Simultaneous three-photon-excited violet upconversion luminescence of Ce\textsuperscript{3+}:Lu\textsubscript{2}Si\textsubscript{2}O\textsubscript{7} single crystals by femtosecond laser irradiation

Yongjun Dong, Jun Xu, Guangjun Zhao, Chenfeng Yan, Guoqing Zhou, Liangbi Su, Luyun Yang, Jianrong Qiu, Lihuang Lin, Xiaoyan Liang, Ruxin Li, and Zhizhan Xu

State Key Laboratory of High Field Laser Physics, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Qinghe Road, 390, Shanghai 201800, China

Qishi Ren
Department of Biomedical Engineering, Shanghai Jiao-Tong University, 800, Dong-Chuan Road, Shanghai 200240, China

Received January 23, 2006; revised April 14, 2006; accepted April 19, 2006; posted April 26, 2006 (Doc. ID 67426)

We found that Ce\textsuperscript{3+}:Lu\textsubscript{2}Si\textsubscript{2}O\textsubscript{7} single crystals could be excited at 800 nm by using a femtosecond Ti:sapphire laser. The emission spectra of Ce\textsuperscript{3+}:Lu\textsubscript{2}Si\textsubscript{2}O\textsubscript{7} crystals were the same for one-photon excitation at 267 nm as for excitation at 800 nm. The emission intensity of Ce\textsuperscript{3+}:Lu\textsubscript{2}Si\textsubscript{2}O\textsubscript{7} crystals was found to depend on the cube of the laser power at 800 nm, consistent with simultaneous absorption of three 800 nm photons. The measured value of the three-photon absorption cross section is $\sigma = 2.44 \times 10^{-77} \text{ cm}^6 \text{s}^2$. © 2006 Optical Society of America

Growing interest in the realization of IR-to-visible frequency-upconversion luminescence by means of three-photon absorption has stimulated investigations of the new irradiation sources and materials. Most investigations of three-photon-induced upconversion luminescence were performed by using pulses of a nanosecond- or picosecond-duration laser pump source. However, it seems that with nanosecond and picosecond sources it is difficult to generate efficient upconversion fluorescence in inorganic solid materials because of low nonlinear effects induced by these sources. A very promising approach to this problem is the use of pulsed lasers operating at a shorter pulse duration and higher peak power as a new irradiation source. In recent years, femtosecond high-peak-power laser systems using a chirped-pulse amplification technique with Ti:sapphire laser crystals have been developed and unquestionably have become a suitable upconversion fluorescence pump source.\textsuperscript{1,2} The advantages of the femtosecond laser are that it provides intense femtosecond pulses at a higher repetition rate from about 690 to 1000 nm, and it offers a shorter pulse duration. The high intensity of the femtosecond laser pulses could cause nonlinear effects, such as simultaneous two- or three-photon absorption, more easily. On the other hand, to date, almost all reports of three-photon-excited upconversion luminescence have been focused on organic compounds, semiconductors, nanocrystals, inorganic glasses, and optical fibers. However, reports of upconversion luminescence in crystals based on three-photon absorption are much fewer.

In this Letter we present experimental results on the simultaneous three-photon-excited violet upconversion luminescence in Ce\textsuperscript{3+}:Lu\textsubscript{2}Si\textsubscript{2}O\textsubscript{7} single crystals induced by using femtosecond laser irradiation at 800 nm. The Ce\textsuperscript{3+}:Lu\textsubscript{2}Si\textsubscript{2}O\textsubscript{7} single crystals were characterized, and a preliminary investigation of their applications as scintillators was conducted.\textsuperscript{3} This result extends the applications of Ce\textsuperscript{3+}:Lu\textsubscript{2}Si\textsubscript{2}O\textsubscript{7}, single crystals and suggests opportunities for a three-photon process in frequency-upconversion lasers, optical communication, high-density three-dimensional optical data storage, display, IR quantum counters, and three-dimensional fluorescence imaging.

