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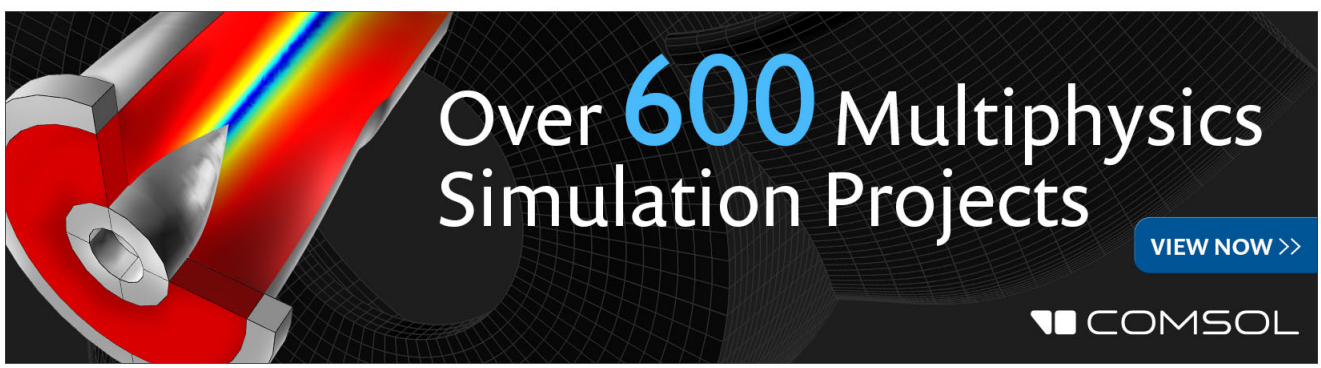

Single and two-photon fluorescence control of Er^{3+} ions by phase-shaped femtosecond laser pulse

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We experimentally demonstrate the control of the single and two-photon fluorescence (SPF and TPF) in Er^{3+} ions by shaping the femtosecond laser pulse with a π or square phase modulation. With the low laser intensity (8.4×10^{10} W/cm^2), SPF keeps a constant while TPF is effectively suppressed by the two control schemes. With the high laser intensity (1.2×10^{13} W/cm^2), both SPF and TPF are simultaneously enhanced or suppressed by the π phase modulation, and SPF is enhanced while TPF is effectively suppressed by the square phase modulation. The up/down-conversion fluorescence enhancement, suppression, or tuning by the optical control method can greatly expand its applications in various related fields. © *2014 AIP Publishing LLC*.
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The up/down-conversion fluorescence in rare-earth ions has attracted considerable interest because of its wide applications on laser sources,[1,2] fiber optic communications,[3,4] light-emitting diodes,[5] color displays,[6–9] and biolabels.[10–12] If the up/down-conversion fluorescence can be artificially enhanced, suppressed, or tuned, its applications can be greatly extended. Nowadays, various schemes have been proposed to experimentally realize the up/down-conversion fluorescence control. The previous studies mainly focus on varying material property, such as controlling dopant-host combination,[13,14] nanoparticle size,[15–17] or dopant concentration.[12,18,19] Recently, we proposed a femtosecond pulse shaping technique to control the up-conversion fluorescence[20] and showed that the two-photon fluorescence in Er^{3+} ions can be significantly suppressed by a π phase modulation. In this Letter, we further show that the single and two-photon fluorescence (SPF and TPF) in Er^{3+} ions can be effectively controlled by shaping the femtosecond laser pulse with a π or square phase modulation under the low and high laser intensities. Our experimental results indicate that rational design of the laser intensity and the laser spectral phase can realize that both SPF and TPF can be enhanced or suppressed, or SPF is enhanced or remains unchanged while TPF is effectively suppressed. By this optical control method, the up/down-conversion fluorescence enhancement, suppression, or tuning can be obtained in a material, which is different from previous works that the up/down-conversion fluorescence control is realized in a variety of materials.[12–19]

