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Femtosecond Laser-Induced Upconversion Luminescence in Rare-Earth Ions by Nonresonant Multiphoton Absorption

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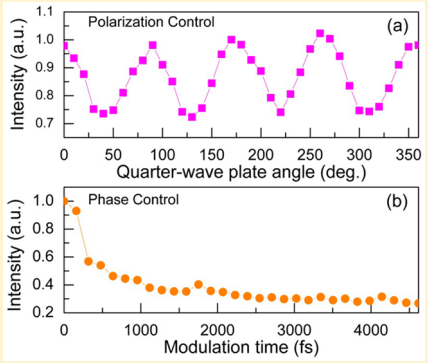
ABSTRACT: The upconversion luminescence of rare-earth ions has attracted considerable interest because of its important applications in photoelectric conversion, color display, laser device, multiplexed biolabeling, and security printing. Previous studies mainly explored the upconversion luminescence generation through excited state absorption, energy transfer upconversion, and photon avalanche under the continuous wave laser excitation. Here, we focus on the upconversion luminescence generation through a nonresonant multiphoton absorption by using the intense femtosecond pulsed laser excitation and study the upconversion luminescence intensity control by varying the femtosecond laser phase and polarization. We show that the upconversion luminescence of rare-earth ions under the intense femtosecond laser field excitation is easy to be obtained due to the nonresonant multiphoton absorption through the nonlinear interaction between light and matter, which is not available by the continuous wave laser excitation in previous works. We also show that the upconversion luminescence intensity can be effectively controlled by varying the femtosecond pulsed laser phase and polarization, which can open a new technological opportunity to generate and control the upconversion luminescence of rare-earth ions and also can be further extended to the relevant application areas.



1. INTRODUCTION

The upconversion luminescence of rare-earth ions doped luminescent material has become the research hotspot in recent years and has been successfully applied in a lot of research areas, such as color display,[1,2] laser source,[3,4] multiplex biolabeling,[5,6] high-density optical storage,[7,8] photovoltaic cell,[9−11] and security printing.[12,13] The upconversion luminescence refers to such a process that the luminescent materials absorb the low-frequency photons and emit the high-frequency photons. Compared with the downconversion luminescence, which converts the high-frequency stimulation to the low-frequency emission, there are many advantages for the upconversion luminescence. For example, the upconversion luminescence usually employed the near-infrared laser excitation but not ultraviolet laser excitation and therefore can significantly suppress the autofluorescence, photobleaching, and photodamage, which are very important for biomedical applications,[14] because the biological specimens are more vulnerable to the exposure of the high-frequency laser. Moreover, the upconversion luminescence contains the two or more photon absorption, which is a nonlinear optical effect, and so it is easy to be controlled by a quantum coherent control method.[15,16]

In previous studies, the continuous wave laser was usually used as the excitation source of the upconversion luminescence of rare-earth ions. In this case, there are usually three generation mechanisms for the upconversion excitation process, including excited state absorption (ESA),[17,18] energy transfer upconversion (ETU),[19−21] and photon avalanche (PA),[22,23] as shown in Figure 1a−c. Because of the large absorption cross section and long excited state lifetime, the upconversion luminescence efficiency of rare-earth ions under the continuous wave laser excitation is usually high. Recently, the femtosecond pulsed laser excitation has been proposed to produce the upconversion luminescence of rare-earth ions doped luminescent materials.[15,16] The femtosecond pulsed laser has the high

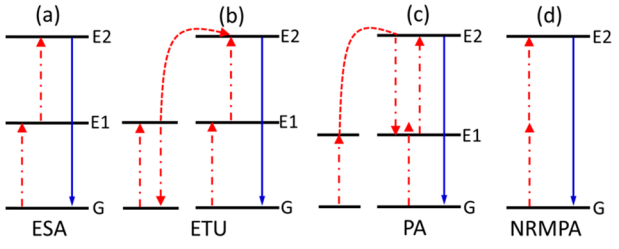


Figure 1. Principle upconversion processes for lanthanide-doped luminescent materials: (a) excited state absorption (ESA); (b) energy transfer upconversion (ETU); (c) photon avalanche (PA); and (d) nonresonant multiphoton absorption (NRMPA).

