Blue upconversion luminescence generation in Ce^{3+}:Gd_2SiO_5 crystals by infrared femtosecond laser irradiation

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Abstract: Blue frequency-upconversion fluorescence emission has been observed in Ce^{3+}-doped Gd_2SiO_5 single crystals, pumped with 120-fs 800 nm IR laser pulses. The observed fluorescence emission peaks at about 440nm is due to 5d→4f transition of Ce^{3+} ions. The intensity dependence of the blue fluorescence emission on the IR excitation laser power obeys the cubic law, demonstrating three-photon absorption process. Analysis suggested that three-photon simultaneous absorption induced population inversion should be the predominant frequency upconversion mechanism.

OCIS codes: (160.5690) Rare earth doped materials; (190.4180) Multiphoton processes; (190.7220) Upconversion; (320.2250) Femtosecond phenomena

References and links

1. R. Scheps, "Upconversion laser processes," Prog. Quant. Electron. **20**, 271-358 (1996).
2. G. S. He, L. Yuan, Y. Cui, M. Li, and P. N. Prasad, "Studies of two-photon pumped frequency-upconverted lasing properties of a new dye material," J. Appl. Phys. **81,** 2529-2537 (1997).
3. W. Tutt and T. F. Boggess, "A review of optical limiting mechanisms and devices using organics, fullerenes, semiconductors and other materials," Prog. Quantum Electron. **17,** 299-338 (1993).
4. J. E. Ehrlich, X. L. Wu, I.-Y. S. Lee, Z.-Y. Hu, H. Rockel, S. R. Marder, and J. W. Perry, "Two-photon absorption and broadband optical limiting with bis-donor stilbenes," Opt. Lett. **22,** 1843-1845 (1997).
5. E. Downing, L. Hesselink, J. Raltson, R. Macfarlane, "A three-color, solid-state, three-dimensional display," Science **273,** 1185-1189 (1996).
6. J. S. Chivian, W. E. Case, D. D. Edden, "The photon avalanche: A new phenomenon in Pr^{3+}-based infrared quantum counters," Appl. Phys. Lett. **35**, 124-125 (1979).
7. R. S. Niedbala, H. Feindt, K. Kardos, T. Vail, J. Burton, B. Bielska, S. Li, D. Milunic, P. Bourdelle, and R. Vallejo, "Detection of Analytes by Immunoassay using up-converting phosphor technology," Anal. Biochem. **293,** 22-30 (2001).
8. S. Maruo, O. Nakamura, and S. Kawata, "Three-dimensional microfabrication with two-photon-absorbed photopolymerization," Opt. Lett. **22,** 132-134 (1997).
9. A. M. R. Fisher, A. L. Murphree, and C. J. Gomer, "Clinical and preclinical photodynamic therapy," Laser Surg. Med. **17,** 2-31 (1995)
10. W. Denk, J. H. Strickler, and W. W. Webb, "Two-photon laser scanning fluorescence microscopy," Science **248,** 73-76 (1990).
11. M. E. Koch, A. W. Kueny, and W. E. Case, "Photon avalanche upconversion laser at 644 nm," Appl. Phys. Lett. **56**, 1083-1085 (1990).
12. S. C. Goh, R. Pattie, C. Byrne, and D. Coulson, "Blue and red laser action in Nd^{3+}:Pr^{3+} co-doped fluorozirconate glass," Appl. Phys. Lett. **67**, 768-770 (1995).
13. F. Lahoz, I. R. Martin, and J. M. Calvilla-Quintero, "Ultraviolet and white photon avalanche upconversion in Ho^{3+}-doped nanophase glass ceramics," Appl. Phys. Lett. **86**, 051106-051108 (2005).

