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INDIRECT UP-CONVERSION SENSITIZATION LUMINESCENCE OF Tm(0.1) Yb(10.9): OXYFLUORIDE VITROCERAMICS INDUCED BY 800nm DIODE LASER*

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This paper reports researches about the indirect up-conversion sensitization luminescence of Tm(0.1)Yb(10.9): oxyfluoride vitroceramics(TmYb:FOV) induced by 800nm diode laser. From the initial comparison research of indirect up-conversion sensitization luminescence between TmYb:FOV and Tm(0.1)Yb(10.9): oxyfluoride glass (TmYb:FOG), it is found that the up-conversion luminescence intensity of TmYb:FOV is much higher than that of TmYb:FOG. It is shown that this is an effective method to e5nhance up-conversion efficiency. It is found also that the fluorescence branch ratio and the meticulous structures are different between vitroceramics and glass. This disparity comes from cluster effect resulting from micro crystallization of the material.

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I. INTRODUCTION

The research of frequency up-conversion has been developed greatly according to social desire for its applying technology and the development of diode laser and up-conversion materials.[1−5]

The ZBLAN material (Zr-Ba-La-Al-Na fluoride glass) has achieved rather high up-conversion efficiency. However, it is not perfect enough and has some gap for practical mass application. Moreover, those shortcomings of ZBLAN system, such as just passable chemical stability, considerable low laser damage threshold, weak mechanical strength and difficulty in processing, are jeopardizing the development of up-conversion practical application very much. This results in a dilemma for the up-conversion research and application. It is no doubt that to seek some special new methods and channels through some new mechanisms and new materials to achieve higher up-conversion performance is one of core-problem for the up-conversion research.

This paper reports the researches of the common photoluminescence induced by Xe lamp and indirect up-conversion sensitization luminescence of Tm(0.1)Yb(10.9):oxyfluoride vitroceramics[6] (Tm Yb:FOV) induced by 800nm-diode laser firstly. From the initial comparison study of indirect up-conversion sensitization luminescence between TmYb:FOV and Tm(0.1)Yb(10.9):glass (TmYb:FOG), it is found that the up-conversion luminescence intensity of TmYb:FOV is much higher than that of TmYb:FOG. The micro-structures of them are different also. This disparity comes from the cluster effect resulting from micro crystallizing of material. So micro crystallization may be regarded as an effective method to enhance up-conversion efficiency.

II. RESEARCH OF COMMON SPECTRA

The common photoemission and excitation spectra[7] of TmYb:FOV are measured by Fluorolog-2 fluorescence photospectrometer. The photoemission spectra of 357.5, 470.5 and 681nm fluorescence of $^1D_2$,$^1G_4$ and $^3F_3$ energy levels are given in Fig.1. The 720nm Peak of "curve *a*" and 590nm peak of "curve *b*" in Fig.1 are harmonic noises of pumping light. From Fig.1, it is easy to point out that the fluorescence of 451.5nm(curve *a*), 649.0nm (curve *b*), 772.5, 783nm (curve *b*) and 777.5, 800.5nm (curve *c*) are the transitions of $^1D_2 \rightarrow {}^3F_4$, $^1G_4 \rightarrow {}^3F_4$, $^1G_4 \rightarrow {}^3H_5$, and $^3H_4 \rightarrow {}^3H_6$, respectively (see Fig.6).

The common photo-excitation spectrum is given in Fig.2. The "curve *b*" of Fig.2 is just the excitation spectrum of 800.5nm fluorescence of $^3H_4$ energy level, in which the peaks of 357.5(462.5, 470.5) 656.5 and

