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Sequential three-step three-photon near-infrared quantum splitting in β -NaYF₄:Tm³⁺

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We report on sequential three-step three-photon near-infrared (NIR) quantum splitting in Tm³⁺-doped β -NaYF₄, where an incident blue photon around 470 nm is split into three NIR photons (1165, 1466, and 1800 nm). The underlying mechanism is analyzed by means of static and dynamic photoemission spectroscopy. Here, an experimental total quantum yield of $\sim 32\%$ is obtained. When quenching due to residual hydroxyl groups and other defect species can be overcome, numerical analyses indicate a theoretical maximum quantum yield of 158%, suggesting application in efficient spectral converters.

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Efficient phosphor materials are key requisites for modern lighting and display devices.¹ Typically, they rely on optical down-conversion of incident high-energy radiation to photons of lower energy. Since the energy of a vacuum ultraviolet (VUV) photon is more than twice that of a visible photon, it is theoretically possible to split such a VUV photon into two visible photons, yielding a hypothetical quantum yield (QY) of up to 200%. Such two-(or more) photon luminescence phenomena have been referred to as quantum splitting (QS) or photon cascade emission (PCE).² Since the first demonstration of QS for deep-blue emission of Pr³⁺-doped fluorides,^{3–5} numerous studies have been conducted on this area with the specific focus on VUV-excited QS phosphors activated by rare-earth (RE) ions.^{6–10} Similar to VUV-VIS QS, an UV-to-blue photon could be split into three or more near-infrared (NIR) photons.^{2,11–18} If such a conversion process can be conducted efficiently, ideally for splitting one visible photon into three NIR photons, this could pave the way to ultra-efficient spectral converters, e.g., for photovoltaic applications, sensing, etc. Despite the importance of this issue, suitable pairs of activator and matrix material are presently not available.

In the present letter, we discuss the concept of sequential three-step three-photon NIR QS in Tm³⁺ singly doped β -NaYF₄. We demonstrate how upon excitation with a blue photon, three NIR photons can be obtained. Further development of an efficient triply splitting NIR phosphor might open a path towards ultra-efficient low-bandgap solar cells thermo-photovoltaic energy converters.^{19–21}

Powder samples of NaYF₄:1%Tm³⁺ and NaYF₄:1%Tm³⁺, 1%Yb³⁺ were synthesized through a facile hydrothermal procedure.¹⁸ The crystal structure and habitus of the obtained products were characterized by means of x-ray powder diffractometry (XRD, Philips Model PW1830, Cu K α) and scanning electron microscopy (SEM, JEOL JEM-1010). Luminescence spectra were determined on a high-resolution spectro-

fluorometer (Edinburgh FLS920) equipped with a static and a microsecond-pulse xenon (Xe) lamp as excitation sources. For time-correlated single photon counting (TCSPC), visible- and NIR-sensitive photomultiplier tubes (PMTs, Hamamatsu R928 and R5509-72) were employed. In addition and for reference, static mid-infrared (MIR) emission spectra were recorded with a PbSe photoconductive detector on a Horiba Jobin-Yvon Triax320 spectrofluorometer (450 W Xe lamp and 976 nm laser diode, LD, respectively, as the excitation sources). For measurement of the absolute QY, a barium sulfate coated integrating sphere with an inner diameter of 120 mm was mounted on the FLS920 system with the standard Xe lamp for excitation.

XRD patterns of the as-prepared samples generally confirmed the presence of NaYF₄ (JCPDS card no. 16-0334) as sole crystalline phase. As observed by SEM, crystals are present in the form of hexagonal microrods with a mean size of 1 μ m in diameter and several microns in length. In Fig. 1, NIR photoluminescence (PL) spectra of NaYF₄:1%Tm³⁺ and NaYF₄:1%Tm³⁺, 1%Yb³⁺ are shown. For NaYF₄:Tm³⁺ excited at 470 nm, typical emission bands of Tm³⁺ occur at 646 (¹G₄ $\rightarrow$ ³F₄) and 804 nm (³H₄ $\rightarrow$ ³H₆) (inset of Fig. 1(a), see also Ref. 13). Intense NIR PL occurs in three bands at 1165, 1466, and 1800 nm. These bands are assigned to the electronic transitions of ¹G₄ $\rightarrow$ ³H₄, ³H₄ $\rightarrow$ ³F₄ and ³F₄ $\rightarrow$ ³H₆ in Tm³⁺,^{13,22,23} respectively. For a rigorous investigation on the NIR emission process, additional PL spectra were recorded for excitation at 798 nm (monochromator) and 976 nm (LD). When the NaYF₄:Tm³⁺ sample is excited at 798 nm (Fig. 1(b)), only the bands at 1466 and 1800 nm can be observed (³H₄ $\rightarrow$ ³F₄ and ³F₄ $\rightarrow$ ³H₆). In comparison, as shown in Fig. 1(c), in the co-doped sample, only the transition of ³F₄ $\rightarrow$ ³H₆ (Tm³⁺, 1800 nm) is obtained as a result of Stokes energy transfer (ET) from Yb³⁺ when exciting at 976 nm LD.^{24,25} Noteworthy, the spectral response of the detectors which, for the NIR R5509-72 PMT, decreases sharply beyond the range of 1600 nm must be taken into account for data interpretation. For comparison, spectra were recorded also with an PbSe photoconductor with optimal spectral response in this wavelength regime (Fig. 1(c)).^{22,23}

