Three-photon-excited upconversion luminescence of YVO_4 single crystal by infrared femtosecond laser irradiation

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Abstract: We report on the upconversion luminescence of a pure YVO_4 single crystal excited by an infrared femtosecond laser. The luminescent spectra show that the upconversion luminescence comes from the transitions from the lowest excited states $^3T_1$, $^3T_2$ to the ground state $^1A_1$ of the VO_4^{3-}. The dependence of the fluorescence intensity on the pump power density of laser indicates that the conversion of infrared irradiation to visible emission is dominated by three-photon excitation process. We suggest that the simultaneous absorption of three infrared photons promotes the VO_4^{3-} to excited states, which quickly cascade down to lowest excited states, and radiatively relax to ground states, resulting in the broad characteristic fluorescence of VO_4^{3-}.

OCIS codes: (140.7090) Ultrafast lasers; (190.4180) Multiphoton processes; (190.7220) Upconversion

References and links

1. L. F. Johnson, G. J. Guggenheim, "Infrared-Pumped Visible Laser," Appl. Phys. Lett. **19**, 44-47 (1971).
2. D. A. Parthenopoulos and P. M. Rentzepis, "Three-dimensional optical storage memory," Science. **245**, 843-845 (1989).
3. E. Downing, L. Hesselink, J. Ralston, and R. Macfarlane, "A Three-Color, Solid-State, Three-Dimensional Display," Science. **273**, 1185-1189 (1996).
4. W. Denk, J. H. Strickler, and W. W. Webb. "Two-photon laser scanning fluorescence microscope," Science. **248**, 73-76 (1990).
5. J. S. Chivian, W. E. Case, and D. D. Eden, "The photon avalanche: A new phenomenon in Pr^{3+}-based infrared quantum counters," Appl. Phys. Lett. **35**, 124-125 (1979).
6. F. E. Auzel, "Upconversion and Anti-Stokes Processes with f and d Ions in Solids," Chem. Rev. (Washington, D.C.) **104**, 139-174 (2004).
7. S. Heer, M. Wermuth, K. Krämer, and H. U. Güdel, "Upconversion excitation of Cr^{3+} ^2E emission in $Y_3Ga_5O_{12}$ codoped with Cr^{3+} and Yb^{3+}," Chem. Phys. Lett. **334**, 293-297 (2001).
8. W.Kaiser, and C.G.B.Garrett, "Two-Photon Excitation in CaF_2: Eu^{2+}," Phys. Rev. Lett. **7**, 229-231 (1961).
9. G. Blasse and B. C. Grabmaier, *Luminescent Materials*. (Springer-Verlag, Berlin, 1994).
10. H. Ronde and G. Blasse,"The nature of the electronic transitions of the vanadate group," J. Inorg. Nuclear Chem. **40**, 215 (1978).
11. W. Barendswaard, R. T. Weber, and J. H. van der Waals, "An EPR study of the luminescent triplet state of VO_4^{3-} in YVO_4 and $YP_{0.96}V_{0.04}O_4$ single crystals at 1.2 K," J. Chem. Phys. **87**, 3731 (1987).
12. Chang Hsu and Richard C. Powell, "Energy transfer in europium doped yttrium vanadate crystals," J. Luminescence. **10**, 273-293 (1975).
13. L.Y. Yang, Y. J. Dong, D. P. Chen, C. Wang, N. Da, X. W. Jiang, C. S. Zhu, J. R. Qiu, "Upconversion luminescence from 2E state of Cr^{3+} in Al_2O_3 crystal by infrared femtosecond laser irradiation," Opt. Express. **13**, 7893-98 (2005).
14. L. H. Zhang, Y. Hang, D. L. Sun, B. X. Qian, F. S. Li, S. T. Yin, " The color problems of YVO_4 crystal," J. Synth. Cryst. **32**, 24-26 (2003 in chinese).