In our experiments single crystals of Ce\textsuperscript{3+}:Lu\textsubscript{2}Si\textsubscript{2}O\textsubscript{7} were grown by the Czochralski technique. Details of the growth apparatus and procedures have been given previously.\textsuperscript{4} Samples were sliced into disks with a 2 mm thickness for femtosecond laser irradiation and spectral measurements. We used a regenerative-amplified 800 nm Ti:sapphire laser that emits 120 fs, 1 KHz, mode-locked pulses as the irradiation source. The laser beam was focused with a lens (100 mm focal length) onto the sample, and the average power at the focused area could be varied from 10 to 55 mW. The emission spectra excited by the focused femtosecond laser were recorded by a ZOLIX spectrophotometer. The absorption spectra were measured with a JASCO V-570 spectrophotometer, and all of the above measurements were taken at room temperature.

Focusing the laser in the sample resulted in strong violet emission that could be easily observed by the naked eye. This result suggests that violet upconversion fluorescence could be excited by an IR femtosecond laser without the use of UV optics. The emission spectra of Ce\textsuperscript{3+}:Lu\textsubscript{2}Si\textsubscript{2}O\textsubscript{7} single crystals are shown in Fig. 1 for excitation at 800 and 267 nm. The most important result was that the relative fluorescence yield ratios and the corresponding spectral distributions of the measured samples are basically the same for both UV and IR excitation, indicating that emission occurs from the same state independent of
the excitation wavelength. In the Lu$_2$Si$_2$O$_7$ host lattice, Ce$^{3+}$ is substituted for Lu$^{3+}$ sites and acts as the luminescence center. The Ce$^{3+}$ ion has a 4$f$ configuration, and the ground state consists of a doublet ($^2F_{5/2}$ and $^2F_{7/2}$). The broad emission peak located at about 395 nm is characteristic of the interconfigurational electronic transition of the Ce$^{3+}$ ions 5$d$ lowest energy level to the $^2F_{5/2}$ and $^2F_{7/2}$ manifolds split by spin–orbit coupling. Since the measured emission spectra are similar for one- and three-photon excitation we considered the possibility of the presence of the three-photon process when the crystal was illuminated at 800 nm.

We examined the dependence of the emission intensity of the Ce$^{3+}$:Lu$_2$Si$_2$O$_7$ crystal on laser power at 800 nm. According to the theoretical consideration of the multiphoton absorption process, the relationship between the pumping power and the fluorescence intensity can be described as a power law:\[ I \propto P^n, \] 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 log–log relationship of the pumping power of the femtosecond laser and fluorescence intensity of the Ce$^{3+}$:Lu$_2$Si$_2$O$_7$ crystal is shown in Fig. 2. The slope coefficient of the fitted line is 3.08. The emission intensity was found to depend on the cube of the laser power, which indicates that the upconversion luminescence emission is generated by the three-photon excitation process.

Three-photon absorption, which includes two mechanisms, one of which is direct three-photon absorption and the other is two- (one-) photon absorption followed by one- (two-) photon absorption from the excited level, is represented by the same cubic relationship between the pumping power and the fluorescence intensity. To identify these two mechanisms, we investigated the single-photon absorption spectra of Ce$^{3+}$:Lu$_2$Si$_2$O$_7$ single crystals, as shown in Fig. 3. One notices that there is no linear absorption at the one-photon energy of 800 nm radiation. Therefore there is little possibility for one-photon absorption followed by the two-photon absorption process. Another possible process is two-photon absorption followed by one-photon absorption; in this case, the Ce$^{3+}$ ions should have an intermediate state corresponding to absorption at 400 nm. However, the Ce$^{3+}$ ion is characterized by the lack of a real energy level between the 4$f$ ground states and the lowest 5$d$ excited states. Therefore this process could be precluded. However, the three-photon energy of the 800 nm radiation falls into the strong UV absorption band of the Ce$^{3+}$:Lu$_2$Si$_2$O$_7$ crystals, and therefore three-photon simultaneous absorption may be expected.

