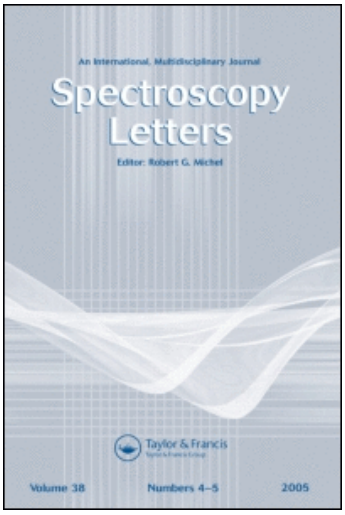

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Up-conversion Luminescence of Terbium(III) in SiO_2 and ZnO-SiO_2 Glasses Induced by Simultaneous Absorption of Three Photons and Saturation

Lixin Yu[ab]; Massayuki Nogami[b]
[a] Key Laboratory of Automobile Materials, Ministry of Education, and College of Materials Science and Engineering, Jilin University, Changchun, People's Republic of China [b] Department of Materials Science and Engineering, Nagoya Institute of Technology, Showa Nagoya, Japan

To cite this Article Yu, Lixin and Nogami, Massayuki(2008) 'Up-conversion Luminescence of Terbium(III) in SiO_2 and ZnO-SiO_2 Glasses Induced by Simultaneous Absorption of Three Photons and Saturation', Spectroscopy Letters, 41: 7, 344 — 348
To link to this Article: DOI: 10.1080/00387010802371478
URL: http://dx.doi.org/10.1080/00387010802371478

Spectroscopy Letters, 41:344–348, 2008

ISSN: 0038-7010 print/1532-2289 online
DOI: 10.1080/00387010802371478

Taylor & Francis
Taylor & Francis Group

Up-conversion Luminescence of Terbium(III) in SiO_2 and ZnO–SiO_2 Glasses Induced by Simultaneous Absorption of Three Photons and Saturation

Lixin Yu[1,2], and Massayuki Nogami[2]

[1]Key Laboratory of Automobile Materials, Ministry of Education, and College of Materials Science and Engineering, Jilin University, Changchun, People's Republic of China
[2]Department of Materials Science and Engineering, Nagoya Institute of Technology, Showa Nagoya, Japan

ABSTRACT Green up-conversion luminescence (UCL) of Tb^{3+} in SiO_2 and ZnO–SiO_2 glasses was observed with femtosecond (fs) laser (800 nm) excitation. The UCL mechanism of Tb^{3+} in both glasses contributed to the simultaneous three-photon absorption. The saturation effect of Tb^{3+} in SiO_2 glass took place. The saturation effect of excited-state levels of Tb^{3+} in SiO_2 glass was associated with the slower decay rate of $^5D_4$ level. This result implied that saturation power of Tb^{3+} in ZnO–SiO_2 glass was higher than that in SiO_2 glass.

KEYWORDS saturation, Terbium, up-conversion

The key feature of UCL of rare earth (RE) ions is their ability to absorb and combine two or more photons of low near-infrared (NIR) energy to emit a higher energy visible photon. UCL of RE ions in transparent hosts has been intensively investigated because it has many potential applications in up-converson laser, displays, fluorescent probe, optical communications and fiber-optic amplifiers, under forth.[1,2] In the past decades, research into UCL was mainly focused on the RE ions with plenty of levels, such as Er^{3+}, Ho^{3+}, Tm^{3+}, and Nd^{3+} ions.[3–5] Reports on UCL of Tb^{3+} were very rare because the energy levels of Tb^{3+} ions cannot easily match those of other RE ions. In previous work, two-photon UCL of Tb^{3+} through energy transfer from Yb^{3+} or ligand to Tb^{3+} at NIR light excitation has been reported.[6–11] But, to our knowledge, virtually nothing has been reported on UCL of Tb^{3+} through three-photon excitation by fs laser. Because Tb^{3+} ion-doped hosts are universally applied to commercial green phosphors, the research on UCL is partly motivated by the technological drive toward novel phosphors and partly because the scientific community would like to understand the fundamental physics. Because ultrafast titanium–sapphire tunable NIR laser can produce fs pulse and provide high density to be used as excitation resource, it is an ideal tool to study the optical

Received 17 April 2007; accepted 17 April 2008.