#9316 - $15.00 USD Received 31 October 2005; revised 28 November 2005; accepted 28 November 2005

15. R. P. Chin, Y. R. Shen, and V. Petrova-koch, "Photoluminescence from Porous Silicon by Infrared Multiphoton Excitation," Science. **270**, 776-778 (1995).
16. Bloembergen. N, "Solid State Infrared Quantum Counters," Phys. Rev. Lett. **2**, 84-85 (1959).
17. Richard Scheps, "Upconversion laser processes," Prog. Quantum Electron. **20**, 271-358 (1996).
18. G. S. He, P. P. Markowicz, T. C. Lin, and P. N. Prasad, "Observation of stimulated emission by direct three-photon excitation," Nature. **415**, 767-770 (2002).
19. J. S. Marchant, G. E. Stutzmann, M. A. Leissring, F. M. LaFerla, and I. Parker, "Multiphoton-evoked color change of DsRed as an optical highlighter for cellular and subcellular labeling," Nat. Biotechnol. **19**, 645-649 (2001).
20. K. Svoboda, W. Denk, D. Kleinfeld, and D.W.Tank, "In vivo dendritic calcium dynamics in neocortical pyramidal neurons," Nature. **385**, 161-165 (1997).
21. H. You and M. Nogami, "Three-photon-excited fluorescence of Al_2O_3-SiO_2 glass containing Eu^{3+} ions by femtosecond laser irradiation," Appl. Phys. Lett. **84**, 2076-78 (2004).
22. H. You and M. Nogami, "Upconversion luminescence of Al2O3–SiO2:Ce^{3+} glass by femtosecond laser irradiation," Appl. Phys. Lett. **85**, 3432-34 (2004)
23. J. Qiu, P. G. Kazansky, J. Si, K. Miura, T. Mitsuyu, K. Hirao, A. L. Gaeta, "Memorized polarization-dependent light scattering in rare-earth-ion-doped glass,"Appl. Phys. Lett. **77**, 1940-42 (2000)
24. P. G. Kazansky, H. Inouye, T. Mitsuyu, K. Miura, J. Qiu, and K. Hirao, "Anomalous anisotropic light scattering in Ge-doped silica glass," Phys. Rev. Lett. **82**, 2199-2202 (1999).

1. Introduction

Upconversion luminescence offers a simple and effective route for conversion of infrared irradiation to the visible and near ultraviolet output and has promising applications on full-color all-solid state display, high-density optical storage, visible laser, and visible detection of infrared radiation [1-4]. In the research field of upconversion, luminescent materials containing active ions have been widely investigated to clarify upconversion processes and to utilize characteristic luminescence of active ions [5-8]. However, little attention has been paid to the upconversion luminescence in intrinsic luminescent materials such as YVO_4, $YNbO_4$, $CaWO_4$, and $PbWO_4$ single crystals. These materials belong to a group of so-called classic phosphors, and the complex of VO_4^{3-}, NbO_4^{3-} and WO_4^{2-} act as luminescent centers [9-12]. The complex of VO_4^{3-}, $NbO_4^{3-}$and WO_4^{2-} are characterized by lack of absorption bands within infrared wavelength band, which is not suited for the requirements for upconversion luminescence from infrared irradiation. There have been no investigations on upconversion luminescence in YVO_4, $YNbO_4$ and $CaWO_4$ single crystals up to now. Recently, we demonstrated that by infrared femtosecond laser irradiation, Cr^{3+}-doped Al_2O_2 [13] and several Ce^{3+}-doped scintillators exhibit strong visible upconversion luminescence. These upconversion mechanisms can be ascribed to two- or three-photon simultaneous absorption. In this paper, we report on the three-photon excited upconversion luminescence in YVO_4 single crystal by infrared femtosecond laser irradiation. To the authors' knowledge, it is the first observation of upconversion luminescence in intrinsic luminescent materials. This observation is useful for the application of YVO_4 single crystal in three dimensional display, and visible detection of infrared radiation etc.

