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Three-photon near-infrared quantum splitting in $\beta\text{-NaYF}_4\text{:Ho}^{3+}$

D. C. Yu,¹ X. Y. Huang,¹ S. Ye,¹ M. Y. Peng,¹ Q. Y. Zhang,^{1,a)} and L. Wondraczek²¹State Key Laboratory of Luminescent Materials and Devices, and Institute of Optical Communication Materials, South China University of Technology, Guangzhou 510641, People's Republic of China²Department of Materials Science, University of Erlangen-Nuremberg, 91058 Erlangen, Germany

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We report on three-step sequential three-photon near-infrared (NIR) quantum splitting in $\beta\text{-NaYF}_4\text{:Ho}^{3+}$, where one absorbed ultraviolet photon is split into three NIR photons with wavelengths 850, 1015, and 1180 nm. The underlying mechanism is analyzed by static and dynamic photoemission and excitation spectroscopy. An internal quantum yield of 124% is estimated on the basis experimental data and theoretical considerations. Further development of an efficient triply splitting NIR phosphor might open up an approach in achieving efficient photonic devices, which enables more photons emitted than absorbed in the excitation process. © 2011 American Institute of Physics. [doi:10.1063/1.3652916]

The recent demonstration of efficient visible quantum splitting (QS) in vacuum ultraviolet (VUV)-excited $\text{LiGdF}_4\text{:Eu}^{3+}$ represents an exciting step towards the development super-efficient phosphors and luminescent devices.^{1,2} Already, since the first report on QS in the VUV spectral region (Pr^{3+} -doped YF_3 and NaYF_4 ,^{3–5}), intense research activities have been devoted to making use of this effect for potential applications in display and lighting.^{6–10} In a QS process, quantum yield (QY) exceeding unity can be obtained by splitting a photon of relatively high energy into two or more low-energy photons, thus enabling more photons to be emitted than were originally involved in the excitation process. If ultraviolet (UV) or visible photons can be split into two (or more) near-infrared (NIR) photons, this would enable exciting potential for efficient photovoltaic energy conversion.^{11–13} Down-conversion phenomena have hence been studied in numerous materials, particularly, for $\text{Ln}^{3+} - \text{Yb}^{3+}$ ($\text{Ln} = \text{Tb}, \text{Tm}, \text{Pr}, \text{Er}, \text{Nd}, \text{and Ho}$)-codoping.^{14–21} However, in most of those cases where NIR luminescence originates from Yb^{3+} through a first-order energy transfer (ET) from Ln^{3+} , QS does actually not occur. Despite the importance of the issue, it appears that there is presently no report on NIR-QS (especially three-photon NIR-QS) in a single-ion activated phosphor. As a consequence, the main mechanisms responsible for NIR-QS not well understood.

Here, we report on the observation of sequential three-step three-photon NIR-QS in $\beta\text{-NaYF}_4\text{:Ho}^{3+}$, where a high-energy UV photon splits into three NIR photons with QY greater than unity. On the basis static and dynamic spectroscopic data, we investigate in detail the underlying optoelectronic mechanism.

Powder sample of NaYF_4 with a Ho^{3+} -concentration of 1.0 mol. % was prepared in a hydrothermal procedure,¹⁶ employing Y_2O_3 , Ho_2O (both 99.99%), HNO_3 , NH_4HF_2 , and NaF (analytical grade) reagents as starting materials. Microstructure of the product was analyzed by powder x-ray diffractometry (XRD, Philips PW1830, $\text{Cu K}\alpha$) and scanning electron microscopy (SEM, JEOL JEM-1010). Photolumi-

nescence (PL) was studied with a high-resolution spectrophotometer (Edinburgh FLS920) fitted with 450 W and μF900 microsecond xenon lamps as the excitation sources and by time-correlated single photon counting (employing photomultiplier tubes Hamamatsu R928 and R5509-72).