Address correspondence to Prof. Massayuki Nogami, Depaprtment of Materials Science and Engineering, Nagoya Institute of Technology, Showa Nagoya 466-8555, Japan. E-mail: nogami@nitech.ac.jp

properties of materials.[12–14] You et al. reported the UCL of Eu^{3+} and Ce^{3+} in sol-gel Al_2O_3–SiO_2 glasses due to three-photon simultaneous absorption.[15,16] In this paper, we report the UCL of Tb^{3+} ions in SiO_2 and ZnO–SiO_2 glasses at fs laser excitation and compare their UCL characteristics. It is important that we observed higher saturation power of Tb^{3+} in ZnO–SiO_2 glass than its SiO_2 glass. It can enrich the understanding of UCL processes of Tb^{3+}.

SiO_2 and 10ZnO–90SiO_2 glasses containing 1% Tb_2O_3 (2.49 mol/m^3) were prepared by a sol-gel method. Tetraethoxysilane (TEOS), $ZnCl_2 \cdot 6H_2O$, and $TbCl_3 \cdot 6H_2O$ were used as starting materials. First, the solution containing TEOS, ethanol, and deionized water (containing 0.15 mol/L HCl) was vigorously stirred for 1 h at room temperature. $ZnCl_2 \cdot 6H_2O$ and $TbCl_3 \cdot 6H_2O$ dissolved in ethanol were added to the above solution and stirred for one-half hour. Then, the mixed solution of H_2O and ethanol with the mole ratio of 4:1 was added, and the resultant solution was stirred for another one-half hour to obtain homogeneous solution. The (obtained above solution) was cast into a plastic container and placed at room temperature for about 4 weeks to form a stiff gel of 1–3 mm thickness. In order to completely hydrolyze the alkoxide, the gel was heated to 150°C in a sealed vessel together with water and held for 30 h. Finally, the gel was sintered at 600°C for 5 h.

The excitation spectra were recorded using monochromator (Jobin Yvon, HR 320, Japan) and a photomultiplier (Hamamatsu, R955). A 500 W xenon lamp with light passed through a monochromator (H20, Jobin Yvon) was used for excitation source. UCL spectra and dynamics processes were measured by fs pulse from a Ti:sapphire regenerative amplifier laser system (Hurricane, Spectra Physics) operating at a wavelength of 800 nm with a 1-kHz repetition rate and approximately 130-fs pulse duration. The power density can be varied from 0.15 to 0.8 W/mm^2.

Figure 1 shows the UCL spectra of SiO_2 and ZnO–SiO_2 containing Tb_2O_3 at femtosecond laser excitation. It is clear that no emission in ZnO–SiO_2 glass with the absence of Tb^{3+} was observed, and strong green emissions were observed in SiO_2 and ZnO–SiO_2 glasses containing Tb^{3+}. Four group lines at 488, 544, 583, and 620 nm were observed, which were from $^5D_4$–^7F_J ($J = 6, 5, 4, 3$) transition emissions.