Figure 1(a) shows the experimental arrangement of SPF and TPF controls by shaping the femtosecond laser pulse. The output femtosecond laser pulse with the central wavelength of 800 nm and the pulse width of about 50 fs is shaped by a programmable 4f-configuration zero-dispersion pulse shaper that is composed of a pair of diffraction gratings with 1200 lines/mm and a pair of concave mirror with 200-mm focal length. A one-dimensional liquid-crystal spatial light

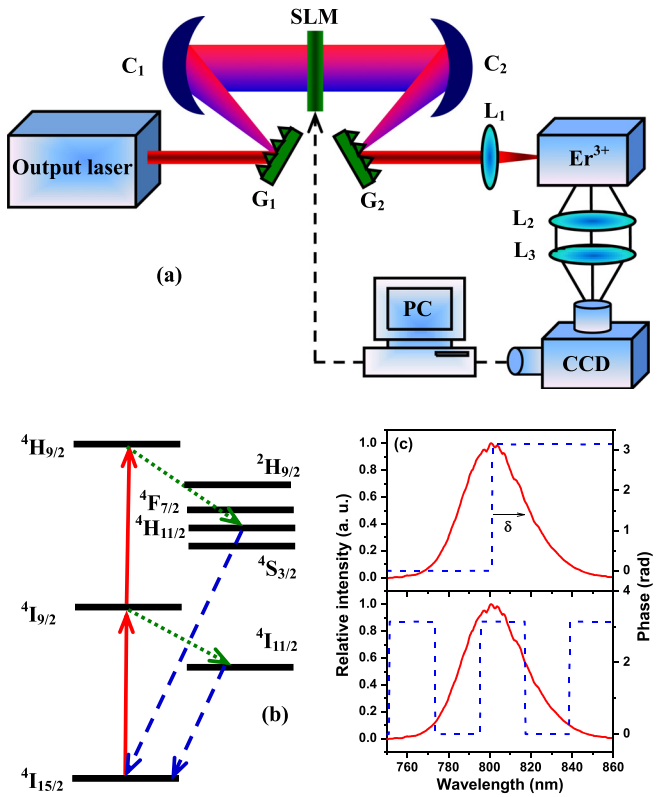

FIG. 1. (a) Schematic diagram of the experimental arrangement. The output femtosecond laser pulse is shaped by a 4f-configuration pulse shaping system. (b) Energy level diagram of the single and two-photon absorption and fluorescence detected schemes in the glass sample $60SiO_2$-$20Al_2O_3$-$20CaF_2$ doped with Er^{3+} ions. (c) The laser spectrum is modulated by a π (upper panel) or square (lower panel) phase modulation.

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modulator (SLM-S320d, JENOPTIK) is placed at the Fourier plane of the pulse shaper and used to vary the spectral phase modulation. The output shaped femtosecond laser pulse is focused into sample with a lens with the focal length of 500 mm. All fluorescence signals radiated from the sample are collected perpendicularly and measured by a spectrometer with charge-coupled device (CCD).

In our experiment, we perform SPF and TPF controls in the glass sample $60SiO_2$-$20Al_2O_3$-$20CaF_2$ doped with Er^{3+} ions, and the excitation and detection scheme is shown in Fig. 1(b), which includes the $^4I_{15/2}$ state as the ground state, the $^4I_{9/2}$ state as the intermediate excited state, and the $^4H_{9/2}$ state as the final excited state. The resonant frequency of the $^4I_{9/2}$ state is $\omega_{4_{I_{9/2}}} = 12563\,cm^{-1}$, corresponding to the wavelength of 796 nm, and the resonant frequency of the $^4H_{9/2}$ state is $\omega_{4_{H_{9/2}}} = 24570\,cm^{-1}$, corresponding to the wavelength of 407 nm. The population excited to the $^4I_{9/2}$ state spontaneously decays to the $^4I_{15/2}$ state through the $^4I_{11/2}$ state, which is corresponding to the single-photon fluorescence (i.e., SPF). However, the population excited to the $^4H_{9/2}$ state spontaneously decays to the $^4I_{15/2}$ state through the four lower $^2H_{9/2}$, $^4F_{7/2}$, $^4H_{11/2}$, and $^4S_{3/2}$ states, which is corresponding to the two-photon fluorescence (i.e., TPF).