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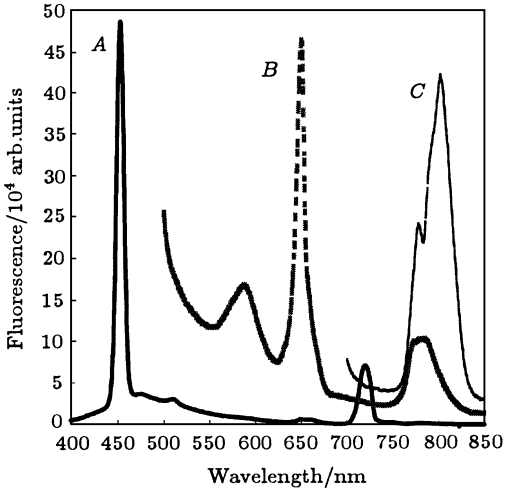


Fig.1. The common photoemission spectrum of TmYb:FOV. The symbol "EM" represents emission spectrum, curve *B* has been multiplied by 20, curve *C* has been multiplied by 200. *A*:357.5EM, *B*:470.5EM, *C*:681EM.

(681, 696.5) nm correspond to the absorption of $^1D_2$, $^1G_4$, $^3F_2$, and $^3F_3$ levels respectively. The "curve *a*" and "curve *c*" of Fig.2 are just the excitation spectra of 451 and 649nm fluorescence of $^1D_2$ and $^1G_4$ energy levels. The excitation spectrum of 451nm fluorescence has only one peak, which corresponds to the absorption of $^1D_2$ level positioned at 357.5nm. The excitation spectrum of 649nm fluorescence has two peaks, corresponding to the absorption of $^1D_2$ level positioned at 357.5nm and that of $^1G_4$ level positioned at (462.5, 470.5)nm.

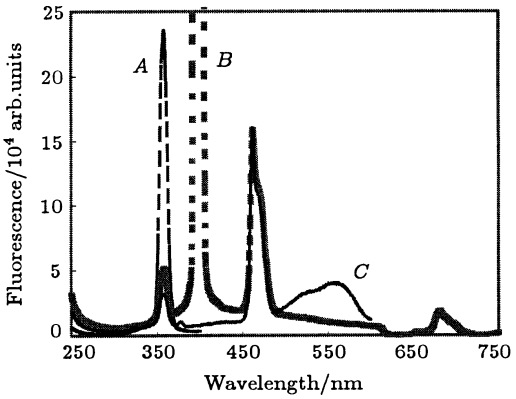


Fig.2. The common photo-excitation spectrum of TmYb:FOV. The symbol "EX" represents excitation spectra, curve *A* has been divided by 10. *A*: 451EX, *B*: 800.5EX, *C*: 649EX

It can be found from Figs. 1 and 2 that the luminescence intensity of $^1D_2 \rightarrow {}^3F_4$ transition when $^1D_2$ level is resonantly excited is about 20 times stronger than that of $^1G_4 \rightarrow {}^3F_4$ transition when $^1G_4$ level is resonantly excited. It is obvious that $^1D_2$ level has rather strong emission ability, and meanwhile the population of $^1G_4$ level is much easy to transfer to lower energy level. As we know, the energy gap between $^1D_2$ level and its close neighbouring lower level $^1G_4$ is very large and similar [8] to that between $^1G_4$ level and its close neighbouring lower level $^3F_2$.Their multi-phonon non-radiating relaxations are similar and very small. So the reason why the population of $^1G_4$ level could be transferred to lower level more efficienty is that the cross-energy transfer of $\{^1G_4(Tm^{3+}) \rightarrow {}^3H_4\ (Tm^{3+}), {}^2F_{7/2}(Yb^{3+}) \rightarrow {}^2F_{5/2}\ (Yb^{3+})\}$ is far stronger than that of $\{^1D_2(Tm^{3+}) \rightarrow {}^1G_4\ (Tm^{3+}), {}^2F_{7/2}(Yb^{3+}) \rightarrow {}^2F_{5/2}\ (Yb^{3+})\}$. This is partly due to the fact that the energy mismatch of the former is rather smaller than that of the later.

Ⅲ. RESEARCH OF INDIRECT UP-CONVERSION SENSITIZATION

In this paper the indirect up-conversion sensitization luminescence phenomenon of the TmYb:FOV is studied firstly. And an initial comparison between TmYb:FOV and TmYb:FOG is made also.

