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Two-wavelength two-photon process for optical selection of rare-earth ions

Xinyue Li [a], Shaoshuai Zhou [a], Xiantao Wei [a, b], Fangfang Hu [a], Yanguang Qin [a], Yonghu Chen [a], Min Yin [a], Changkui Duan [a, *]

[a] Department of Physics, University of Science and Technology of China, Hefei, 230026, China
[b] The Center of Physics Experiment, School of Physical Sciences, University of Science and Technology of China, Hefei, China

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ABSTRACT

The past decades has witnessed the blossom of upconversion, which is based on the ground state absorption (GSA) and excited state absorption (ESA) processes. Herein, we propose a brief strategy based on two-photon process with two simultaneous excitation wavelength for optical selection of rare earth (RE) ions. RE ion can be transferred to its intermediate state with resonant frequency from the first laser, and then furthered to the target state with the second laser of appropriate frequency, and every ion is separately excited by simultaneous two-wavelength independently. Herein, the resulting $^2H_{9/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} in $NaYF_4$ microprisms is employed as a monitoring probe, and this two-photon process is demonstrated by the excitation and emission spectra, and further verified by the dependences on excitation power and the luminescence decay curves. This conception will also provide a new strategy on precise optical selection of RE ions, especially for quantum information technology.

1. Introduction

Recently, rare earth (RE) doped luminescent materials have garnered much attention due to their promising applications in various fields, including photovoltaics, 3D display, data storage, biological imaging, biomedicine, as well as quantum information process [1–7]. In particular, upconversion has been the focus of a growing body of investigation, which characterizes by the absorption of low-energy photons based on the ground state absorption (GSA) and the excited state absorption (ESA), then followed by the emission of high-energy photons [8–10]. On this basis, a brief strategy based on two-photon process with simultaneous two-wavelength excitation [11,12] is proposed for optical selection of RE ions in this work. When excited by two-wavelength from different direction, the excited area in the sample would be reduced to a small volume, and the optical selection could be locked in a light spot. On the other hand, at least three energy levels are involved in this two-photon process, and the RE ions can be resonated to the intermediate level with a resonant wavelength provided by the first laser, and then to the target level by another tuned frequency. Thus the aimed RE ions, which match the two energy gaps strictly, can be perfectly locked and selected by high precision laser through two-photon process. Therefore, it is perfectly suitable for the optical selection of RE ions.

As a proof-of-concept experiment to verify our hypothesis, we utilize $NaYF_4$:Er^{3+} as an example, and the violet emission assigned to $^2H_{9/2} \rightarrow {}^4I_{15/2}$ transition as a monitoring probe. The first-step resonance is accomplished by excited at 1532 nm since Er^{3+} ions have a strong resonant absorption of $^4I_{15/2} \rightarrow {}^4I_{13/2}$. Meanwhile, Er^{3+} ions in excited $^4I_{13/2}$ state need extra energy at least 18043 cm^{-1} to reach the $^2H_{9/2}$ state, then producing violet emission, suggesting the appropriate wavelength for the second laser is approximately 555 nm. Therefore, the excitation and emission spectra, power dependence and lifetime measurements have been investigated under two-wavelength excitation simultaneously, providing insight in this two-photon process, which has potential applications in precise optical selection of RE ions, especially for quantum information technology.

2. Experimental

Hexagonal $NaYF_4$:2 mol% Er^{3+} phosphor was synthesized via hydrothermal method, as described in our previous studies [13,14]. The excitation and emission spectra and the lifetime measurements

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* Corresponding author.
E-mail address: ckduan@ustc.edu.cn (C. Duan).

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were performed with the excitation sources of a 1532 nm diode laser and an Opolette 355 LD laser, which is tunable in the range of 410–2200 nm with a spectral line-width of 4–7 cm^{-1} and pulse duration of 7 ns. The emission was dispersed and detected by a Jobin-Yvon HRD-1 double monochromator equipped with a Hamamatsu R928 photomultiplier. The decay curves were measured with a Tektronix TDS2024 digital storage oscilloscope. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Structural and morphology characterization

The X-ray powder diffraction (XRD) pattern of the $NaYF_4$:Er^{3+} sample is presented in Fig. 1(a). The diffraction peak positions of the sample match well with the standard data of hexagonal $NaYF_4$ (JCPDS No. 16–0334) with space group P63/m. And no additional peaks for other phases can be detected when incorporating Er^{3+} ions as dopants because of the almost same radii of Y^{3+} and Er^{3+} ions, indicating that the pure hexagonal phase of $NaYF_4$ is successfully synthesized. The fairly narrow full width at half maximum and intense diffraction peaks suggest the well crystallization. Furthermore, the morphology and size of the as-synthesized $NaYF_4$ sample are confirmed in the SEM graphs as depicted in Fig. 1(b) and (c), revealing the sample is composed of hexagonal microprisms and spherical crossed microprisms, which could be attributed to the several different growth directions from seed crystals. The microprisms are 3 μm in length and 2 μm in diameter on average.