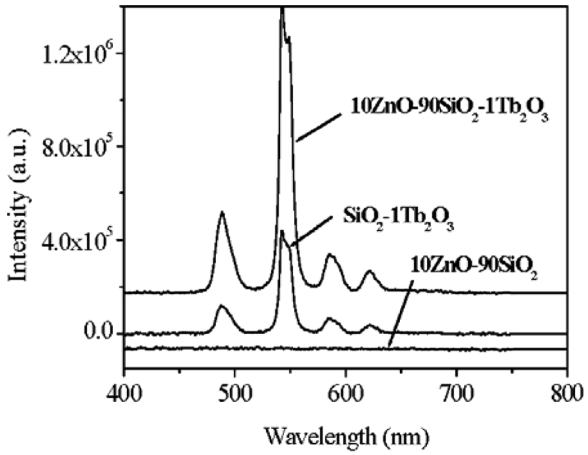

FIGURE 1 **UCL spectra of Tb^{3+} in SiO_2 and ZnO–SiO_2 glasses at femtosecond laser excitation. Excitation wavelength is 800 nm and power is 200 mW/mm^2).**

The strongest emission locating at 544 nm was from $^5D_4$–$^7F_5$ transitions.

To better understand and compare the mechanism of UCL of Tb^{3+} in SiO_2 and ZnO–SiO_2 glasses, the UCL integrated intensity of $^5D_4$–^7F_J transition emissions as a function of the excitation power was studied. The UCL intensity can be expressed as follows,

$$I \propto p^n$$

where I is the integrated intensity of UCL, p is the pump power of fs laser, and n is the number of photons absorbed per visible photon emitted for any UCL mechanism. According to the above equation, n is the slope of the log-log plot between the UCL intensity and pump power. Figure 2 is the UCL intensity as a function of pump power. It can

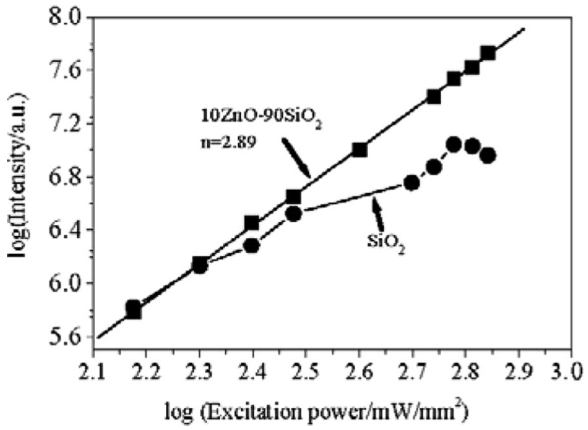

FIGURE 2 **Dependence of UCL intensity on the pump power.**

be seen that the three-photon excited luminescence of Tb^{3+} in SiO_2 glass saturates at high excitation powers. The slope of the logarithmic line is determined by linear fitting to be about 2.89 in ZnO–SiO_2 glass. This result indicated that the three-photon excitation in ZnO–SiO_2 glass predominant.

To clarify the mechanism of UCL processes, the excited-state energy levels should be known. Figure 3 shows the (a) absorption and (b) excitation spectra of Tb^{3+} in glasses monitoring 544 nm emission. In excitation spectra, the broad band ranging from 220 to 290 nm centered at 260 nm was associated with $4f$–$5d$ transitions of Tb^{3+} ions. There existed many weak excitation lines of Tb^{3+} ions in ultraviolet range (300–380 nm), which were associated with $^7F_6$–$^5D_3$, ^5G_J, $^5L_6$ transitions. In absorption spectra (Fig. 3(a)), only $4f$–$5d$ excitation band (200–300 nm) and weak absorption lines (300–380 nm) were observed.

In ZnO–SiO_2 glass, three-photon excitation predominated. To our knowledge, this is the first report on three-photon UCL of Tb^{3+} in glasses or other hosts. For three-photon UCL processes, there existed two possible mechanisms.[17] One is the excited-state absorption (ESA). For ESA mechanisms, the material must have absorption at about 800 nm and 400 nm, respectively. The second is the simultaneous three-photon absorption. Because there is no absorption at 400 nm and 800 nm, thus we can exclude the ESA mechanism. We should further consider the mechanism of the simultaneous three-proton absorption. The simultaneous three-photon absorption requires an excited state that matches the three-photon energy, and high photon density. In previous references, this mechanism attracted little attention.[18] According to excitation spectra, the simultaneous three-photon absorption corresponded with resonant $4f$–$5d$ transitions absorption (about 266 nm) of Tb^{3+} at fs laser (800 nm) excitation. In addition, fs laser can provide ultrafast pulse and high-density laser. Thus we suggested that the UCL mechanism of Tb^{3+} in ZnO–SiO_2 was three-photon simultaneous absorption.