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FIG. 1. NIR PL spectra of $\text{NaYF}_4:\text{Tm}^{3+}$ and $\text{NaYF}_4:\text{Tm}^{3+}, \text{Yb}^{3+}$, respectively. Solid lines are PL spectra recorded on a R5509-72 PMT, and dotted line represents those which were measured with a PbSe detector. The inset of (a) shows visible PL spectrum of $\text{NaYF}_4:\text{Tm}^{3+}$ excited at 470 nm.

In Fig. 2, PL excitation (PLE) spectra of $\text{NaYF}_4:1\%\text{Tm}^{3+}$ in the 440 and 815 nm wavelength range are shown. The PLE bands centered at 470, 690, and 798 nm can readily be assigned to the electronic transitions of $^3\text{H}_6 \rightarrow ^1\text{G}_4$, $^3\text{H}_6 \rightarrow ^3\text{F}_{2,3}$, and $^3\text{H}_6 \rightarrow ^3\text{H}_4$ of Tm^{3+} ,^{13,22} respectively. Monitoring emission at 646 and 1165 nm, respectively, only one excitation band (470 nm) can be detected. On the other hand, monitoring PL at 804, 1466, and 1800 nm, respectively, additional excitation bands are found at 690 and 798 nm (Fig. 2). The bands at 646 and 1165 nm exhibit almost equivalent decay time (230.1 and 226.5 μs , respectively; time after which the band intensity has decreased to 1/e of its initial value). Similarly, the bands at 804 nm (1114.1 μs) and 1466 nm (1113.7 μs) decay with the same rate. The lifetime of the 1800 nm emission ($\text{Tm}^{3+}: ^3\text{F}_4 \rightarrow ^3\text{H}_6$) is 117.6 μs . The underlying decay kinetics of the bands

FIG. 2. PLE spectra of $\text{NaYF}_4:\text{Tm}^{3+}$ monitored at PL wavelengths of 646, 804, 1165, 1466, and 1800 nm, respectively. Solid PLE spectra are recorded on a R5509-72 PMT, and dotted measured with a PbSe detector.

at 646 and 1165 nm, and 804 and 1466 nm, respectively, are hence dominated by the same respective decay reaction. In both cases, this reaction is different from the one leading to 1800 nm emission.²² It may already be speculated that for high-energy photon excitation (470 nm), the simultaneous emergence of 1165, 1466, and 1800 nm photon emissions results from “cascade” radiative transitions through several intermediate levels of the Tm^{3+} ion.^{3,4,18}

The schematic energy-level diagram shown in Fig. 3 illustrates the assumed process of sequential three-step three-photon NIR QS in $\beta\text{-NaYF}_4:\text{Tm}^{3+}$. When exciting Tm^{3+} into the $^1\text{G}_4$ state (Fig. 3(a)), the first NIR photon (1165 nm) may be emitted through the transition of $^1\text{G}_4 \rightarrow ^3\text{H}_4$ (indicated by step 1). Subsequently, the populated $^3\text{H}_4$ state decays to $^3\text{F}_4$, emitting the second NIR photon (1466 nm, indicated by step 2). Finally, the $^3\text{F}_4$ state relaxes to the $^3\text{H}_6$ ground state, accompanied by emission of the third NIR photon (1800 nm, indicated by step 3), thus completing the process of sequential three-step NIR QS. The energy gaps of $^1\text{G}_4 \rightarrow ^3\text{F}_{2,3}$, $^3\text{H}_4 \rightarrow ^3\text{H}_5$, and $^3\text{F}_4 \rightarrow ^3\text{H}_6$ are ~ 6000 , 4000, and 5600 cm^{-1} , respectively, while the maximum phonon energy of NaYF_4 host lattice is about 400 cm^{-1} .¹⁷ According to the energy gap law and the presence of intense emission bands at 646 and 804 nm, radiative decay dominates over multiphonon relaxation for the $^1\text{G}_4$, $^3\text{H}_4$, and $^3\text{F}_4$ states, thereby facilitating the occurrence of sequential three-step relaxation. In contrast, if the $^3\text{H}_4$ state is excited directly at 798 nm (Fig. 3(b)), the two transitions of step 2 and step 3 take place sequentially, with $^3\text{F}_4$ acting as an intermediate level. As depicted in Fig. 3(b), the occurrence of step 3 is well-proven when exciting $\text{Tm}^{3+}: ^3\text{H}_5$ through Stokes ET from $\text{Yb}^{3+}: ^2\text{F}_{5/2}$ in co-doped $\text{NaYF}_4:1\%\text{Tm}^{3+}, 1\%\text{Yb}^{3+}$ pumped with a 976 nm LD.^{24,25}