SEM of the as-prepared product revealed pronounced hexagonal prismatic microrods with an average size of 1 μm in diameter and several microns in length. The XRD pattern readily agrees with $\beta\text{-NaYF}_4$ (Joint Committee on Powder Diffraction Standards 16-0334) as the sole crystalline phase. Figure 1 shows NIR PL spectra of $\text{NaYF}_4\text{:Ho}^{3+}$. Excitation at 287 nm results in four NIR PL peaks, which are located at 850, 965, 1015, and 1180 nm, respectively (Fig. 1(a)). These can be ascribed to the transitions of $^3\text{D}_3 \rightarrow ^3\text{K}_8$, $^5\text{F}_2 \rightarrow ^5\text{I}_7$, $^5\text{S}_2 \rightarrow ^5\text{I}_6$, and $^5\text{I}_6 \rightarrow ^5\text{I}_8$ of Ho^{3+} .^{21,22} A further series of characteristic PL bands in the UV-to-visible region can be also detected, corresponding to intra-4f transitions in Ho^{3+} , inset of Fig. 1(a). The bands at 360 and 850 nm exhibit almost identical lifetimes (96.2 μs and 92.4 μs , respectively). This observation is taken as evidence for similar electronic origin

FIG. 1. (Color online) NIR PL spectra of $\text{NaYF}_4\text{:1\%Ho}^{3+}$ upon excitation of (a) 287 nm, (b) 535 nm, and (c) 880 nm. The insets of Figs. 1(a) and 1(b) show the corresponding visible PL spectra.

^{a)} Author to whom correspondence should be addressed. Electronic mail: qyzhang@scut.edu.cn.

of these two bands, $\text{Ho}^{3+} : {}^3\text{D}_3$.²² For a rigorous investigation of the NIR emission scheme, detailed PL spectra (Figs. 1(b) and 1(c)) were recorded for excitation at 535 and 880 nm. Upon 535 nm excitation, intense NIR emissions peaking at 965, 1015, and 1180 nm (Fig. 1(b)) could be observed clearly, but the 850 nm peak is absent for this excitation wavelength.^{21,22} Luminescence occurs in the visible, peaked at 650 nm (${}^5\text{F}_5 \rightarrow {}^5\text{I}_8$) and 750 nm (${}^5\text{S}_2, {}^5\text{F}_4 \rightarrow {}^5\text{I}_7$), shown in the inset of Fig. 1(b). For 880 nm excitation, however, only the NIR PL peak at 1180 nm could be detected, originating from ${}^5\text{I}_6 \rightarrow {}^5\text{I}_8$ in Ho^{3+} (Fig. 1(c)).

In Fig. 2, PL excitation (PLE) spectra of $\text{NaYF}_4:1\%\text{Ho}^{3+}$ is shown for the wavelength range of 250–670 nm. The pronounced, overlapped PLE bands at 275 and 287 nm correspond to the transitions of ${}^5\text{I}_8 \rightarrow {}^3\text{P}_0$ and ${}^5\text{I}_8 \rightarrow {}^3\text{G}_3, {}^3\text{L}_8$,²² respectively. These two bands are the only ones visible when monitoring emission at 410 nm (${}^3\text{D}_3 \rightarrow {}^5\text{I}_6$) and 850 nm, respectively, while for other emission bands, a variety of further excitation peaks can be detected (obviously related to intra-4f transitions from the ${}^5\text{I}_8$ ground state to the corresponding intermediate states,^{21,22}). This may confirm that the 850 nm NIR emission band only appears when exciting the ${}^3\text{P}_0$ and ${}^3\text{G}_3, {}^3\text{L}_8$ states. Comparing the individual PLE spectra to each other, no PLE band occurs at 640 nm (${}^5\text{I}_8 \rightarrow {}^5\text{F}_5$) when monitoring the 1015 nm emission. This further indicates that only the states of ${}^5\text{S}_2, {}^5\text{F}_4$, and above yield NIR 1015 nm emission.²¹ At this point, it may already be speculated that for high-energy excitation (that is, at 287 nm), the simultaneous appearance of the 850, 1015, and 1180 nm emission bands originates from “cascade” radiative transitions through several intermediate levels in Ho^{3+} .^{3–5}

The schematic energy-level diagram of Ho^{3+} shown in Fig. 3 illustrates the sequential three-step three-photon NIR-QS process. Upon excitation of the 287 nm light, the ${}^3\text{D}_3$ state of Ho^{3+} populated by fast multiphonon relaxation can emit efficiently the first 850 nm NIR photon through the ${}^3\text{D}_3 \rightarrow {}^3\text{K}_8, {}^5\text{F}_2$ transition (step 1). On the basis of the energy gap law²³ and the intense visible emission bands shown in the inset of Fig. 1(a), the excited ${}^3\text{D}_3$ state is proven to be the long-lived level because of the large energy gap of

FIG. 2. (Color online) PLE spectra monitored at various PL wavelengths of $\text{NaYF}_4:1\%\text{Ho}^{3+}$ phosphor.