#10172 - $15.00 USD Received 6 January 2006; revised 15 February 2006; accepted 18 February 2006

14. S. Q. Man, E. Y. B. Pun, and P. S. Chung, "Upconversion luminescence of Er^{3+} in alkali bismuth gallate glasses," Appl. Phys. Lett. **77**, 483-485 (2000).
15. D. C. Nguyen, G. E. Faulkner, M. E. Weber, and M. Dulick, "Blue upconversion thulium laser," in *Solid State Lasers*, George Dube Ed., Proc. SPIE **1223**, 54-63 (1990).
16. R. R. Jacobs, W. F. Krupke, and M. J. Weber, "Measurement of excited-state-absorption loss for Ce^{3+} in $Y_3Al_5O_{12}$ and implications for tunable $5d \rightarrow 4f$ rare-earth lasers," Appl. Phys. Lett. **33**, 410-412 (1978).
17. N. Sarukura, Z. Liu, and Y. Segawa, "Ultraviolet subnanosecond pulse train generation from an all-solid-state Ce:LiCAF laser," Appl. Phys. Lett. **67**, 602-604 (1995).
18. J. Qiu, Y. Shimizugawa, Y. Iwabuchi, and K. Hirao,"Photostimulated luminescence of Ce^{3+}-doped alkali borate glasses," Appl. Phys. Lett. **71**, 43-45 (1997).
19. A. P. Davey, E. Bourdin, F. Henari, and W. Blau, "Three photon induced fluorescence from a conjugated organic polymer for infrared frequency upconversion," Appl. Phys. Lett. **67**, 884-885 (1995)
20. G. S. He, J. Dai, T.-C. Lin, P. P. Markowicz, and P. N. Prasad, "Ultrashort 1.5-μm laser excited up converted stimulated emission based on simultaneous three-photon absorption," Opt. Lett. **28**, 719-721 (2003).
21. L. Wang, Z. Cheng, Q. Ping, and X. Hou, "Three-photon photoemission from GaAs–O–Cs negative electron affinity surfaces induced by 2.06 μm nanosecond laser pulses," Appl. Phys. Lett. **67**, 91-93 (1995).
22. J. W. M. Chon, M. Gu, C. Bullen and P. Mulvaney, "Three-photon excited band edge and trap emission of CdS semiconductor nanocrystals," Appl. Phys. Lett. **84**, 4472-4474 (2004).
23. K. S. Bindra, H. T. Bookey, A. K. Kar, B. S. Wherrett, X. Liu and A. Jha, "Nonlinear optical properties of chalcogenide glasses: Observation of multiphoton absorption," Appl. Phys. Lett. **79**, 1939-1941 (2001).
24. 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**, 2076-2078 (2004).
25. M. Watanabe, S. Juodkazis, H. B. Sun, S. Matsuo, and H. Misawa, "Two-photon readout of three-dimensional memory in silica," Appl. Phys. Lett. **77**, 13-15 (2000).
26. W. H. Zhou, S. M. Kuebler, K. L. Braun, T. Y. Yu, J. K. Cammack, C. K. Ober, J. W. Perry, and S. R. Marder, "An efficient two-photon-generated photoacid applied to positive-tone 3D microfabrication," science **296**, 1106 -1109(2002).
27. K. Svoboda, W. Denk, D. Kleinfeld, and D. W. Tank, "In vivo dendritic calcium dynamics in neocortical pyramidal neurons," Nature **385**, 161-165 (1997).
28. J. Bewersdorf, R. Pick, and S. W. Hell, "Multifocal multiphoton microscopy," Opt. Lett. **23**, 655-657 (1998).
29. L.-Y. Yang, Y.-J. Dong, D.-P. Chen, C. Wang, N. Da, X. W. Jiang, C. 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**, 7893-7898 (2005). http://www.opticsexpress.org/abstract.cfm?URI=OPEX-13-20-7893.
30. L. Yang, C. Wang, Y. Dong, N. Da, X. Hu, D. Chen, J. Qiu, "Three-photon-excited upconversionluminescence of YVO4 single crystal by infrared femtosecond laser irradiation," Opt. Express. **13**, 10157-10162 (2005). http://www.opticsexpress.org/abstract.cfm?URI=OPEX-13-25-10157.
31. H. You and M. Nogami, "Upconversion luminescence of Al_2O_3–SiO_2:Ce^{3+} glass by femtosecond laser irradiation," Appl. Phys. Lett. **85**, 3432-3434 (2004).
32. R. P. Chin, Y. R. Shen, and V. Petrova-koch, "Photouminescence from Porous Silicon by Infrared Multiphoton Excitation," Science **270**, 776-778 (1995).

