Nonlinear properties of upconversion YVO$_4$:Yb$^{3+}$, Er$^{3+}$ nanoparticles

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Abstract. Nonlinear character of upconversion processes can be revealed via a measurement of power dependent steady-state emission intensity depicted in the In-In plot, where a slope indicates the degree of nonlinearity. As a rule observed values of the slope for YVO$_4$ :Yb, Er nanoparticles are less than 2 that interprets as a saturation effect due to high pump laser intensity. Here we based on a numerical analysis show that a life time of the Er$^{3+}$ ion metastable state $4_{11/2}$ is also responsible for deviation of the slope from 2 even in the case when Yb$^{3+}$-Er$^{3+}$ upconversion system is far away from saturation mode.

1. Introduction

Upconversion nanoparticles (UCNPs) are a class of optical nanomaterials doped with lanthanide ions enabled to up-convert few lower-energy photons into one high-energy photon [1-3]. This property opens up the unique perspective of using them in a broad range of applications as highly sensitive fluorescent nanoprobes. As is known, Yb$^{3+}$ and Er$^{3+}$ ions co-doped nanoparticles can absorb near infrared radiation and emit visible luminescence. In such a system the upconversion process is a result of energy transfer from Yb$^{3+}$ ion with high absorption cross section at 980 nm firstly to the $4_1^{11/2}$ level of Er$^{3+}$ ion and finally to the $4F_{7/2}$ level (see figure 1). The relaxation processes depopulate $2H_{15/2}$ and $4S_{3/2}$ levels of the Er$^{3+}$ ion and cause green and red luminescence. One of the most interesting type of UCNPs is oxide nanocrystals YVO$_4$ doped with lanthanide ions. Their low toxicity makes them promising in biological applications. Another attractive property is low sensitivity to surface luminescence quenchers that results in bright luminescence in water solutions. Although synthesis and luminescence properties of such UCNPs are well described in literature the detailed study of the energy transfer and relaxation processes is desirable, particularly for developing highly efficient luminescence nanoprobes for biological applications.

One of the most commonly used methods to confirm upconversion process is monitoring power-dependent luminescence $I_L \propto I_P^n$, where $I_L$ is the luminescence intensity, $I_P$ is laser power density. The value of the slope $n$ in the ln-ln plot indicates the degree of nonlinearity. According to published reports the slope for YVO$_4$ :Yb, Er UCNPs lies within the range from 1.15 to 2 [4-7]. In [8] it was theoretically shown by using simplified model where the Er$^{3+}$ ion activator treated as a three level system that in principle the value of the slope varies in the range $1 \leq n \leq 2$ and depends on the life times of the Yb$^{3+}$ and Er$^{3+}$ levels $4F_{5/2}$ and $4I_{11/2}$ (see figure 1). According to [9] the modeling of energy transfer processes contributing to upconversion luminescence of YVO$_4$ :Yb, Er UCNPs requires accounting at least 8 levels of Er$^{3+}$ ions and Er$^{3+}$-Er$^{3+}$ energy migrations. Although it is widely believed that for YVO$_4$ :Yb, Er UCNPs the slope $n = 2$ reflects two-photon upconversion luminescence and saturation is mainly
responsible for observed deviation from 2, this question is still not clear and needs accurate theoretical study.

\[ \alpha = W_{52}P_1 + W_{56}P_4 + W_{57}P_5, \]
\[ \beta = W_{54} + W_{52}P_1 + W_{24}P_2 + W_{56}P_4 + 2W_{57}P, \]
\[ \gamma = W_{65} + W_{62}P_1 - W_r, \]
\[ \delta = W_{56} + W_{72}P + W_r, \]

where the rate constant \( \varepsilon \) describes the absorption transition, and the numbers \( N_{Yb} \) and \( N_{Er} \)

\[ P_1 + P_2 = N_{Yb}, \]
\[ \sum_{i=3}^{7} P_i = N_{Er}, \]
are the total populations of Yb$^{3+}$ and Er$^{3+}$ ions, respectively. As was done in [9-11], the model (1) treats the $^4F_{7/2}$, $^2H_{11/2}$, $^4S_{3/2}$ excited levels as one due to fast cascade non-radiative transitions from $^4F_{7/2}$ level to $^4S_{3/2}$ level.