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laser intensity and broad spectral bandwidth, and therefore, compared with the continuous wave laser excitation, the femtosecond pulsed laser excitation can additionally produce a upconversion excitation process, that is, nonresonant multiphoton absorption (NRMPA), as shown in Figure 1d. In this upconversion excitation process, the rare-earth ions can simultaneously absorb many photons to the target excited state without the intermediate excited state. Obviously, the femtosecond pulsed laser can provide a more flexible method to generate and control the upconversion luminescence of rare-earth ions since more upconversion excitation processes are included.

In our previous works, we have obtained the upconversion luminescence in rare-earth ions doped glass or glass ceramics via the excited state absorption and energy transfer upconversion under the intense femtosecond pulsed laser excitation[24,25] and realized the upconversion luminescence enhancement or color tuning by varying the spectral phase, laser polarization, and repetition rate.[26,27] In this work, we focus on the generation and control of the upconversion luminescence in the rare-earth ions via the nonresonant multiphoton absorption by using the femtosecond pulsed laser excitation. Our experimental results show the upconversion luminescence in the glass doped with Eu^{3+} ions can be obtained via the nonresonant two-photon absorption under the 800 nm femtosecond pulsed laser excitation and this upconversion luminescence intensity can be effectively controlled by varying the femtosecond pulsed laser phase and polarization. Compared with our previous study via the excited state absorption (i.e., resonant-mediated two-photon absorption) in the glass doped with Dy^{3+} ions,[26] the control efficiency via the nonresonant two-photon absorption in this work is much higher. Our work reveals a new and efficient excitation pathway to control the upconversion luminescence efficiency in the rare-earth ions by modulating the femtosecond pulsed laser, which will be very meaningful in the upconversion luminescence generation and control.

2. EXPERIMENT ARRANGEMENT

In our experiment, we take the glass doped with Eu^{3+} ions as our study object. Here, the glass is used as the matrix materials, which is due to the excellent uniformity, machinability, and stability of glass material. The Eu^{3+}-doped glass sample preparation method is the same as that in our previous works,[26] and here only the simple description is given. The precursor sample is prepared with the composition in mol % of $40SiO_2/25Al_2O_3/18Na_2CO_3/10YF_3/7NaF/1EuF_3$. The original materials are mixed and melted in a covered platinum crucible at the temperature of 1450 °C for 45 min in the ambient atmosphere and then are cast into a brass mold followed by annealing at the temperature of 450 °C for 10 h and cooling inside the furnace. Finally, the glass sample is cut and polished for optical measurement in our experiment.

The experimental arrangement for the upconversion luminescence generation and control in Eu^{3+}-doped glass is shown in Figure 2. A Ti−sapphire mode-locked regenerative amplifier (Spitfire, Spectra Physics) provides the femtosecond laser pulse with the central wavelength of 800 nm, pulse width of 50 fs, and repetition rate of 1 kHz. A programmable femtosecond pulse shaping setup is utilized to modulate the spectral phase of the femtosecond laser pulse, which is consist of a pair of diffraction gratings (G_1 and G_2) with 1200 lines/mm, a pair of concave mirrors (C_1 and C_2) with focal length of

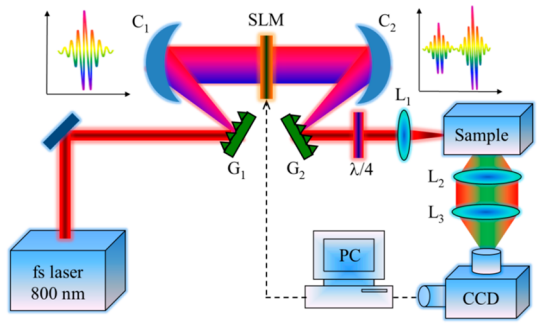

Figure 2. Experimental arrangement for the upconversion luminescence generation and control of Eu^{3+}-doped glass by the femtosecond laser pulse excitation, where a spatial light modulator (SLM) is used to control the spectral phase and a quarter-wave plate ($\lambda/4$) is used to vary the laser polarization.