The laser device used is the 800nm semiconductor one and the fluorescence collecting and conducting system is a SPEX Fluorolog-2 fluorescence photospectrometer. The fluorescence-collecting direction is perpendicular to the laser. All the samples are 3mm thick. The schematic diagram of experimental setup is shown in Fig.3. The measuring condition and status of various samples are kept the same so as to enable the comparison on their relative intensities.

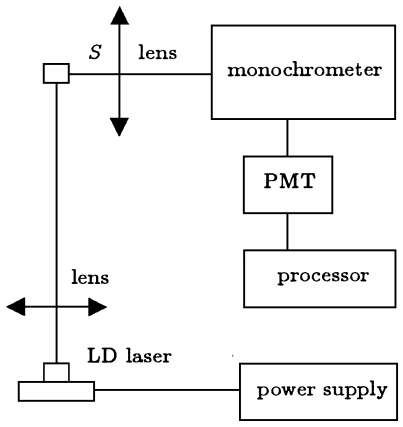


Fig.3. Schematic diagram of the experimental setup.

The indirect up-conversion sensitization luminescence of TmYb:FOV and TmYb:FOG samples is measured under the excitation of the 800nm laser. It is

found that there are mainly two luminous peaks positioned at 475 and 647nm respectively. The luminous spectra and relative intensities are presented in Fig.4 and Table 1. The relative intensities listed in Table 1 are the values of relative intensity of the indirect up-conversion sensitization luminescence of TmYb:FOV divided by that of TmYb:FOG. And fluorescence branch ratio $\beta = L(475)/L(647)$ is the value of 475nm fluorescence intensity divided by that of 647nm fluorescence. lmproving the condition of measurement, the micro structures of $^1G_4 \rightarrow {}^3H_6$ up-conversion luminescence of TmYb:FOV and TmYb:FOG samples are measured carefully also, the results are shown in Fig.5. According to the energy structure of Tm^{3+}ion[8], as shown in Fig.6, it is easy to point out that they are $^1G_4 \rightarrow {}^3H_6$ and $^1G_4 \rightarrow {}^3F_4$ transitions. The variation of up-conversion luminescence intensities with the 800nm-laser power (as shown in Fig.7) is measured also. It is found that the log-log F-P curve of 475nm $^1G_4 \rightarrow {}^3H_6$ fluorescence (F) against the 800nm-laser power (P) is a straight line with a slope γ=1.88. The results prove that the up-conversion luminescence of Tm^{3+} ion's $^1G_4$ level when excited by 800nm laser is a two-photo fluorescence.

Table 1. The relative intensities of up-conversion fluorescence of TmYb:FOV and TmYb:FOG induced by a 800nm diode laser.

Sample	Relative intensity of 475nm $^1G_4 \rightarrow {}^3H_6$ fluorescence	Relative intensity of 647nm $^1G_4 \rightarrow {}^3F_4$ fluorescence	Fluorescence branch ratio $\beta = L(475)/L(647)$
TmYb:FOV	6.73×10^6	1.39×10^5	48.42
TmYb:FOG	3.89×10^6	4.65×10^4	83.66
Intensity proportion	1.73	2.99	

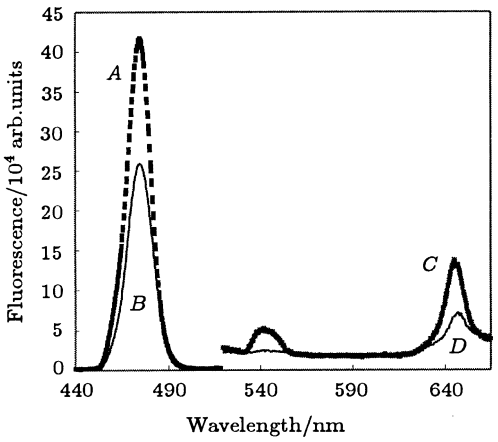


Fig.4. The up-conversion fluorescence of TmYb:FOV and TmYb:FOG.(relative strength are comparable,"×10" represents multiplied by 10.) A : TmYb:FOV, B : TmYb:FOG, C : TmYb:FOV×10, D : TmYb:FOG×10.