To further verify the three-photon simultaneous excitation process, we need to exclude the possibility of other upconversion mechanisms. Until 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 (CU), and photon avalanche (PA). It should be noted that both
ETU and ESA processes need at least one metastable intermediate level that acts as a storage reservoir for the pump energy. The Ce$^{3+}$ ions in Lu$_2$Si$_2$O$_7$ single crystals, which involves a single ground state 4$f$ and a single excited state 5$d$, cannot generate violet up-conversion luminescence by ETU or ESA processes because of the lack of metastable intermediate levels. CU is a process by which two rare-earth ions that are both excited to the higher manifold interact. To generate the upconversion fluorescence by the CU mechanism, one basic condition is that the upconversion emission peaks are about at half the wavelength of the IR absorption peaks. However, it can be seen from the absorption spectra of Ce$^{3+}$:Lu$_2$Si$_2$O$_7$ crystals that Ce$^{3+}$ ions did not show any absorption band located at the IR region. Thus the CU mechanism can be precluded. One important characteristic of the PA process is that an excitation power threshold clearly separates two different regimes. Below threshold the upconverted fluorescence intensity is weak, and above threshold the fluorescence increases by several orders of magnitude. However, from our experiments, the PA process should not be involved in the upconversion process because there was no transmittance decrease and the upconversion signal grew nonlinearly with increasing pump power phenomena. These facts, as well as the low possibility of sequential stepwise multiphoton excitation processes, enable us to suggest that the femtosecond-laser-induced violet upconversion luminescence mechanism in Ce$^{3+}$:Lu$_2$Si$_2$O$_7$ crystals is dominated by the three-photon simultaneous absorption process.

Using the intensity-dependent transmission measurement, we measured the three-photon absorption coefficient of Ce$^{3+}$:Lu$_2$Si$_2$O$_7$ single crystals at an 800 nm wavelength. According to the basic theoretical consideration, the intensity change of an excitation beam along the optical propagation path $z$ can be expressed as

$$ I(z) = I_0/(1 + 2\gamma z I_0)^{1/2}, $$

where $\gamma$ is the three-photon absorption coefficient of the sample and $I_0$ is the incident intensity of the excitation beam. The measured transmitted intensity as a function of the incident intensity is shown in Fig. 4. Equation (2) is adequate for a cw incident beam or a pulsed beam with a rectangular temporal profile. In our case the incident pulses had a quasi-Gaussian temporal profile; therefore we could further assume an equivalent rectangular pulse shape to give a rough estimate of intensity $I_0$ or $I(z)$. The solid line is the theoretical curve predicted by Eq. (2) by using a best-fit parameter of $\gamma = 1.07 \times 10^{-23} \text{ cm}^6 \text{ W}^{-2}$. Based on the known $\gamma$ value of the measured sample, the absorption cross section (in the units of cm$^6$ s$^{-2}$) for the Ce$^{3+}$:Lu$_2$Si$_2$O$_7$ crystal is obtained by

$$ \sigma'_3 = \frac{\gamma}{N_A d_0 \times 10^{-3}} \left( \frac{hc}{\lambda} \right)^2, $$

where $N_A$ is the Avagadro constant, $d_0$ is the concentration of doped Ce$^{3+}$ ions in Lu$_2$Si$_2$O$_7$ single crystals (in the units of moles per liter), and $h(c/\lambda)$ is the energy of an incident photon at 800 nm. Thus the value of the three-photon cross section of Ce$^{3+}$:Lu$_2$Si$_2$O$_7$ crystals can be estimated as $\sigma'_3 = 2.44 \times 10^{-27} \text{ cm}^6 \text{ s}^{-2}$.

In conclusion, we observed emission from Ce$^{3+}$:Lu$_2$Si$_2$O$_7$ single crystals excited with a femtosecond Ti:sapphire laser at 800 nm. The emission spectra were found to be identical for one- and three-photon excitation. The dependence of luminescence intensity on incident laser power indicates a three-photon process. When the intensity-dependent transmission measurement was used, the three-photon cross section of the crystal was determined to be $2.44 \times 10^{-27} \text{ cm}^6 \text{ s}^{-2}$.

This work is supported by the National Basic Research Program of China (grant 2005CB724302). J. Xu’s e-mail address is xujun@mail.shcnc.ac.cn; Q. Ren’s e-mail address is renqsh@sjtu.edu.cn.

References