200 mm, and a one-dimension liquid−crystal spatial light modulator (SLM-S320d, JENOPTIK), and here the spatial light modulator is located at the Fourier plane to control the spectral phase or amplitude in the frequency domain. A quarter-wave plate is used to vary the laser polarization from linear through elliptical to circular by rotating the plate angle. Finally, the modulated femtosecond pulsed laser is focused into the Eu^{3+}-doped glass sample using a lens with focal length of 50 mm. All the upconversion luminescence signals are collected on the side by a telescope system, and measured by a spectrometer with charge-coupled device (CCD).

3. RESULTS AND DISCUSSION

The UV−vis-NIR absorption spectrum of Eu^{3+}-doped glass sample is shown in Figure 3a, which is measured by a UV−vis

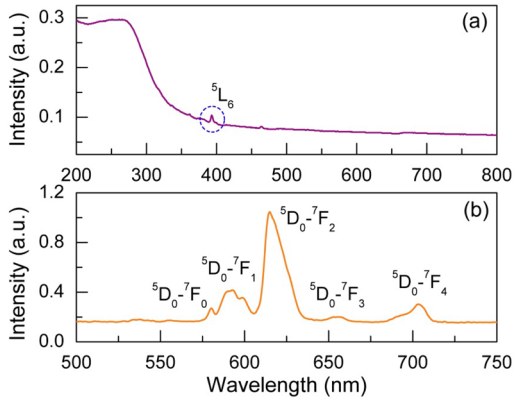

Figure 3. UV−vis-NIR absorption spectrum (a) and upconversion luminescence spectrum under the 800 nm femtosecond pulsed laser excitation (b).

spectrophotometer (TU-1901, Purkinje). There is an obvious absorption peak at 394 nm, which is corresponding to the transition from the ground state $^7F_0$ to the excited state $^5L_6$. The upconversion luminescence spectrum under the 800 nm femtosecond pulsed laser excitation is shown in Figure 3b. One can see that five upconversion luminescence peaks are respectively observed at 580, 593, 615, 654, and 703 nm, which are contributed to the transitions from the excited state $^5D_0$ to these states $^7F_0$, $^7F_1$, $^7F_2$, $^7F_3$ and $^7F_4$. We also utilize the 800 nm continuous wave laser to excite the Eu^{3+}-doped glass sample, but no upconversion luminescence is observed under

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the same laser energy. This experimental observation shows that the femtosecond pulsed laser excitation has a greater advantage in inducing the upconversion luminescence compared with the continuous wave laser excitation under the same laser energy.

In order to demonstrate the upconversion luminescence generation process of Eu^{3+}-doped glass sample in our experiment, we present the energy level diagram of Eu^{3+} ions and possible upconversion excitation pathways under the 800 nm femtosecond pulsed laser excitation, as shown in Figure 4.

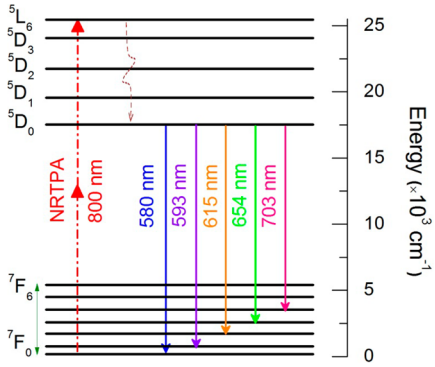

Figure 4. Energy level diagram of Eu^{3+} ion and possible upconversion process by nonresonant two-photon absorption (NRTPA) in our experiment.

The population in the ground state $^7F_0$ is pumped to the excited state $^5L_6$ via nonresonant two-photon absorption (NRTPA). Here, as long as the sum of the energies of the two photons is equal to the energy difference between the ground state $^7F_0$ and the excited state $^5L_6$, the nonresonant two-photon absorption can occur under the intense femtosecond pulsed laser excitation. The population in the excited state $^5L_6$ can spontaneously decay to these states $^7F_0$, $^7F_1$, $^7F_2$, $^7F_3$ and $^7F_4$ through the lower excited state $^5D_0$ and emits the upconversion luminescence signals with different wavelengths in Figure 3b. One can see that these upconversion luminescence signals come from the relaxation of the same excited state $^5L_6$, and therefore their intensity control efficiencies should be the same.