2. Experiment

Crystal of YVO_4 was grown by czochralski method. The starting materials of high purity Y_2O_3, and V_2O_5 were used to synthesize stoichiometric YVO_4. The apparatus and detailed crystal-growth procedure have been described elsewhere [14]. The crystal obtained was cut and polished into samples with various thickness from 1mm to 4mm for femtosecond laser irradiation and spectral measurements. The crystal samples were yellow. No inclusions or other light scattering centers were observed by the optical microscope.

A regeneratively amplified 800 nm Ti: sapphire laser that emits 120 femtosecond, 1 kHz, mode-locked pulses was used as the irradiation source. To achieve a high power density, the laser beam was focused into samples by objective lens or optical lens. When using objective lens, the focal point can be monitored by a confocal microscope system linked to a charge coupled device system. The position of the focal point was beneath the sample surface. In fact, the laser beam can be focused into any place within the sample. The spot size can be

#9316 - $15.00 USD Received 31 October 2005; revised 28 November 2005; accepted 28 November 2005

controlled at least below several microns by choosing appropriate objective lens or optical lens and adjusting the power density of laser beam. The fluorescence spectra excited by focused femtosecond laser were recorded by a spectrophotometer of ZOLIX SBP300. The scanning rate of this spectrophotometer was 100nm/min. The fluorescence spectra were measured at ~90^o direction with respect to the pump beam. The fluorescence spectra excited by a 267nm monochromatic light from a xenon lamp were measured by a JASCO FP6500 spectrophotometer. In addition, the absorption spectra were obtained by a JASCO V-570 spectrophotometer. All the measurements were preformed under room temperature.

Under focused femtosecond laser irradiation, strong blue emission was seen near the focused spot by naked eyes. The emission spectrum irradiated by the femtosecond laser with a power density of 5.6TW/cm^2 is shown in Fig. 1. The laser beam was focused by an optical lens with focal length of 100mm. The thickness of the sample used was 1.5mm. The Fig. 1 also shows the luminescent spectrum of YVO_4 irradiated by 267nm monochromatic light from a xenon lamp. The inset in Fig. 1 is a photograph of the crystal sample irradiated by focused femtosecond laser. The brightest spot in the middle of the crystal corresponds to the place irradiated by femtosecond laser. The two bright spots on the edges of the crystal are the light scattering spots.

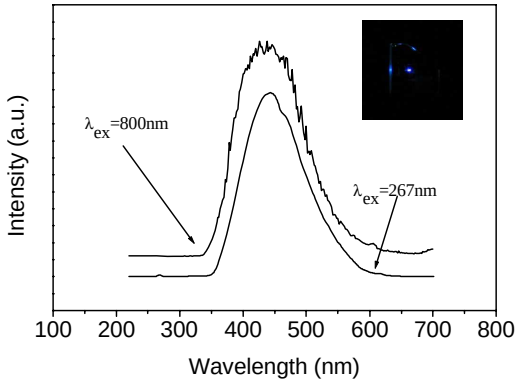

Fig. 1. Emission spectra of the YVO_4 crystal sample under focused femtosecond laser irradiation and 267nm monochromatic light excitation. The inset was the photograph of the YVO_4 crystal sample irradiated by focused femtosecond laser, which was taken in darkroom.

The spectrum of YVO_4 crystal irradiated by the femtosecond laser exhibits a broad emission band peaking at 438nm and a shoulder peak at 464nm, which is similar to those of YVO_4 crystal excited by 267nm monochromatic light. All these peaks can be assigned to the characteristic emission of YVO_4 single crystal.

For vanadate group in YVO_4 single crystal, there are one ground state of $^1A_1$ with configuration $t_1^6e^0t_2^0$, and four excited states of $^3T_1$, $^3T_2$, $^1T_1$, and $^1T_2$ with configuration $t_1^5e^1t_2^0$ [10.11]. The transitions from $^1A_1$ ($t_1^6e^0t_2^0$) to $^1T_1$ ($t_1^5e^1t_2^0$) and $^1T_2$ ($t_1^5e^1t_2^0$) are allowed by an electric dipole mechanism, which correspond to two absorption bands in absorption spectrum of YVO_4 crystal.