1. Introduction

Considerable interest has recently been focused on the conversion of infrared radiation into visible or ultraviolet light through frequency upconversion in rare-earth-doped materials, for a wide variety of applications including infrared-pumped visible laser [1, 2], optical power limiting [3, 4], high-density 3D optical data storage, display [5], infrared quantum counters [6], biological nanolables [7], 3D lithographic microfabrication [8], photodynamic therapy [9], and (3D) fluorescence imaging [10]. Among doped trivalent rare-earth ions, praseodymium [11], neodymium [12], holmium,[13] erbium,[14] and thulium [15] have been paid much attention and a wide range of upconversion wavelengths between 380 and 750 nm involving the transition within the $4f^n$ levels were produced in different hosts. In all these cases, upconversion fluorescence have been pumped using different excitation mechanisms such as energy transfer upconversion (ETU), excited-state absorption (ESA), cooperative upconversion, and photon avalanche, all of which involve the use of metastable intermediate levels which act as a storage reservoir for the pump energy. The trivalent cerium ions, Ce^{3+}, which involving a single ground $4f$ and a single excited state $5d$, exhibit broad ultraviolet or visible luminescence in many crystals hosts [16-18] due to the allowed $5d \rightarrow 4f$ electric dipole transition. It is, therefore, a suitable candidate for ultraviolet upconversion luminescence

#10172 - $15.00 USD Received 6 January 2006; revised 15 February 2006; accepted 18 February 2006

applications. However, there are few published reports of infrared-pumped upconversion luminescence based on Ce^{3+} ions due to the lacking of metastable intermediate levels and efficient upconversion mechanisms.

Multiphoton absorption is a well-known phenomenon and it can involve a variety of mechanisms, such as simultaneous multiphoton absorption and two or more photon absorption followed by successive absorption of photons with real intermediary excited states. Upconversion fluorescence induced by multiphoton absorption has been shown in organic compound [19 20], semiconductors [21], nanocrystals [22], and inorganic glasses [23, 24]. Multiphoton absorption mechanism can contribute to the absorption of light at irradiance levels of interest and makes it possible the realization of upconversion luminescence of Ce^{3+} doped materials based on the direct absorption of multiphoton. Despite many recent progresses on multiphoton absorption studies in numerous materials, the upconversion luminescence in Ce^{3+} doped crystals via direct multiphoton absorption has been paid little attention.

Due to its potential application in multiphoton optical data storage [25], three dimensional microfabrication [26], and multiphoton excited upconverted fluorescence [27, 28], research in multiphoton absorption processes generated by IR femtosecond lasers has been very active in recent years. More recently, we demonstrated that the use of femtosecond laser irradiation to obtain upconversion luminescence in Cr^{3+} doped Al_2O_3 and YVO_4 crystals [29, 30]. In addition, femtosecond laser induced upconversion luminescence has been shown in Ce^{3+} ions doped glass [31]. Combining the promising advantages of multiphoton absorption and femtosecond laser, the study of the frequency upconversion processes of Ce^{3+} ions doped crystal is important. Here, we report a strong simultaneous three-photon absorption blue upconversion luminescence of Ce^{3+}-doped Gd_2SiO_5 single crystals excited by ultrashort femtosecond laser pulses at 800 nm.

2. Experiments

Single crystals of Ce^{3+}-doped Gd_2SiO_5 were grown by the Czochralski method in inductively heated iridium crucible under a high purity nitrogen atmosphere. The high purity powders of Gd_2O_3 (≥99.99%), Ce_2O_3 (≥99.99%) and SiO_2 (≥99.999%) were used as starting materials. The raw materials were fired at 1000℃ for more than 10 h prior to weighing and mixing to remove moisture, then pressed into pellets and sintered at 1200℃ before loading into the iridium crucible. A pulling rate of 2 mm/h and rotation rate of 12 rpm were adopted in the growth experiments. Samples with thickness of 1mm for femtosecond laser irradiation and spectral measurements were cut from the as-grown crystals perpendicularly to the growth axis and polished on both sides.