In order to further confirm that the upconversion luminescence of Eu^{3+}-doped glass sample under the 800 nm femtosecond pulsed laser excitation is due to the nonresonant two-photon absorption process, we measure the dependence of the upconversion luminescence intensity at the wavelength of 615 nm on the femtosecond pulsed laser intensity and the experimental result is shown in Figure 5. Here, these experimental data are linearly fitted. As can be seen, the fitting slope is 1.94, which completely satisfied the relationship of the luminescence intensity and laser intensity in the nonresonant two-photon absorption. Furthermore, as shown in Figure 4, there is no state transition corresponding to the 800 nm laser wavelength in the Eu^{3+}-doped glass sample, which can further illustrate that the population in the ground state $^7F_0$ can only be excited by the nonresonant multiphoton transition. Additionally, we also observe the upconversion luminescence intensities at other wavelengths by varying the femtosecond pulsed laser intensity, and find that all these upconversion luminescence signals have the same evolution behavior, which can verify above theoretical prediction that these upconversion luminescence signals result from the same upconversion excitation process, that is, nonresonant two-photon absorption.

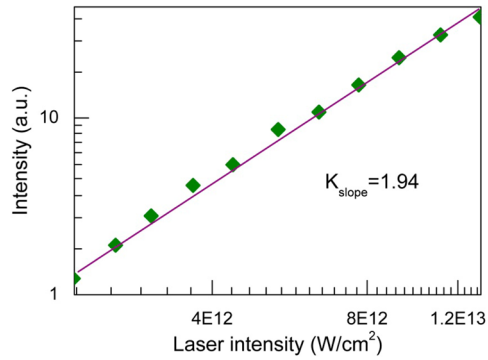

Figure 5. Upconversion luminescence intensity at the wavelength of 615 nm by varying the laser intensity, together with the linear fitting (purple solid line).

Because the upconversion luminescence of Eu^{3+}-doped glass under the 800 nm femtosecond pulsed laser excitation comes from the contribution of the nonresonant two-photon absorption, its intensity can be effectively controlled by varying the spectral phase of the femtosecond pulsed laser, which is similar to the two-photon fluorescence control in atomic or molecular system.[28,29] Here, we utilize a square phase modulation to control the upconversion luminescence intensity. Mathematically, the square phase modulation can be defined as follows[30]

$$\Phi(\omega) = \frac{\Delta}{2} + \frac{2\Delta}{\pi}\sum_{m=1}^{\infty}\frac{\sin[\Gamma(2m+1)(\omega-\omega_0)]}{2m+1}$$

where Δ and Γ, respectively, represent the modulation depth and time, and ω_0 is the laser central frequency. The square phase modulation will lead to the formation of subpulse train with a controllable temporal separation and relative intensity.[31] The modulation depth Δ is to control the relative intensity between the central subpulse and those side subpulses, and the modulation time Γ is to vary the temporal separation of these subpulses. Here, we fix the modulation depth $\Delta = \pi$ and vary the modulation time Γ to control the upconversion luminescence intensity in the Eu^{3+}-doped glass sample. Figure 6 shows the normalized upconversion luminescence intensity at the wavelength of 615 nm by varying the modulation time Γ of the square phase modulation. One can see that the control

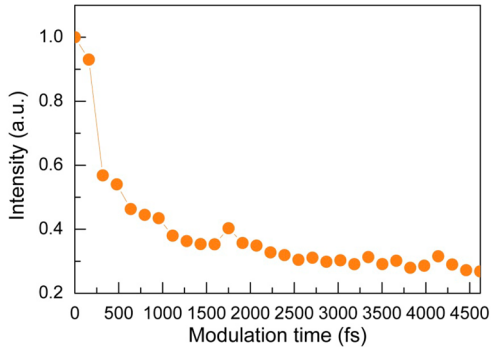

Figure 6. Normalized upconversion luminescence intensity at the wavelength of 615 nm by varying the modulation time Γ of the square phase modulation.

