved that the cooperative up-conversion green luminescences may result from the $Yb^{3+}$-$Tb^{3+}$ cooperative effect.[9] Even the sol-gel material can provide a good coupled chance for the $Yb^{3+}$ ion to form the $Yb^{3+}$–$Yb^{3+}$ clusters, and further improvement is urgently needed because the phonon energy of this material is high and its electron–phonon interactions are strong. This results in its small up-conversion luminous efficiency. The cooperative up-conversion luminescence intensity in Ref.[8] is also small due to the larger energy transfer up-conversion from the $Yb^{3+}$ ion to the $Er^{3+}$ ion, and a fast unidirectional energy transfer occurs from the $Yb^{3+}$–$Yb^{3+}$ clusters to the resonant $^4F_{7/2}$ level of the $Er^{3+}$ ions. The large cooperative up-conversion blue luminescence of the $Yb^{3+}$–$Yb^{3+}$ clusters obtained in this paper results from the better coupled chance of the $Yb^{3+}$–$Yb^{3+}$ clusters within the FOV material and the smaller amount of phonon-relaxation and cross-relaxation. Furthermore, the large cooperative up-conversion luminescence of Yb(5):FOV also comes from its higher concentration 5 mol% of the activator $Yb^{3+}$ ions because the cooperative up-conversion luminescence intensity varies linearly against the square of the concentration of $Yb^{3+}$ ions in the range of 0.5–5 mol% (see Fig.7 and Table 2). Also, the cooperative up-conversion luminescence can be well enhanced by a large diode-laser pumping power, as indicated in Fig.9, showing a very good linear relation without saturation.

## 7. Conclusion

We have found that the Yb:FOV exhibits excellent cooperative up-conversion blue luminescence. A strong blue 479.1 nm cooperative up-conversion luminescence of Yb:FOV is revealed, which results from the coupled states of the $Yb^{3+}$–$Yb^{3+}$ clusters formed by two adjacent $Yb^{3+}$ ions. The measured up-conversion luminescence main peak 479.1 nm in this article is different from the characteristic fluorescence main peak of $Tb^{3+}$ ion positioned at about 495–504 nm wave-range and coincides with those in

the published correct papers, whose cooperative up-conversion luminescence main peaks of the direct $Yb^{3+}$–$Yb^{3+}$ clusters are all located at about the 476–480 nm range. All of these show that the strong cooperative up-conversion blue luminescence of the direct $Yb^{3+}$–$Yb^{3+}$ clusters discovered in this paper is clearly seen and stable. This further proves that the cooperative up-conversion green luminescence results from the $Yb^{3+}$-$Tb^{3+}$ cooperative effect.[9] In particular, the cooperative up-conversion blue-luminescence strength of Yb(5):FOV is 230 times greater than that of fluoride glass Yb(3):ZBLAN. And the co-doped $Ho^{3+}$ ion causes obvious reduction of the cooperative blue up-conversion luminescence of the $Yb^{3+}$–$Yb^{3+}$ clusters, implying that the impurities, some kind of co-doped ions or the ions mixed in the manufacture procedure, may seriously reduce the cooperative up-conversion luminescence intensity due to the cross-relaxation from the $Yb^{3+}$–$Yb^{3+}$ clusters. Our results also show that strong cooperative up-conversion blue luminescence can be achieved by using good materials such as oxyfluoride vitroceramics, which can provide a better opportunity to form better $Yb^{3+}$–$Yb^{3+}$ clusters and have less relaxation to gain more efficient up-conversion luminescence. Meanwhile, the cooperative up-conversion blue luminescence could be improved further by pure $Yb^{3+}$ ion-doped materials that have as little impurities as possible to reduce cross-relaxation from the $Yb^{3+}$–$Yb^{3+}$ clusters. The strong cooperative up-conversion blue luminescence of Yb(5):FOV also comes from its higher concentration (5 mol%) of the activator $Yb^{3+}$ ions, which act perfectly because the cooperative up-conversion luminescence intensity varies linearly against the square of the concentration of the $Yb^{3+}$ ion in the range of 0.5–5 mol%. Moreover, the cooperative up-conversion blue luminescence could be enhanced further by a high diode-laser pumping power, based on the experimental double-logarithmic plot log $F$–log $P$ curves exhibiting a very good straight-line relation without saturation. Finally, we can say that the improvement of the cooperative up-conversion blue luminescence results from the comprehensive enhancement in the aspects of good coupled opportunity of the $Yb^{3+}$–$Yb^{3+}$ clusters, less cross-relaxation, higher concentration of $Yb^{3+}$ activators, non-saturation, and better up-conversion luminescence efficiency. The results of this paper may be significant for both the up-conversion research and its related applications.

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