Figure 4 shows time-resolved fluorescence spectra of $\text{NaYF}_4:\text{Tm}^{3+}$ in the wavelength range of 1100–1650 nm under 470 nm pulsed excitation. In the initial period, only the

FIG. 3. Energy-level diagrams presenting the concept of a sequential three-step three-photon NIR QS: (a) for $\text{NaYF}_4:\text{Tm}^{3+}$ excited by 470 and 798 nm, and (b) for a 976 nm LD pumping Yb^{3+} to excite Tm^{3+} through a Stokes ET in $\text{NaYF}_4:\text{Tm}^{3+}, \text{Yb}^{3+}$. (1) the first-step, $^1\text{G}_4 \rightarrow ^3\text{H}_4$ at 1165 nm, (2) the second-step, $^3\text{H}_4 \rightarrow ^3\text{F}_4$ at 1466 nm, and (3) the third-step, $^3\text{F}_4 \rightarrow ^3\text{H}_6$ at 1800 nm. Solid and dotted arrows represent optical transition and NR processes, respectively.

FIG. 4. Time-resolved emission spectra of NaYF₄:Tm³⁺ with delay times 112, 152, 360, 700, 1100, and 1800 μ s in the 1100 and 1700 nm wavelength range upon 470 nm pulsed excitation with a μ F900 microsecond Xe flashlamp.

transition of $^1G_4 \rightarrow ^3H_4$ at 1165 nm emerges (delay time of 112 μ s). After a delay of $\sim 152 \mu$ s, an additional band grows in at 1466 nm, corresponding to the $^3H_4 \rightarrow ^3F_4$ transition. With progressing time, the intensity of the $^1G_4 \rightarrow ^3H_4$ emission band decreases relative to that of the $^3H_4 \rightarrow ^3F_4$ transition: the 1G_4 state relaxes stepwise to 3H_4 and 3F_4 intermediate levels, first emitting a 1165 nm photon and subsequently a 1466 nm photons. The third step of the relaxation process cannot be observed directly in the dynamic experiments because of the working range of the employed NIR R5509-72 PMT (Figs. 1(a) and 1(b)).

The internal QY (η_{QY}) of the emission process is defined as the ratio of the number of re-emitted photons to that of absorbed photons. In principle, it comprises a part of visible emission and a part of NIR emission, η_{VIS} and η_{NIR} .^{11–18} For the three-step emission process which is considered here, a theoretical estimate of η_{QY} can be obtained from the Judd-Ofelt parameters of the emission process. These are available for LiYF₄:Tm³⁺ crystals which, as an assumption, exhibit great similarity to the present case of NaYF₄:Tm³⁺ ($\Omega_2 = 2.42 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 1.28 \times 10^{-20} \text{ cm}^2$, $\Omega_6 = 0.90 \times 10^{-20} \text{ cm}^2$),^{18,26}

$$\eta_{QY} = \eta_{VIS} + \eta_{NIR} = \eta_{^1G_4} + (\beta_{^1G_4 \rightarrow ^3F_{2,3}} + \beta_{^1G_4 \rightarrow ^3H_4})\eta_{^3H_4}^* + (\beta_{^1G_4 \rightarrow ^3H_5} + \beta_{^1G_4 \rightarrow ^3F_4})\eta_{^3F_4}^*, \quad (1)$$