Detailed UCL processes in ZnO–SiO_2 glass are shown in Fig. 4. First, the electrons at the ground state $^7F_6$ level were resonantly excited onto upper $5d$ excited state through the simultaneous three-photon absorption. Then electrons at $5d$ excited state may nonradiatively relax fast $^5D_1$, $^5D_3$, and $^5D_4$ level, and as a consequence $^5D_4$–^7F_J transition emissions follow.

In SiO_2 glass, no absorption at 800 nm and 400 nm was observed. Two-photon excitation cannot take place, and three-photon excitation resonantly matched $4f$–$5d$ absorption. We suggest that UCL mechanism of Tb^{3+} in SiO_2 glass was also simultaneous three-photon absorption. Detailed UCL process was similar with that in ZnO–SiO_2 glasses. According to Fig. 2, in SiO_2 glass, saturation effect occurred. This contributed to the competition between the decay of $^5D_4$ level and the feed from higher excited state, leading to the saturation of $^5D_4$ level. Due to ultrafast pulse and high density of

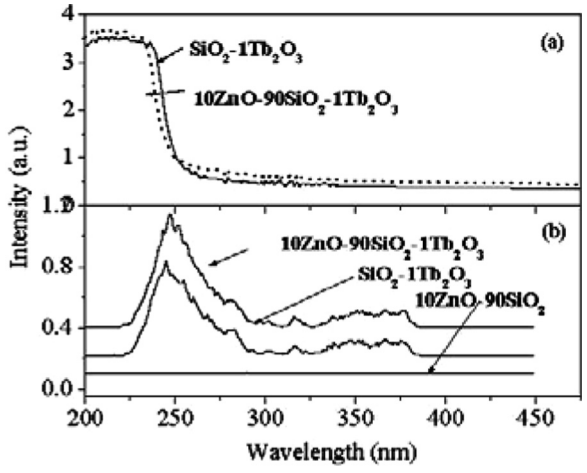

FIGURE 3 The (a) absorption and (b) excitation spectra of Tb^{3+} monitoring 544 nm emission.

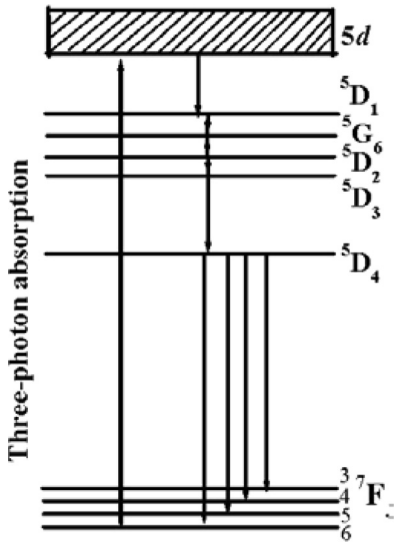

FIGURE 4 The level diagram of Tb^{3+} and UCL process.