We used an regeneratively amplified 800 nm Ti:Al_2O_3 laser that emits 120 femtosecond, 1 kHz, mode-locked pulses as the irradiation source. A chirped pulse with 10Hz, ~ 220 picosecond, and central wavelength of ~ 800nm from Ti:Al_2O_3 laser was used for comparison. The chirped pulse is generated from the preamplifier chain of an optical parametric amplification system. Laser beam was focused into sample by 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. The spot size can be controlled at least below several microns by choosing appropriate objective lens or optical lens and adjusting the average power of laser beam. In this study, the femtosecond and picosecond laser beam was focused by an optical lens with a focal length of 100 mm. The fluorescence spectra excited by focused femtosecond laser were recorded by a spectrophotometer of ZOLIX. The fluorescence spectra excited by a 266 nm monochromatic light from a xenon lamp were measured by JASCO FP6500 spectrophotometer. In addition, the absorption spectra were measured with a JASCO V-570 spectrophotometer. All the measurements were taken at room temperature.

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3. Results and discussion

Figure 1 shows the emission spectra of Ce^{3+}:Gd_2SiO_5 irradiated by focused femtosecond laser at 800 nm. Strong blue light emission was observed clearly by the naked eye on the focused spot when focusing the femtosecond laser on the sample. The luminescence spectrum exhibits a typical broad emission band peaking at about 440 nm. For comparison, we also show the emission spectrum of Ce^{3+}:Gd_2SiO_5 crystals excited at 267 nm (800/3) by monochromatic light from a xenon lamp. The emission spectra show that the corresponding spectral distributions of the measured samples are basically the same for both single-photon and multiphoton excitations. The structure of Gd_2SiO_5 belongs to the monoclinic space group $P2_1/c$, and in Ce^{3+}:Gd_2SiO_5 crystal, Ce^{3+} is substituted for Gd^{3+}. Ce^{3+} ion has a $4f^1$ configuration, the ground state consists of a doublet ($^2F_{5/2}$ and $^2F_{7/2}$). Since the radial wave function for the excited 5*d* electron of Ce^{3+} ions extends spatially well beyond the closed $5s^25p^6$ shells, 5*d* states are strongly perturbed by the ligand field of the host, and the lower excited states are the crystal-field components of the 5*d* configuration. Above results indicates that the blue luminescence of Ce^{3+}:Gd_2SiO_5 crystals induced by femtosecond laser irradiation is due to interconfiguration transitions from the lowest level of the 5*d* configuration to the $4f^1$ ground state of Ce^{3+} ions.

It should be noted that a slightly red shift of the near IR excited fluorescence was observed. This can be explained by the reabsorption effect induced by multiphoton absorption. In one-photon spectroscopy, the luminescence emission is characteristic of the surface rather than of the crystalline volume because of the drastic attenuation of the radiation as it propagates into the sample. Therefore, the reabsorption effect can be neglected. Due to the significantly smaller values of the multiphoton absorption coefficients, the reabsorption effect plays its roles during the femtosecond laser irradiation process and red shift occurred. In fact, similar phenomena have also been observed in organic compound [19].