We utilize a π or square phase modulation to control SPF and TPF, and the simple spectral phase modulation is shown in Fig. 1(c). The π or square phase modulation has been successfully applied in quantum coherent control of atomic and molecular systems[21–26] and has played a prominent role in the development of quantum control concepts and techniques. Here, the π phase modulation is defined by the function of $\Phi(\omega) = \frac{\pi\sigma(\omega-\delta)}{2}$, where $\sigma(\omega-\delta)$ denotes the signum function which takes the value -1 for $\omega < \delta$ and 1 for $\omega > \delta$, and thus $\Phi(\omega)$ is characterized by a phase jump from $-\pi/2$ to $\pi/2$ at the phase step position δ. The square phase modulation is defined by the function of $\Phi(\omega) = \frac{\pi}{2} + 2\sum_{m=0}^{\infty} \frac{\sin[\Gamma(2m+1)(\omega-\omega_0)]}{2m+1}$, where Γ is the modulation time and ω_0 is the laser central frequency, and thus the modulation period of the square phase modulation can be continuously changed by varying the modulation time Γ. In our experimental study, we control SPF and TPF in the glass sample doped with Er^{3+} ions by varying the step position δ of the π phase modulation and the modulation time Γ of the square phase modulation.

Figure 2 shows the absorption (a) and fluorescence spectra (b) of the glass sample doped with Er^{3+} ions. One can see from Fig. 2(a) that there are two obvious absorption peaks around the wavelength of 800 and 400 nm, which are corresponding to the $^4I_{9/2}$ and $^4H_{9/2}$ states. As shown in Fig. 2(b), five fluorescence signals can be observed at the wavelength of 404, 482, 526, 546, and 978 nm. The four fluorescence signals in the visible region are corresponding to the two-photon fluorescence (i.e., TPF), which result from these state transitions $^2H_{9/2} \rightarrow {}^4I_{15/2}$, $^4F_{7/2} \rightarrow {}^4I_{15/2}$, $^4H_{11/2} \rightarrow {}^4I_{15/2}$, and $^4S_{3/2} \rightarrow {}^4I_{15/2}$, respectively. However, the fluorescence signal in the near-infrared region is corresponding to the single-photon fluorescence (i.e., SPF), which results from the state transition $^4I_{11/2} \rightarrow {}^4I_{15/2}$.

We first demonstrate SPF and TPF controls of the glass sample doped with Er^{3+} ions with the low laser intensity. Figure 3 presents the normalized SPF (green squares) and TPF (red circles) intensities as the function of the step position δ of the π phase modulation (a) and the modulation time Γ of the square phase modulation (b) with the lower laser intensity of $8.4 \times 10^{10}\,W/cm^2$. All data are normalized by the corresponding fluorescence intensity induced by the transform-limited laser pulse, and hereafter the same method is employed. As can be seen, by both the two control schemes, TPF can be effectively suppressed but cannot be enhanced, while SPF is uncontrollable. That is to say, TPF can be continuously tuned, while SPF remains unchanged. It can be seen that TPF intensity can be maximally reduced by ~50% by the π phase modulation and ~90% by the square phase modulation. Obviously, these results are the same as that obtained in molecular system.[21]

However, SPF and TPF controls show the different behavior under the excitation with the high laser intensity. Figure 4 presents the normalized SPF (green squares) and TPF (red circles) intensities as the function of the phase step position δ of the π phase modulation (a) and the modulation