3.2. Excitation and emission spectra

Fig. 2 shows the excitation spectra of $NaYF_4$:Er^{3+} microprisms monitoring the emission at 407 nm measured with the 1532 nm diode laser being turned on (red solid curve) or off (black dashed curve). The output power of the 1532 nm diode laser adopted was 24 mW, which alone does not cause any observable upconversion emission. Without the 1532 nm excitation, Er^{3+} ions exhibit intense absorption transitions from $^4I_{15/2}$ to $^4S_{3/2}$, $^2H_{11/2}$, $^4F_{7/2}$, $^4F_{5/2}$ and $^4F_{3/2}$, which are subsequently upconverted to higher levels to produce violet emission, as reported in Refs. [15,16]. When the 1532 nm excitation is turned on to excite Er^{3+} ions to $^4I_{13/2}$, three extra bands appear in the red solid curves ca 18011 cm^{-1}, 19880 cm^{-1} and 20938 cm^{-1}, i.e., 555.2 nm, 503.0 nm and 477.6 nm in wavelength, agreeing with the energy gaps of $^2H_{9/2}$-$^4I_{13/2}$, $^4G_{11/2}$-$^4I_{13/2}$ and $^4G_{9/2}$-$^4I_{13/2}$, respectively.

The emission spectra under the simultaneous excitations of 1532 nm and 555.2 nm, 503.0 nm or 477.6 nm are shown in Fig. 3(a–c), respectively. In Fig. 3(a), the 407 nm emission originated from the $^2H_{9/2} \rightarrow {}^4I_{15/2}$ transition shows up as a result of the $^4I_{15/2} \rightarrow {}^4I_{13/2}$ transition by 1532 nm excitation followed by the $^4I_{13/2} \rightarrow {}^2H_{9/2}$ transition by 555.2 nm excitation. This emission disappears when the 1532 nm laser was turned off. The schematic diagram of the process is shown in the inset of Fig. 3(a), and every Er^{3+} ion is separately excited by simultaneous two-wavelength independently. In addition, when the second laser is tuned to 503.0 nm, an emission band centered at 407 nm appears as expected (Fig. 3(b)), as well as an additional band centered at 378 nm, which is originated from the $^4G_{11/2} \rightarrow {}^4I_{15/2}$ transition. In this case, the two lasers populated Er^{3+} ions to the level $^4G_{11/2}$ at ca 26400 cm^{-1}, which relaxed subsequently to the $^2H_{9/2}$ level due to multiphonon nonradiative relaxation. The emission spectrum in Fig. 3(c) when the second laser is turned to 477.6 nm is similar to Fig. 3(b), apart from an extra weak emission band centered at 400 nm. This extra band corresponds to the $^2P_{3/2} \rightarrow {}^4I_{13/2}$ transition, as reported in Refs. [18,19], and maintains its intensity when the 1532 nm is turned off, and is due to solely the excitation of Er^{3+} ions by 477.6 nm.

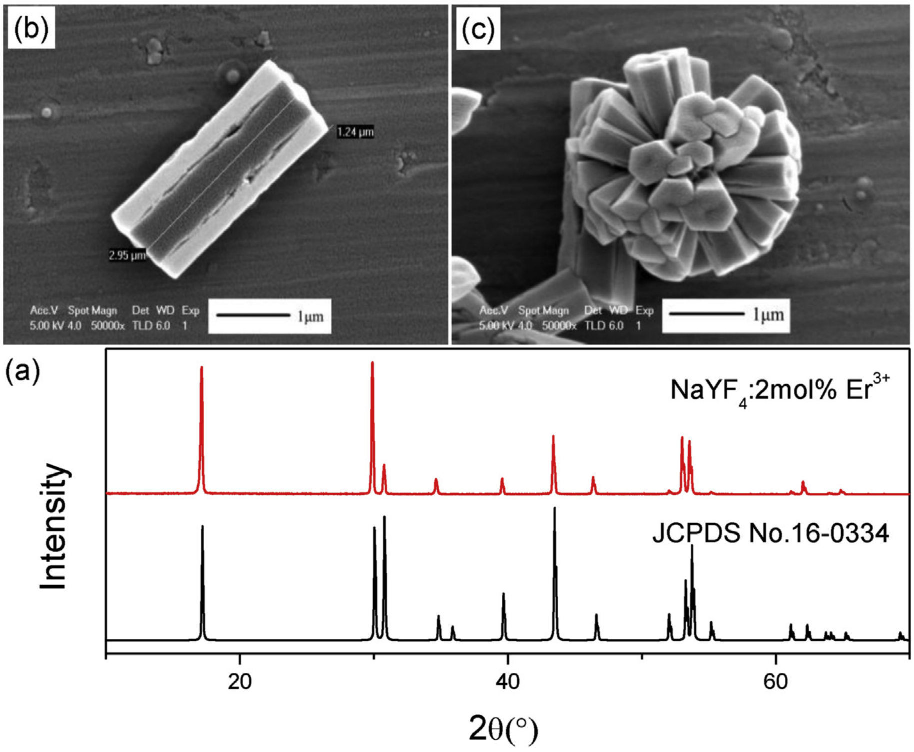

Fig. 1. XRD patterns (a) and SEM micrographs (b, c) of the $NaYF_4$:Er^{3+} microprisms.