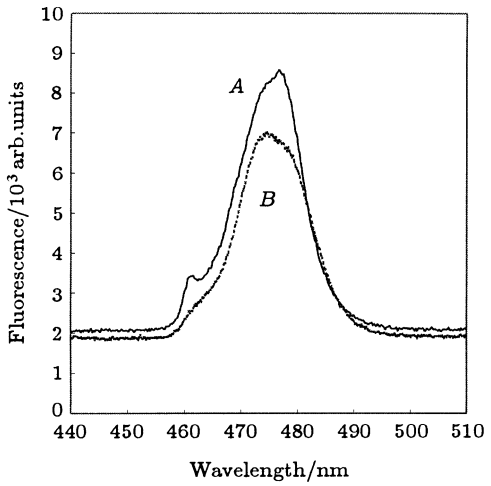


Fig.5. The micro structure of up-conversion fluorescence of TmYb:FOV and TmYb:FOG. (relative strengths are not comparable.) A : TmYb:FOV, B : TmYb:FOG.

There is a general phenomenon for the up-conversion fiber laser achieved in mono-doped rare earth ion materials. That is, the power of two-photon up-conversion laser is not increased quadratically with the linear increase of the pumping laser power, but usually is with a power exponent less than 2.[9] Sometimes, even the up-conversion luminescence is increased linearly with the pumping laser power.[10,11]

The "indirect up-conversion sensitization" mechanism has been proposed independently by authors of Ref.[12], which was published nearly at the same time as the first international work.[13] It has vast advantage in this field. The excitation mechanism is: For the rare earth activator center(Tm^{3+} ion in this work) and sensitizer center Yb^{3+} ion con-doped luminous materials, when laser wavelength is resonant with the $^3H_6 \rightarrow {}^3H_4$ absorption of Tm^{3+} ions, first the activator Tm^{3+} ions are excited to $^3H_4$ level. Then the first-step energy transfer from the $^3H_4$ level of Tm^{3+}

to Yb^{3+} would take place and result in a certain population on the $^2F_{5/2}$ level of Yb^{3+} ion. And then the second-step energy transfer from the $^2F_{5/2}$ level of sensitizer Yb^{3+} ion to the $^1G_4$ level of activator Tm^{3+} ions could occur. So some population of Tm^{3+} ion ground state $^3H_6$ is excited indirectly to $^1G_4$ level and blue up-conversion fluorescence would be radiated finally. We call this process as indirect up-conversion sensitization, which is also shown in Fig. 6.

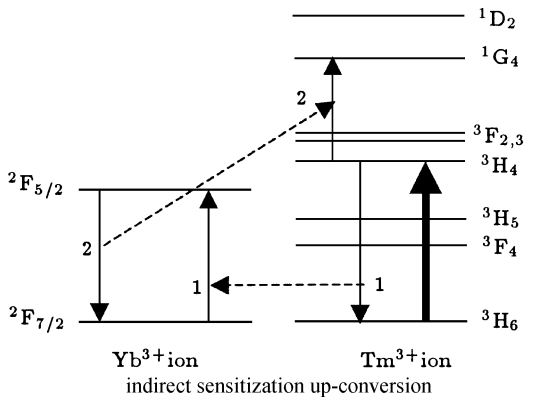


Fig.6. Schematic diagram of indirect sensitization up-conversion processes in Yb^{3+} and Tm^{3+} codoped systems. $1 \longrightarrow 1$ represents first-step energy transfer, $2 \longrightarrow 2$ represents second-step enertgy transfer.