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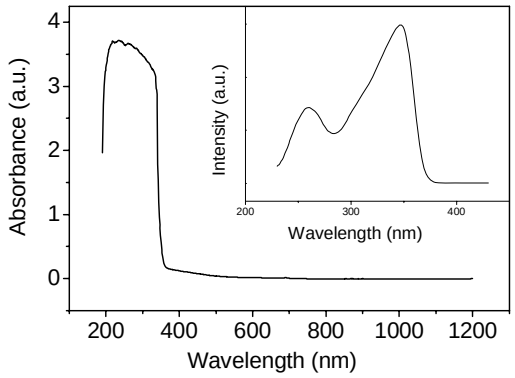

Fig. 2. Absorption spectrum and the excitation spectrum (the inset) of the YVO_4 crystal sample.

Figure 2 shows the absorption spectrum of YVO_4 crystal. This spectrum shows a strong absorption band below 350nm, which is a superposition of the intrinsic absorption of YVO_4 crystal and the absorption of vanadate group. To manifest the absorption of vanadate group, we measured the excitation spectrum of vanadate group by monitoring the fluorescence at 443nm. The excitation spectrum clearly presents two strong absorption bands. These two bands usually act as efficient pumping bands [12]. Exciting any of these bands produces electron population in excited states of $^1T_1$, and $^1T_2$. Then, the electrons can nonradiatively relax to the lowest excited states of $^3T_1$, and $^3T_2$, from which, the characteristic emission occurs. At room temperature, the fluorescence appears as broad bands from 350nm to 650nm. From the above results, it seems that the focused infrared femtosecond laser may act as a spatially confined ultraviolet source in the interior of bulk of YVO_4 crystal.

Generally, conversion of infrared radiation to the visible emission can be ascribed to a multiphoton absorption process. The relationship between the pumping power density and the fluorescence intensity can be described as [15]:

$$I \propto I_{\mathrm{in}}^{\mathrm{n}}$$

Where, I is the integrated intensity of the upconversion luminescence, I_{in} is the pump power density of the infrared laser, and n is the photon number. The number of photons must satisfy that the total energy of n photons exceeds or equals to the excitation energy required by excited states. The n can be experimentally determined from the slope coefficient of linear fitted line of logarithmic plot of the pumping power density and fluorescence intensity. The pumping power density was controlled below 25TW/cm^2. No degradation of the PL or damage to the sample was observed. The log-log relationship between pumping power density of femtosecond laser and fluorescence intensity of YVO_4 crystal is shown in Fig. 3. It can be seen that the slope coefficient of the fitted line is 2.93. Similar results were obtained by using the samples with thickness of 2mm; 3mm and 4mm.These results indicate that the upconversion may be a three-photon absorption process.

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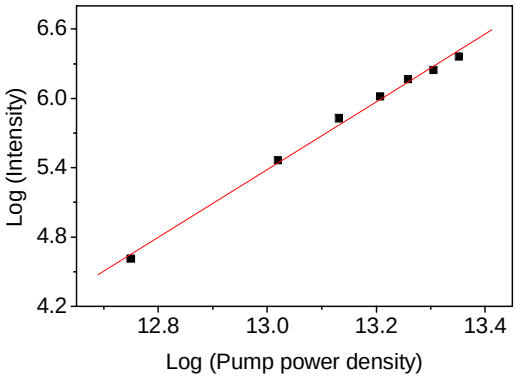

Fig. 3. Fluorescence intensity of the transition from $^3T_1$, and $^3T_2$ to $^1A_1$ of VO_4^{3-} as function of the femtosecond laser pump power density.