**Figure 2.** The calculated dependence of the level 7 population $P_7$ on the absorption transition $\varepsilon$

The main process populating the level 2 is pump absorption (1→2). The energy back-transfers (5→3, 1→2), (7→5, 1→2) and (6→4, 1→2) also contribute to the population of the level 2. The radiative decay (2→1) and the three direct energy transfers from Yb$^{3+}$ ion to Er$^{3+}$ ion (2→1, 3→5), (2→1, 4→6) and (2→1, 5→7) decrease the population of the level 2. The radiative transitions (7→3) from the $^2H_{11/2}$ and $^4S_{3/2}$ levels are responsible for green emission. The transitions (2→1, 5→7) and (5→3, 5→7) are the two processes populating the level 7. The non-radiative transition (7→6) and the back energy transfer (7→5, 1→2) reduce its population and first one is the main energy channel pumping the level 6, which is the source of the red emission (6→3). The energy back-transfer process (6→4, 1→2) also contributes to depopulation of the level 6. It should be noted, that the cascade of non-radiative transitions (7→6→5→4) with multiphonon mechanism depopulate the upper levels and populate lower levels of Er$^{3+}$ ion. The transition (6→5) passes through the non-emitting state $^4I_{9/2}$. Since larger energy gap between $^4F_{9/2}$ and $^4I_{9/2}$ compared with the energy gap between $^4I_{9/2}$ and $^4I_{11/2}$, the rate of the transition (6→5) is limited by the rate of multiphonon transition $^4F_{9/2}\rightarrow^4I_{9/2}$ [9, 11]. Thus, for the sake of simplicity, the $^4I_{9/2}$ state is omitted. The $^4I_{11/2}$ (the level 5) plays principal role in the energy transfer from Yb$^{3+}$ ion to Er$^{3+}$ ion (2→1, 3→5) and provides upconversion transitions (2→1, 5→7), (2→1, 4→6) because it matches well with the $^4F_{7/2}$ level of Yb$^{3+}$ ion. The emission (5→3) and the energy back transfer (1→2, 5→3) as well as non-radiative transition (5→4) depopulate the level 5. The level 4 takes part in the IR emission (4→3) and upconversion process (2→1, 4→6).

The distances between nearest Er$^{3+}$ ions allow energy migration among them. According to [9] the most efficient Er-Er energy pathways are (5→3, 5→7) and (5→3, 4→6). Other possible pathways due to extremely slow transitions are not taken into account.

It is often assumed that the rates of the green (7→3) and red (6→3) emissions are negligible compared to the non-radiative multiphonon rates $W_{76}$ and $W_{65}$ [9] and can be omitted $W_r \approx 0$. Such assumption is quite reasonable because the observed decay rate of the $^4S_{3/2}$ state is about $80 – 150$ ms$^{-1}$ [4, 12, 13] and rates of radiative transitions are $0.1 – 0.2$ ms$^{-1}$ [4, 14].
We interested in a solution for a steady-state regime $\frac{d}{dt}P = 0$ with constant pump laser power density. In the case when the laser intensity is much lower than the intensity causing saturation effect $\varepsilon \ll W_{21}$, it is reasonable to use following expressions for the populations of the two Yb$^{3+}$ ion levels:

$$
P_1(\varepsilon) = N_{Yb} \frac{W_{21}}{\varepsilon + W_{21}},
$$

$$
P_2(\varepsilon) = N_{Yb} \frac{\varepsilon}{\varepsilon + W_{21}}. 
$$

(3)

In this way the (1) transforms into the nonlinear system of equations, which can be easily solved numerically with the rate constants taken from [9] and collected in tab. 1.

**Figure 3.** The calculated dependence of the level 7 population $P_7$ on the absorption transition $\varepsilon$ (solid lines); the nonlinear function $f(\varepsilon) = \varepsilon^n$, $n = 1.76, 1.93$ (dashed lines); $W_{54} = 31.25$ and $W_{54} = 31.25 \cdot 10^2$ were used in calculations presented by black and red lines, respectively.

### 3. Results

It should be noted, that since the green luminescence intensity is proportional to the level 7 population $I_L \propto P_7$ and the absorption transition rate (1→2) is proportional to the laser intensity $\varepsilon \propto I_p$ the function $P_7 \propto \varepsilon^n$ reflects the same photophysical processes as $I_L \propto I_p^n$. The results of numerical calculations are presented in figures 2–3, where for the sake of simplicity it is assumed $N_{Yb} = N_{Er} = 1$. The calculation in figure 2 is performed for the very weak pump power $\varepsilon/W_{21} \leq 5 \cdot 10^{-5}$. The steady-state solutions $P_1 < 0.994 \cdot N_{Yb}$ and $P_3 < 0.997 \cdot N_{Er}$ show that the system is far away from a saturation mode. This weak excitation results in a quadratic dependence of the luminescence intensity on the pump power $n = 2$ as it is commonly expected.