FIG. 3. (Color online) Schematic energy-level diagram of Ho^{3+} showing the concept of sequential three-step NIR-QS under excitation of 287, 535, and 808 nm, respectively. (1) the first step, ${}^3\text{D}_3 \rightarrow {}^3\text{K}_8, {}^5\text{F}_2$ at 850 nm; (2) the second step, ${}^5\text{S}_2, {}^5\text{F}_4 \rightarrow {}^5\text{I}_6$ at 1015 nm; and (3) the third step, ${}^5\text{I}_6 \rightarrow {}^5\text{I}_8$ at 1180 nm. Solid arrow represents optical transition, and short-dotted arrow is NR process.

${}^3\text{D}_3 \rightarrow {}^5\text{G}_2$ ($\sim 2800 \text{ cm}^{-1}$) but small maximum phonon energy of NaYF_4 host lattice ($\sim 400 \text{ cm}^{-1}$).²⁴ Following the ${}^5\text{S}_2, {}^5\text{F}_4$ states populated by phonon-assisted nonradiative relaxation (NR) from the excited ${}^3\text{K}_8, {}^5\text{F}_2$ states, relaxation to ${}^5\text{I}_6$ occurs radiatively by emission of a second 1015 nm photon (step 2). Finally, ${}^5\text{I}_6$ relaxes by emission of a third photon with a wavelength of 1180 nm (step 3), completing a process of three-photon NIR-QS. The typical energy gaps of around 2900 and 3500 cm^{-1} enable radiative decay to dominate over multiphonon relaxation of ${}^5\text{S}_2, {}^5\text{F}_4$, and ${}^5\text{I}_6$ states. Hence, these levels serve as intermediate levels of the QS process.²³ In contrast, if ${}^5\text{S}_2, {}^5\text{F}_4$ states are directly excited at 535 nm, the sequential two-step transitions of 2 and 3 occur, where ${}^5\text{I}_6$ acts as intermediate level. Completing this picture, only step 3 is detected for direct excitation to ${}^5\text{I}_5$ state excited by 880 nm (Fig. 3).

Figure 4(a) shows time resolved emission spectra of $\text{NaYF}_4:1\%\text{Ho}^{3+}$, excited at 287 nm with a pulsed source. It can be seen that the bands at 360 and 410 nm dominate initially (at delay time of $59.5 \mu\text{s}$). As already noted, they correspond to the transitions of ${}^3\text{D}_3 \rightarrow {}^5\text{I}_7$ and ${}^3\text{D}_3 \rightarrow {}^5\text{I}_6$ of Ho^{3+} and, hence, appear after sufficient population of the ${}^3\text{D}_3$ level via NR from the excited ${}^3\text{G}_3, {}^3\text{L}_8$ states. The 485 nm emission band (${}^5\text{F}_3 \rightarrow {}^5\text{I}_8$) emerges after a delay time of $60.5 \mu\text{s}$ and the band at 540 nm (${}^5\text{S}_2, {}^5\text{F}_4 \rightarrow {}^5\text{I}_8$) grows in clearly after $70.0 \mu\text{s}$. The latter then increases dramatically relative to the intensity of all other emission bands related to the ${}^3\text{D}_3$ state. These dynamic processes of ET indicate that the excited ${}^3\text{D}_3$ state might be faster depopulated to the ${}^3\text{K}_8, {}^5\text{F}_2$ states through a one-step NIR transition of ${}^3\text{D}_3 \rightarrow {}^3\text{K}_8, {}^5\text{F}_2$ (step 1, 850 nm) rather than via stepwise NR decay. As the delay time increases, densely populated ${}^3\text{K}_8, {}^5\text{F}_2$ states relax nonradiatively to the following ${}^5\text{F}_3$ state, which then decays either to the ${}^5\text{I}_8$ ground state by emitting a 485 nm photon or depopulates non-radiatively to ${}^5\text{S}_2, {}^5\text{F}_4$ due to the small energy gap between those states ($\sim 1800 \text{ cm}^{-1}$). The excited ${}^5\text{S}_2, {}^5\text{F}_4$ states

FIG. 4. (Color online) Visible (a) and NIR (b) time resolved emission spectra excited at 287 nm with a μ F900 microsecond xenon lamp; # refers to that recorded in a fine time interval of 0.2 μ s.

then would sequentially emit the second 1015 nm NIR photon (2) and the third 1180 nm NIR photon (3).