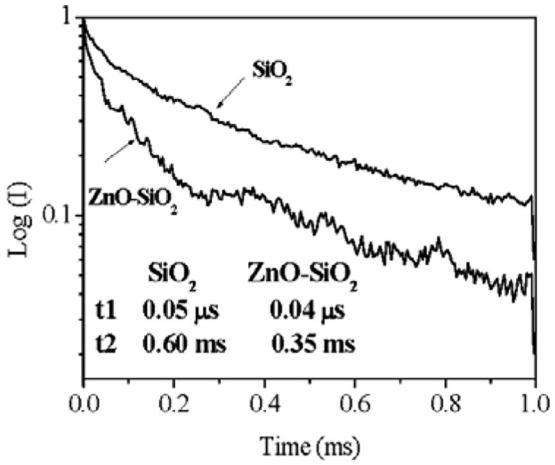

FIGURE 5 Decay curves of Tb^{3+} monitoring 544 nm at femtosecond laser excitation.

fs laser, the excitation of three-simultaneous absorption and nonradiative relaxation from 5*d* excited state to $^5D_3$, followed to $^5D_4$ is fast. The intensity of $^5D_4$–^7F_J on pump power mainly depended on the decay of $^5D_4$ level. Figure 5 shows the decay curves of Tb^{3+} monitoring 544 nm. It can be seen that $^5D_4$ level second-exponentially decayed. The lifetimes were obtained by second-exponential fitting and are listed in Fig. 5. The fast process was attributed to the nonradiative relaxation from $^5D_4$ to some quenching centers. The slow process corresponded with $^5D_4$–^7F_J transitions. The lifetime of fast and slow process of Tb^{3+} in SiO_2 glass was longer than that in ZnO–SiO_2 glass, indicating slower decay rate in SiO_2 glass, leading to the observation that the saturation of $^5D_4$ level of Tb^{3+} in SiO_2 glass is easier to occur than is that in ZnO–SiO_2 glass. Thus the UCL was the dominant depletion mechanism of $^5D_4$ in SiO_2 glass, leading to saturation effect to occur. This saturation effect of UCL was also observed in Er^{3+} -Yb^{3+} codoped Gd_2O_3 nanocrystals.[19] It implied that higher saturation power of Tb^{3+} is obtained in ZnO–SiO_2 glass in comparison with SiO_2 glass.

In conclusion, SiO_2 and ZnO–SiO_2 glasses containing terbium ions were prepared by a sol-gel method, and their UCL of Tb^{3+} ions was analyzed and compared at fs laser excitation. In both glasses, the intensive green UCL of Tb^{3+} was observed. The results of dependence of UCL intensity on pump power indicated that the three-photon UCL processes in ZnO–SiO_2 glass predominated and saturation effect took place in SiO_2 glass. In view of the energy level of Tb^{3+}, the mechanism of UCL of Tb^{3+} in both glasses is simultaneous three-photon excitation. However, the saturation of $^5D_4$ population of Tb^{3+} ions in SiO_2 glass occurred as a result of their slow decay rate in this glass, leading to a marked deviation from the cubic dependence of the emission intensity on the excitation power.

ACKNOWLEDGMENTS

The authors are grateful for the financial support from the NITECH 21st Century COE Program for Environment-Friendly Ceramics and from the NSFC (no. 10504030).