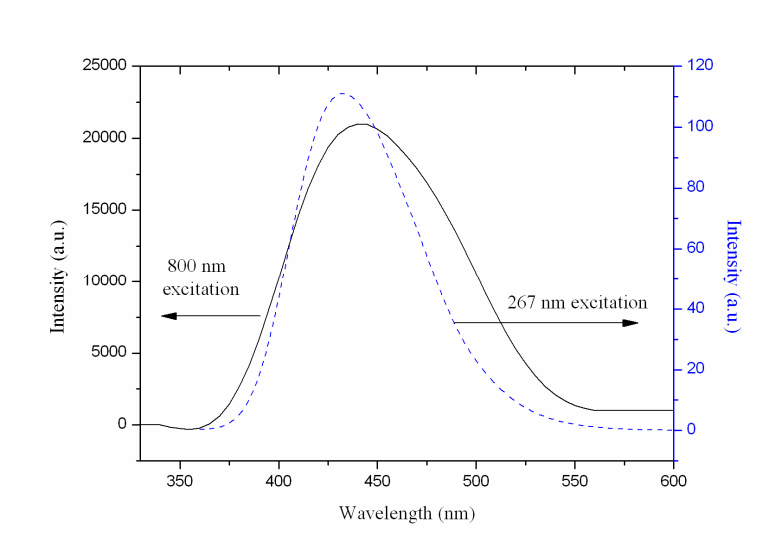

Fig. 1. Emission spectra of Ce^{3+}:Gd_2SiO_5 irradiated by femtosecond laser at 800 nm (solid line) and xenon lamp at 267 nm (dashed line).

Up to now, it has been shown that the predominant mechanisms of the upconversion on rare-earth doped materials are energy transfer upconversion (ETU), excited-state absorption (ESA), cooperative upconversion, and photon avalanche. It was believed that these

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mechanisms were not involved in Ce^{3+}:Gd_2SiO_5 crystals under femtosecond laser irradiation due to the lacking of two excited states or no transmittance decrease and upconversion signal grows nonlinearly with increasing pump power. Apart from these predominant mechanisms, multiphoton simultaneous absorption is also a mechanism for upconversion luminescence although little attention has been paid to this mechanism in the solid-state materials containing rare earth ions.

According to the theoretical consideration of multi-photon absorption process, the relationship between the pumping power and the fluorescence intensity can be described as a power law:[32] $I \propto P^n$. Where, I is the integrated intensity of the upconversion luminescence, P is the average power of the pumping 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 by varying the pumping power of femtosecond laser at fixed focused point. Here, the number of photons n can be determined as a slope coefficient of the linear fitted line by plotting the logarithmic transformation of the pumping power and fluorescence intensity. The log-log relationship of pumping power of femtosecond laser and fluorescence intensity of Ce^{3+}:Gd_2SiO_5 is shown in Fig. 2. It can be seen that the slope coefficient of the fitted line is 2.97, which indicates that the upconversion luminescence emission is generated by the three-photon absorption process.

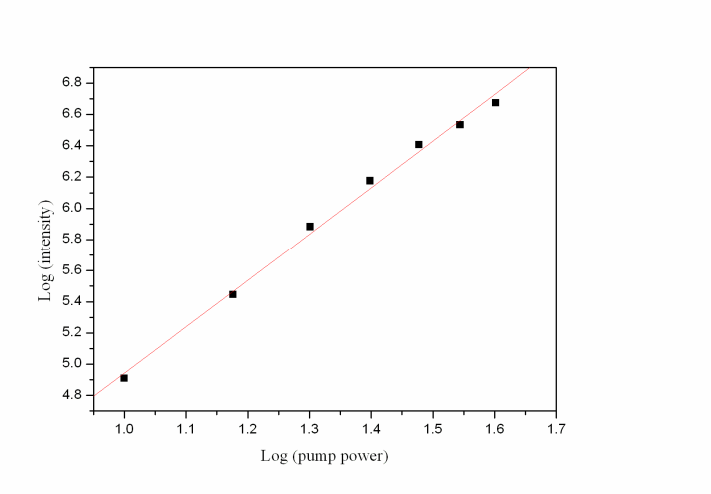

Fig. 2. Log-log plot of luminescence intensity as a function of pump power.