A second set of delay spectra is shown in Fig. 4(b) for 287 nm pulsed excitation. In the early stage of relaxation (delay time of 9.0 μ s), only the 850 nm NIR PL band can be detected, corresponding to $^3D_3 \rightarrow ^3K_8, ^5F_2$ transition (step 1). Subsequently, after 110.0 μ s, the 1015 nm band ($^5S_2, ^5F_4 \rightarrow ^5I_6$, step 2) and the 965 nm emission band ($^5F_5 \rightarrow ^5I_7$) can be observed. The final band of $^5I_6 \rightarrow ^5I_8$ at 1180 nm (step 3) occurs after a delay time of 200.0 μ s and increases in intensity with progressing delay. These results provide further direct evidence for the assumed sequential three-step NIR-QS in Ho^{3+} , with the $^3K_8, ^5F_2$, and 5I_6 states serving as intermediate levels.

Total QY (η_{QY}) of $\text{NaYF}_4:\text{Ho}^{3+}$ can be estimated from the PL spectrum ($\lambda_{\text{ex}} = 287$ nm). Thereby, η_{QY} is defined as the number of photons re-emitted per number of absorbed UV photons. Hence, visible QY (η_{VIS}) and NIR QY (η_{NIR}) may be distinguished NIR-QS.^{14–21} The integral fluorescence intensities of all visible PL bands were calculated. By taking into account, the emission mechanism (Fig. 3), η_{QY} can be appropriately estimated as follows:^{11,12}

$$\eta_{QY} = \eta_{\text{VIS}} + \eta_{\text{NIR}} = \beta_{^3D_3 \rightarrow ^5I_7} + 2 \sum_{J=4,5,6} \beta_{^3D_3 \rightarrow ^5I_J} + \beta_{^5F_5 \rightarrow ^5I_8} + \eta_{QY}^* \left(\sum_{J=7,8} \beta_{^5S_2, ^5F_4 \rightarrow ^5I_J} + \beta_{^5F_5 \rightarrow ^5I_8} \right), \quad (1)$$

where β_{exp} are the luminescence branching ratios measured in our experiment. Using the Judd-Ofelt parameters of $\text{LiYF}_4:\text{Ho}^{3+}$ single crystal ($\Omega_2 = 1.03 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 2.32 \times 10^{-20} \text{ cm}^2$, $\Omega_6 = 1.93 \times 10^{-20} \text{ cm}^2$),²⁴ the total QY of $^5S_2, ^5F_4$ states, η_{QY}^* , can be rationally evaluated from¹²

$$\eta_{QY}^* = \eta_{^5F_4, ^5S_2} + (\beta_{^5F_4, ^5S_2 \rightarrow ^5F_5}^* + \sum_{J=4,5,6} \beta_{^5F_4, ^5S_2 \rightarrow ^5I_J}^*) \eta_{^5F_4, ^5S_2} \eta_{^5I_6}, \quad (2)$$

where QY for the $^5F_4, ^5S_2$ (5I_6) states, $\eta_{^5F_4, ^5S_2}$ ($\eta_{^5I_6}$), is set to unity, neglecting NR processes, and $\beta^* = A_J / \sum_i A_{ji}$ (A is the

radiative transition rates) refers to the relative intensities of transitions from the excited levels ($^5F_4, ^5S_2$) to all terminal levels. The reduced matrix elements were adopted from Ref. 24, the refractive index of NaYF_4 is 1.486.²⁵ Accordingly, η_{QY}^* of $\sim 110\%$ is obtained, resulting in η_{QY} of about 124% for the three-step NIR-QS in Ho^{3+} . Here, the approximate value of η_{QY} would represent just the lower end of the expected real value of total QY because QY of the $^3D_3 \rightarrow ^3K_8, ^5F_2$ transition is completely neglected by assuming that the $^5S_2, ^5F_4$ states only populate by fast NR from the excited 3D_3 .

In summary, a sequential three-step three-photon NIR-QS has been demonstrated in Ho^{3+} doped $\beta\text{-NaYF}_4$. Upon excitation with a UV photon, cascading emission of three NIR photons at 850, 1015, and 1180 nm occurs. The electronic states of $^3K_8, ^5F_2$, and 5I_6 in Ho^{3+} act as intermediate levels. Theoretical estimation indicates a total QY of about 124%. It is believed that the low phonon energy of NaYF_4 of $\sim 400 \text{ cm}^{-1}$ is a key prerequisite for the sequential three-step three-photon NIR-QS in Ho^{3+} . As such, the concept of triply splitting NIR-QS may offer an interesting route towards the design of efficient photonic devices.

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