REFERENCES

1. Wermuth, M.; Riederer, T.; Gudel, H. Spectroscopy and upconversion mechanisms of $CsCdBr_3:Dy^{3+}$. *Phys. Rev. B.* **1998**, *57*, 4369–4376.
2. Auzel, F. Upconversion and anti-stokes processes with f and d ions in solids. *Chem. Rev.* **2004**, *104*, 139–174.
3. Patra, A.; Friend, C. S.; Kapoor, R.; Prasa, P. Effect of crystal nature on upconversion luminescence in $Er^{3+}:ZrO_2$ nanocrystals. *Appl. Phys. Lett.* **2003**, *83*, 284–286.
4. Yi, G.; Chow, G. Colloidal LaF_3:Yb, Er, LaF_3:Yb, Ho, LaF_3:Yb,Tm nanocrystals with multicolor upconversion fluorescence. *J. Mater. Chem.* **2005**, *15*, 4460–4464.
5. Patra, A.; Ghosh, P.; Saha, P.; Alencar, M.; Lozano, W.; Rakov, N.; Maciel, G. Red to Blue tunable upconversion in Tm^{3+}-doped ZrO_2 nanocrystals. *J. Phys. Chem. B.* **2005**, *109*, 10142–10146.
6. Noginov, M. A.; Venkateswarlu, P.; Mahdi, M. Two-step upconversion luminescence in Yb:Tb:YSGG crystal. *J. Opt. Soc. Am. B.* **1996**, *13*, 735–737.
7. Vermelho, M. V. D.; Santos, P. V.; Araújo, M. T. A.; Gouveia-Neto, S. F.; Cassanjes, C. S.; Ribeiro, J. L.; Messaddeq, Y. Thermally enhanced cooperative energy-transfer frequency upconversion in terbium and ytterbium doped tellurite glass. *J. Lumin.* **2003**, *102*, 762–767.
8. Luo, L.; Po-Wan Lai, W.; Wong, K.; Wong, W.; Li, K.; Cheah, K. Green upconversion fluorescence in terbium coordination complexes. *Chem. Phys. Lett.* **2004**, *398*, 372–376.
9. Lakowicz, J. R.; Piszczek, G.; Maliwal, B.; Gryczinski, I. Multiphoton excitation of lanthanides. *Chem. Phys. Chem.* **2001**, *2*, 247.
10. White, G. F.; Litvinenko, K. L.; Meech, S. R.; Andrews, D. L.; Thomson, A. J. Multonphoton-excited luminescence of a lanthanide ion in a protain complex:Tb^{3+} bound to transferring. *PhotoChem. Photobio. Sci.* **2004**, *3*, 47.
11. Wers, M.; Nerambourg, N.; Pelegry, D.; Le Grand, Y.; Blanchard-Desce, M. Action cross sections of two-photon excited luminescence of some Eu(III) and Tb(III) complexes. *PhotoChem. Photobio. Sci.* **2005**, *4*, 531.
12. Qiu, J.; Miura, K.; Suzuki, T.; Mitsuyu, T. Permanent photoreduction of Sm^{3+} to Sm^{2+} inside a sodium aluminoborate glass by an infrared femtosecond pulsed laser. *Appl. Phys. Lett.* **1999**, *74*, 10–12.
13. Bewersdorf, J.; Denk, R.; Kleinfeld, D.; Tank, D. Multifocal multiphoton microscopy. *Opt. Lett.* **1998**, *23*, 655–657.
14. Zhou, W.; Kuebler, S.; Braun, K.; Yu, T.; Cammack, J.; Ober, C.; Perry, J.; Marder, S. An efficient two-photon-generated photoacid applied to positive-tone 3D microfabrication. *Science.* **2002**, *296*, 1106.

15. You, H.; Nogami, M. Three-photon-excited fluorescence of Al_2O_3-SiO_2 glass containing Eu^{3+} ions by femtosecond laser irradiation. *Appl. Phys. Lett.* **2004**, *84*, 2076–2078.
16. You, H.; Nogami, M. Upconversion luminescence of Al_2O_3-SiO_2:Ce^{3+} glass by femtosecond laser irradiation. *Appl. Phys. Lett.* **2004**, *84*, 3432–3434.
17. Blasse, G.; Grabmaier, C. *Luminescent Materials*. Springer: Berlin, 1994, 196.
18. Song, F.; Zhang, G.; Shang, M.; Tan, H.; Yang, J.; Meng, F. Three-photon phenomena in the upconversion luminescence of erbium–ytterbium-codoped phosphate glass. *Appl. Phys. Lett.* **2001**, *79*, 1748–1750.
19. Lei, Y.; Song, H.; Yang, L.; Yu, L.; Liu, Z.; Pan, G.; Bai, X.; Fan, L. pconversion luminescence, intensity saturation effect, and thermal effect in Gd_2O_3:Er^{3+}, Yb^{3+} nanowires. *J. Chem. Phys.* **2005**, 123–174710.