Upconversion luminescence has been widely investigated for several decades, and the two-photon excited upconversion luminescence is a ubiquitous phenomenon. The predominated upconversion processes can be classified into several mechanisms such as energy transfer, excited-state absorption, cooperative upconversion, and photon avalanche [5,6,16,17]. These mechanisms operate only on the condition that the active center has metastable states that are intermediate in energy between the ground state and the emitting state. Pumping photons are absorbed sequentially rather than simultaneously. For mechanisms of energy transfer, excited-state absorption, and cooperative upconversion, a rigorous condition is that the pump photon must be resonant with the transition from the ground state to the intermediate metastable state. This means that the absorbing centers must have an absorption band corresponding to the energy of pump photon. However, we found that the YVO_4 single crystal has no any absorption near 800nm, which can be seen in the absorption spectrum of YVO_4. Therefore, these mechanisms can be precluded for the upconversion processes. In addition, the photon avalanche can also be ruled out, because a characteristic power threshold for an avalanche process has not been observed in our experiment. Another possible mechanism may be such a process: first, the VO_4^{3-} was pumped into a real intermediate level by simultaneously absorption of two pump photons; then, the VO_4^{3-} at intermediate level was promoted to the upper excited states. In this case, the YVO_4 should have an intermediate energy level near 400nm. However, there is a lack of real energy level at 400nm in YVO_4 crystal [10,11]. Therefore, this mechanism can also be ruled out. Additionly, we confirmed that, on this irradiation condition, there was no optical breakdown and no any absorption change before and after femtosecond laser irradiation. Moreover, we measured the electron spin resonance spectra of the crystal before and after laser irradiation, and no apparent peak was observed. Thus, we suggest that the upconversion is not due to the absorption of the intermediate metable state existed beforehand or induced by the femtosecond laser irradiation.

Due to the high peak power of the femtosecond laser, the effect of self-focusing should be taken into consideration when we discuss the dependence between the luminescence intensity and pump power density. The critical power for causing self-focusing can be estimated to be ~10^6 W for YVO_4 crystal. The peak power of the laser we used for the experiments is almost 10^7 W, higher than the critical power for self-focusing. However, from our experiments, we got the similar value of slope coefficient n even when we use various samples with different thickness and optical lens with focal length of 50mm. It indicates that the effect of surface and self-focusing which may have influence on the luminescent behavior is not dominant in the upconversion process.

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A three-photon simultaneous absorption can be responsible for the actual upconversion processes. Though upconversion luminescence based on two- or three- photon simultaneous absorption have been investigated in organic materials for many years [18-20], there are few reports concerning the similar phenomenon in inorganic materials [13,21-24], especially, in crystals. Previous research shows that the requirements for efficient three-photon excited upconversion luminescence can be associated to two aspects. First, the active centers should have excited state that can be excited by three pump photons. In addition, the pumping photon density must be high, which can be easily reached by using femtosecond laser [22]. In this experiment, the $VO4^{3-}$ has two excited states corresponding to the strong absorption bands from 240nm to 350nm. Excitation by focused infrared femtosecond laser, the $VO4^{3-}$ ions can be promoted from ground states to excited states, which nonradiatively relax to the lowest excited states. Thereafter, these ions radiatively relax to the ground state, generating the characteristic broad band luminescence of VO_4^{3-}.

4. Conclusions

In summary, we have experimentally demonstrated upconversion luminescence in pure YVO_4 single crystal by using focused infrared femtosecond laser irradiation. The relationship between the fluorescence intensity and the pump power density shows that the pump process is a three-photon excitation process. The analysis reveals that the absorption of three photons is simultaneous rather than sequential. This result provides an efficient route to produce upconversion luminescence in intrinsic luminescence materials, and has potential applications in visible lasers, optical data storage, three-dimensional displays, etc.

Acknowledgments

This work is supported by National Natural Science Foundation of China (Grants No.50125258 and No.60377040), and by Shanghai Nanotechnology Promote Center (Grants No. 0352nm042 and No.04XD14018). We thank Dr. C. J. Zhao, Q. T. Zhao, and X. W. Jiang for enlightening discussions.

#9316 - $15.00 USD Received 31 October 2005; revised 28 November 2005; accepted 28 November 2005