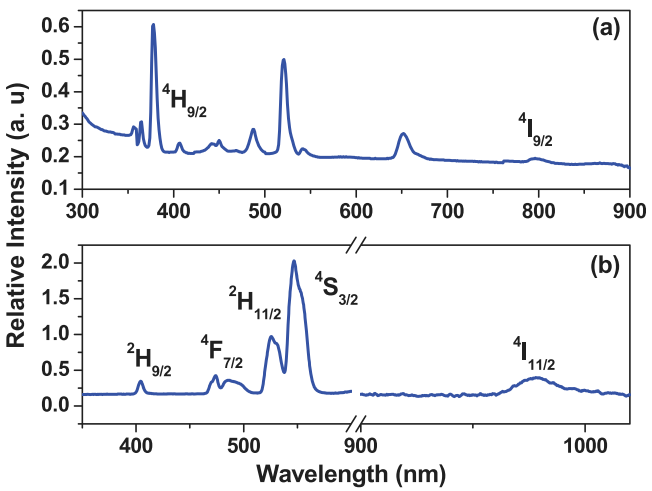

FIG. 2. The absorption (a) and fluorescence spectra (b) of the glass sample $60SiO_2$-$20Al_2O_3$-$20CaF_2$ doped with Er^{3+} ions.

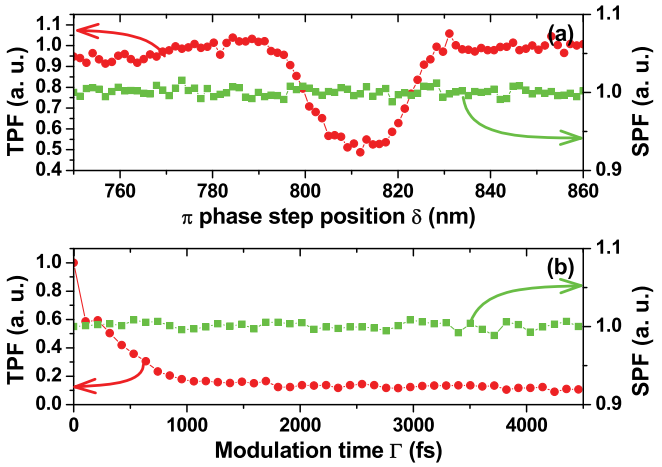

FIG. 3. The normalized SPF (green squares) and TPF (red circles) intensities as the function of the step position δ of the π phase modulation (a) and the modulation time Γ of the square phase modulation (b) with the lower laser intensity of $8.4 \times 10^{10}\,W/cm^2$.

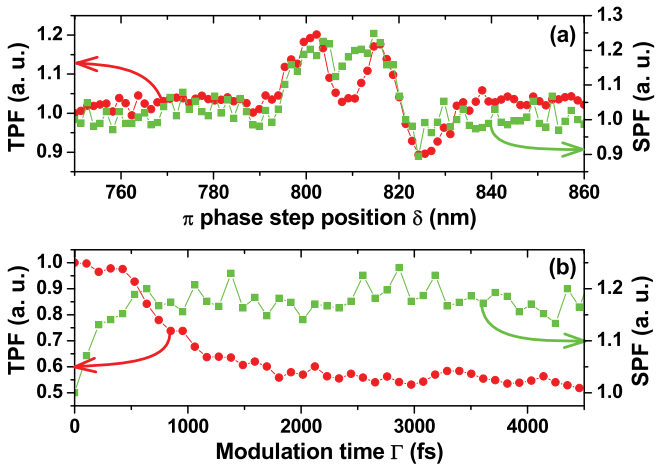

FIG. 4. The normalized SPF (green squares) and TPF (red circles) intensities as the function of the step position δ of the π phase modulation (a) and the modulation time Γ of the square phase modulation (b) with the higher laser intensity of 1.2×10^{13} W/cm^2.