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efficiency of the upconversion luminescence can reach about 75%, here the control efficiency is defined by such a function of $\eta = (I_{max} - I_{min})/I_{max}$, where I_{max} and I_{min} are the maximal and minimal upconversion luminescence intensities by the square phase modulation. Obviously, the upconversion luminescence via the nonresonant two-photon absorption can be effectively controlled by varying the femtosecond laser phase, which is highly desired in some related application areas, such as color display.

In the nonresonant two-photon absorption process, the two photons are simultaneously absorbed to excite the population from the ground state to the excited state without the intermediate state, and thus the two photons must have the same polarization direction.[32,33] It is easy to verify that the nonresonant two-photon absorption is maximal value for the linear polarization and minimal value for the circular polarization under the same laser intensity. Obviously, the femtosecond laser polarization is also an important parameter to affect the upconversion luminescence intensity via the nonresonant two-photon absorption. Figure 7 shows the

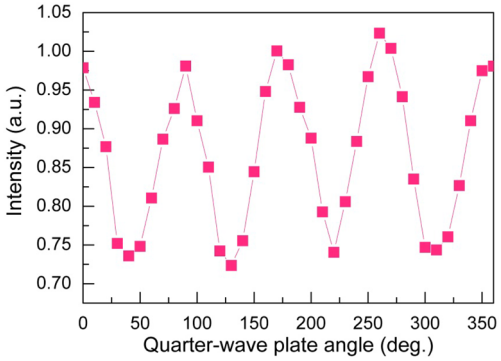

Figure 7. Normalized upconversion luminescence intensity at the wavelength of 615 nm by varying the quarter-wave plate angle.

normalized upconversion luminescence intensity at the wavelength of 615 nm in the Eu^{3+}-doped glass sample by rotating the quarter-wave plate angle (i.e., varying the laser polarization. Here, the femtosecond laser is linear polarization when the quarter-wave plate angle is the integral multiple of $\pi/2$ (i.e., $\theta = m\pi/2$) and is the circular polarization when the quarter-wave plate angle is an odd number of $\pi/4$ (i.e., $\theta = (2m + 1)\pi/4$). In our experiment, the quarter-wave plate rotation angle does not affect the out laser intensity. As expected, the upconversion luminescence intensity decreases when the laser polarization is changed from linear through elliptical to circular, and the control efficiency can be up to 26%. By comparison, it can be found that this control efficiency is much higher than that of Dy^{3+}-doped glass in our previous work,[26] where the control efficiency is only 7%. The fundamental reason is that the upconversion luminescence of Dy^{3+} ions is a resonant-mediated two-photon absorption process with the intermediate state, which contains the on-resonant two-photon absorption (i.e., excited state absorption) and near-resonant two-photon absorption (i.e., nonresonant two-photon absorption), and the on-resonant two-photon absorption is independent of the laser polarization. Therefore, we can make such a conclusion that the upconversion luminescence only via the nonresonant two-photon absorption can be most effectively controlled by varying the femtosecond laser polarization.

4. CONCLUSIONS

In summary, we have experimentally achieved the upconversion luminescence via a nonresonant two-photon absorption in the Eu^{3+}-doped glass under the intense 800 nm femtosecond pulsed laser excitation and realized the effective control of the upconversion luminescence by varying the femtosecond pulsed laser phase and polarization. The nonresonant multiphoton absorption can simultaneously absorb multiple photons with identical or different frequencies to excite the rare-earth ions from the ground state to the target excited state without the intermediate states, which can open a new upconversion excitation process in the luminescent materials doped with rare-earth ions. Furthermore, the nonresonant multiphoton absorption is a nonlinear optical effect, which is very sensitive to the femtosecond pulsed laser phase and polarization, and therefore it can provide a good method to control the upconversion luminescence via the nonresonant multiphoton absorption. Our work offers a new research direction to realize the upconversion luminescence generation and control, which is significant for the further applications of the luminescent materials doped with rare-earth ions.

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Notes

The authors declare no competing financial interest.

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