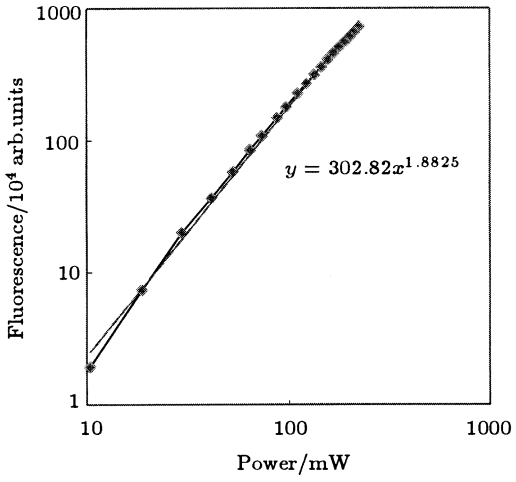


Fig.7. Variation of up-conversion fluorescence intensity F of TmYb:FOV with 800nm LD laser power P(slope r=1.88).

As we know, there is rather small absorption and very high power density in a fiber because of small transverse and large longitudinal size. The sensitizer Yb^{3+} ions act as population reservoir under the condition of indirect up-conversion sensitization, which would not enhance the absorption of the pumping or oscillating laser greatly and would not destroy the pumping or oscillating uniformity. And the absorption saturation problem of activators [9−11] would be solved also.[12] Furthermore this system could be driven by a cheap and powerful diode laser. This is especially benefited in improvement of the property of the up-conversion fiber laser and would be valuable to the development of compact blue solid laser.[14]

It could be seen from Table 1 that the 475nm $^1G_4 \rightarrow ^3H_6$ two-photon up-conversion fluorescence of TmYb:FOV is 1.73 times stronger than that of TmYb:FOG, and the 647nm $^1G_4 \rightarrow ^3F_4$ up-conversion fluorescence of TmYb:FOV is 2.99 times stronger than that of TmYb:FOG. This means that the fluorescence branch ratio is changed also. In addition, the micro structures of $^1G_4 \rightarrow ^3H_6$ up-conversion fluorescence between TmYb:FOV and TmYb:FOG are quite different also. It is obvious that all of these result from the change of material structure caused by micro crystallizing of material.

This oxyfluoride vitroceramics used in our experiment is produced from oxyfluoride glass through high temperature heat-treatment, forming $Pb_xCd_{1-x}F_2$ fluoride micro-crystallines[6], and the rare earth ions tend to concentrate in the micro-crystalline. On the other hand, the scattering action for visible light by small and uniform micro-crystallines might be quite small also.

As we know, the larger the phonon energy of matrices, the stronger the multi-phonon non-radiative relaxation of rare earth ions, and the weaker the up-conversion. In the structure of oxyfluoride glass, rare earth ions with F^- ion together are easily coupled by the non-bridging oxygen on the strong O—Si and O—Al bonds because they usually have larger electric field strength. These coupling would accelerate multi-phonon non-radiative relaxation and reduce the lifetime of relative level involved in the up-conversion process. So the efficiency of stepwise or direct sensitization up-conversion of oxyfluoride glass is rather low, just like the general oxide glasses. However, if rare earth ions preferentially resided in the $Pb_xCd_{1-x}F_2$ micro-crystallines in the oxyfluoride vitroceramics, they would be shielded by the $Pb_xCd_{1-x}F_2$ micro-crystallines and not couple with the non-bridging oxygen on the strong O—Si and O—Al bonds. Thus the up-conversion efficiency would nearly be equal to that of fluoride glass or crystal. For those rare earth ions that preferentially reside in the $Pb_xCd_{1-x}F_2$ micro-crystallines, the distance between rare earth ions is re-

duced considerably, and especially the coupling groups made up of two or more rare earth ions emerge. So the very strong exchange interaction would appear, so do the violent energy transfer[15] and cluster effect. That is the reason why the up-conversion luminescence of TmYb:FOV is enhanced very much.

In brief, the cluster effect of oxyfluoride vitroceramics produced by micro-crystallization from oxyfluoride glass is an effective method to enhance the up-conversion efficiency.

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