time Γ of the square phase modulation (b) with the higher laser intensity of 1.2×10^{13} W/cm^2. As shown in Fig. 4(a), by the π phase modulation, both SPF and TPF can be effectively controlled, which can be enhanced or suppressed. It is noteworthy that the enhancement and suppression for SPF and TPF occur at the same step position δ, in other words, SPF and TPF are simultaneously enhanced or suppressed. SPF and TPF are, respectively, enhanced by ~25% and ~22%, and both are suppressed by ~10%. As shown in Fig. 4(b), by the square phase modulation, SPF is enhanced while TPF is effectively suppressed. SPF is enhanced by ~23%, and TPF is suppressed by ~50%. Comparing with the low laser intensity (see Fig. 3), SPF and TPF controls with the high laser intensity are more flexible and variable, which depend on the laser spectral phase shape.

In theory, SPF and TPF controls in Figs. 3 and 4 can be explained as follows. The weak-field N-photon absorption involves initial-to-final excitation pathways that are composed of N absorbed photons, while the strong-field N-photon absorption also involves additional resonance-mediated excitation pathways that are composed of N + 1 absorbed photons and one emitted photon,[27] corresponding to the higher order nonlinear optical effect, and thus the single or two-photon absorption in strong field regime is coherently induced by the single or two-photon transitions as well as by additional resonance-mediated three or four-photon transitions. With low laser intensity (8.4×10^{10} W/cm^2), the higher order nonlinear optical effect does not occur, which is corresponding to the perturbation regime, and therefore SPF and TPF modulation can be well described by the quantum interference of different optical excitation pathways connecting the initial and final states based on time-dependent perturbation theory, which has been demonstrated in our previous works.[20] However, with high laser intensity (1.2×10^{13} W/cm^2), the contribution of the higher order nonlinear optical effect becomes very evident, and thus the inter- and intragroup interferences involving the single (or two) and three-photon (or four-photon) excitation pathways lead to SPF (or TPF) enhancement or suppression. In the previous study, TPF enhancement with the high laser intensity due to the four-photon absorption has been experimentally and theoretically demonstrated in sodium (Na) atom.[27]

As shown in Figs. 3 and 4, by rationally designing the laser intensity and the laser spectral phase, both SPF and TPF can be effectively controlled, such as TPF is effectively suppressed while SPF keeps a constant, or both SPF and TPF are simultaneously enhanced or suppressed, or SPF is enhanced while TPF is effectively suppressed. Consequently, the coherent control strategy by making use of the femtosecond pulse shaping technique provides a well-established tool to realize the enhancement or suppression of SPF and TPF in Er^{3+} ions and their tuning. This optical control method is different from previous works, where the up/down-conversion fluorescence enhancement, suppression, or tuning are mainly realized by varying the material property of dopant-host combination, nanoparticle size, and dopant concentration,[12–19] and therefore this up/down-conversion fluorescence control is realized in a variety of materials. However, by varying the laser intensity and the laser spectral phase in our experiment, the up/down-conversion fluorescence can be controlled in one material, which illustrates that this optical control method in the preparation of the material has more advantageous.

In summary, we have experimentally demonstrated that SPF and TPF in Er^{3+} ions can be effectively controlled by shaping the femtosecond laser pulse with a π or square phase modulation under the low and high laser intensities. We showed that, by properly designing the laser intensity and the laser spectral phase, TPF is effectively suppressed while SPF keeps a constant, or both SPF and TPF are simultaneously enhanced or suppressed, or TPF is suppressed while SPF is enhanced. This up/down-conversion fluorescence enhancement, suppression, or tuning are realized in one material, which is very useful in its future applications. Our experimental schemes can also be further extended to control the multi-photon fluorescence in various rare-earth ions. This optical control method opens a new opportunity to control the up/down-conversion fluorescence enhancement, suppression, or tuning, which may have a significant impact on the up/down-conversion fluorescence applications of rare-earth ions.

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