The three photon absorption, which includes two mechanisms, one of which is direct three photon absorption and the other is two photon absorption followed by one photon absorption from the excited level, are also represented by a cubic relationship between the pumping power and the fluorescence intensity. In our case, the direct three-photon absorption can be considered to be responsible for the upconversion emission in Ce^{3+}:Gd_2SiO_5 crystals. A more detailed understanding of the three-photon simultaneous absorption upconversion process can be gained by examination of the linear absorption and excitation spectra of the Ce^{3+}:Gd_2SiO_5 crystals. The measured one-photon absorption spectrum of the Ce^{3+}:Gd_2SiO_5 crystal is shown in Fig. 3. For the $4f \rightarrow 5d$ transition of Ce^{3+}, the electron-phonon interaction is strong because the $5d$ electrons are outermost, so that the broad absorption bands attributed to Ce^{3+} ions appear in the absorption spectra. One can find that the two strong broad absorption bands located at 285 and 345 nm in the 190–400 nm range are due to the Ce^{3+} ions. But the absorption is also included the absorption peaks of Gd^{3+} ions. In order to identify others absorption peaks of Ce^{3+} ions, we shown the excitation spectra of Ce^{3+}:Gd_2SiO_5 crystal when

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emission at 345 nm, as that shown in the inset of Fig. 3. It is clear that the 248 nm band is also associated with Ce^{3+} ions. We can see that there is no linear absorption at the one-photon energy or the two-photon energy of 800-mm radiation. Here, the processes of simultaneous absorption of photons in Ce^{3+}:Gd_2SiO_5 crystals only involving a single ground and a single excited state of Ce^{3+} ions. Therefore, it is very unlikely that two photon absorption followed by one photon absorption from real intermediary excited states. In addition, the three-photon energy of the near-IR radiation at 800 nm falls within the strong absorption band of the Ce^{3+} ions, and therefore direct three-photon absorption in the sample may be expected.

To form efficient three-photon simultaneous absorption, the photon density should be high. This is confirmed by the picosecond laser experiments. We performed the experiments using a chirped pulse with 10Hz, 220 picosecond, and 800nm Ti:Al_2O_3 laser as irradiation source. It is interesting to note that no any visible luminescence emission was observed on the Ce^{3+}:Gd_2SiO_5 crystal when focused the 800nm picosecond laser with the same pulse power density before focus as that of femtosecond laser irradiation experiments. Above results indicate that the high photon density generated by focused femtosecond laser may make three-photon simultaneous absorption possible.

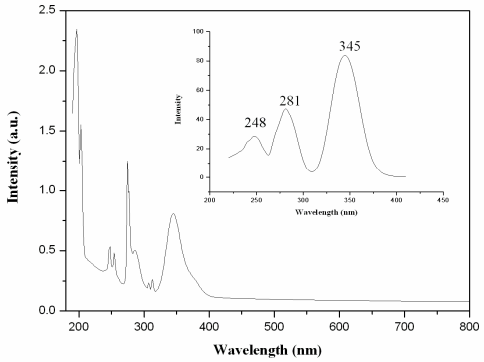

Fig. 3. One-photon absorption and excitation spectrum of Ce^{3+}:Gd_2SiO_5 single crystals.

The process of the direct three photon induced fluorescence of Ce^{3+}:Gd_2SiO_5 by femtosecond laser irradiation may be as follows: first, the simultaneous absorption of three photons by Ce^{3+}:Gd_2SiO_5 leading to population of the upper 5*d* excited state. Second, the excited state relaxes nonradiatively to the zeroth vibronic level-the bottom of the 5*d* state before returning to the $^2F_{5/2}$ ground state via emission of a single photon. The population inversion is created between the lower emitting state, 5*d*, and the ground state, $^2F_{5/2}$.

4. Conclusions

In conclusion, the blue upconversion luminescence in Ce^{3+} ions doped Gd_2SiO_5 single crystal has been experimentally demonstrated by infrared femtosecond laser irradiation. No blue luminescence was observed when focused the 800nm picosecond laser with different pulse power density on the Ce^{3+}:Gd_2SiO_5 crystal. The relationship between the fluorescence intensity and the pumping power shows that the upconversion luminescence is a three-photon excitation process. The analysis reveals that direct three photons absorption should responsible for the upconversion luminescence. Femtosecond three-photon generation of blue upconversion luminescence in Ce^{3+}-doped Gd_2SiO_5 single crystals reveals potential applications in ultraviolet upconversion laser, date storage, display, and imaging.

#10172 - $15.00 USD Received 6 January 2006; revised 15 February 2006; accepted 18 February 2006