with luminescence branching ratios $\beta = A_j / \sum_i A_{ji}$ and the radiative transition rates A . The values of β refer to the relative intensities of the respective transition from an excited level (1G_4) to all terminal levels. $\eta_{^1G_4}$ is the QY of the 1G_4 state. Its value is set to unity by neglecting all nonradiative relaxation (NR) processes. $\eta_{^3H_4}^*$ is the internal QY of the excited 3H_4 state sequentially emitting 1466 and 1800 nm photons with 3F_4 acting as the intermediate level. The value of $\eta_{^3H_4}^*$ is estimated from^{3,4,18}

$$\eta_{^3H_4}^* = \eta_{^3H_4} + (\beta_{^3H_4 \rightarrow ^3H_5} + \beta_{^3H_4 \rightarrow ^3F_4})\eta_{^3F_4}^* \quad (2)$$

with the internal QY of the 3H_4 (3F_4) state, $\eta_{^3H_4}$ ($\eta_{^3F_4}$). Here again, the values of the latter two are set to unity, neglecting NR relaxation. For $\eta_{^3H_4}^*$, a value of $\sim 112\%$ is obtained. The value of η_{QY} is then $\sim 158\%$. This value corresponds to the theoretical maximum QY which can be expected for NIR emission from NaYF₄:Tm³⁺, using the Judd-Ofelt parameters of LiYF₄:Tm³⁺ as an approximation. Due to the forbidden nature of $4f-4f$ transitions, Tm³⁺ exhibits narrow absorption linewidth and low absorption cross-section. In addition, the employed matrix materials does not have a significant influence on the value of β .^{1,11,15} This means that in a desired application such as broadband solar spectral conversion, the introduction of broadband sensitizers is highly desirable.

Experimental QY is obtained from^{27,28}

$$\eta = \frac{\varepsilon}{\alpha} = \frac{\int L_{\text{NaYF}_4:1\%\text{Tm}^{3+}} - \int L_{\text{NaYF}_4}}{\int E_{\text{NaYF}_4} - \int E_{\text{NaYF}_4:1\%\text{Tm}^{3+}}}, \quad (3)$$

where $\varepsilon(\alpha)$ is the number of photons emitted (absorbed) by the sample, $L_{\text{NaYF}_4:1\%\text{Tm}^{3+}}$ is the PL spectrum of NaYF₄:1%Tm³⁺, L_{NaYF_4} is the PL spectrum of NaYF₄, and E_{NaYF_4} , $E_{\text{NaYF}_4:1\%\text{Tm}^{3+}}$ are the respective excitation spectra. As described above, data are collected with an integrating sphere. For excitation at 470 nm, absolute QY of NaYF₄:1%Tm³⁺ in the visible range of 600–850 nm is obtained directly from the ratio of the integrated emission intensity over the integrated absorption spectrum, both recorded on the R928 PMT (see above). For NIR emission, the NIR-sensitive R5509-72 PMT was employed accordingly, except that the normalization of the integrated intensity of the PL peak at 804 nm, recorded by R928 and R5509-72 PMTs, respectively, was first done to correct the relative sensitivity of the two different detectors.²⁸ Due to the limited spectral response of the R5509-72 PMT, the absolute QY of the 1800 nm PL band had to be evaluated via normalizing to the integrated intensity of the 1466 nm peak recorded with the PMT and the PbSe MIR detector. We expect significant experimental uncertainty for the quantitative analyses of the MIR data. In this way, a value of $\sim 11\%$ was estimated for the absolute QY in the spectral range of 600–850 nm, and $\sim 32\%$ for the total absolute QY. This value is much below the theoretical optimum of $\sim 158\%$, what is attributed to three primary factors: (i) cross-relaxation occurring between the abundant electronic levels of neighboring Tm³⁺ species,²³ (ii) phonon-assisted NR processes caused by residual hydroxyl groups (-OH) which are incorporated into the material as a result of the hydrothermal synthesis procedure,^{1,29} and, (iii) quenching via defects such as oxygen impurities.¹⁵ Significant improvement of experimental QY appears in reach when these aspects are targeted.

In summary, Tm³⁺-doped β -NaYF₄ has been demonstrated as an efficient material for splitting an incident blue photon into three NIR photons. Sequential depopulation of the excited 1G_4 state occurs via the intermediate states of 3H_4 and 3F_4 , accompanied by emission of photons at 1165, 1466, and 1800 nm. The theoretical maximum of the total

QY of this process is $\sim 158\%$, estimated from numerical analyses. Experimentally, an absolute value of QY of $\sim 32\%$ was observed. Triply splitting NIR emission presents an intriguing path for the design of ultra-efficient optical converters, e.g., for application in low-bandgap solar cells and thermo-photovoltaic energy conversion.

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