Figure 3 (black solid line) shows another excitation regime, where the pump power upper limit is 35-fold increased $\varepsilon/W_{21} \leq 0.2$ relative to previous case. Nevertheless it is still not sufficient for the saturation, because the inequalities $P_1 < 0.828 \cdot N_{Yb}$ and $P_3 < 0.981 \cdot N_{Er}$ hold for this excitation. One can see the essential deviation from quadratic character, because the slope $n$ becomes not constant and its average value is close to 1.76.
Table 1. Rate constants of transitions and energy transfers in YVO₄:Yb, Er UCNPs (taken from [9])

| Transitions between levels | Rate constant | Value (s⁻¹) | Transitions between levels | Rate constant | Value (s⁻¹) |
|----------------------------|---------------|-------------|----------------------------|---------------|-------------|
| 1→2                        | W₂₁           | 3571        | 2→1, 3→5                  | W₂₅           | 43.3        |
| 7→6                        | W₇₆           | 111111      | 1→2, 7→5                  | W₇₂           | 0.02        |
| 6→5                        | W₅₅           | 1754.4      | 1→2, 6→4                  | W₆₂           | 401         |
| 5→4                        | W₅₄           | 31.25       | 1→2, 5→3                  | W₅₂           | 40.5        |
| 4→3                        | W₄₃           | 455         | 5→3, 5→7                  | W₅₇           | 1.7         |
| 2→1, 5→7                   | W₂₇           | 6347        | 5→3, 4→6                  | W₅₆           | 189         |
| 2→1, 4→6                   | W₂₆           | 118         |                            |               |             |

According to [8] such deviation could be associated with the life time τ₅ of the metastable level 5 (⁴¹₁₁/₂ state of Er³⁺ ion). In our system the life time τ₅ is determined by the non-radiative transition W₅₄, the energy back-transfer W₅₂ and the Er-Er energy migration W₅₆ and W₅₇. In order to prove that the deviation of the slope depends on the life time τ₅, we performed the numerical calculation where the rate constant W₅₄ was 100-fold increased, that considerably shortened τ₅ value. The calculation result P₇(ε) represented by the red solid line in figure 3 is very close to the quadratic function.

Thus the calculations revealed that the slope η depends on the life time τ₅ of the Er³⁺ ion level ⁴¹₁₁/₂ and conclusion done in [8] of the slope η variation is actual for YVO₄:Yb, Er UCNPs. Also it is worth noting that the presented here calculations clearly indicate that the deviation of the slope η from 2, which is often observed in YVO₄:Yb, Er UCNPs, occurs at relatively weak laser power density far away from saturation mode. Interestingly, that this deviation reflects energy transfer processes through the level ⁴¹₁₁/₂ of Er³⁺ ion playing principal role in upconversion efficiency and that needs to be taken into account in analysis of traditional spectroscopic measurements to get valuable information on upconversion mechanism in YVO₄:Yb, Er UCNPs.

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References
[1] Wen S, Zhou J, Zheng K, Bednarkiewicz A, Liu X, Jin D 2018 Nat. Commun. 9 2415
[2] Chen B, Wang F 2020 Trends in Chemistry 2 427
[3] Jia F, Li G, Yang B, Yu B, Shen Y, Cong H 2019 Nanotechnol. Rev. 8 1
[4] Xu W, Chen B, Yu W, Zhu Y, Liu T, Xu S, Min X, Bai X, Song H 2012 Dalton Trans. 41 13525
[5] Mahata M K, Tiwari S P, Mukherjee S, Kumar K, Rai V K. J. 2014 Opt. Soc. Am. B 31 1814
[6] Mialon G, Turkcan S, Dantelle G, Collins D P, Hadjipanayi M, Taylor R A, Gacoin T, Alexandrou A, Boilot J P 2010 J. Phys. Chem. C 114 22449
[7] Zharkov D K, Shmelev A G, Leontyev A V, Nikiforov V G, Lobkov V S, Alkahtani M H, Hemmer P R, Samartsev V V 2020 Laser Phys. Lett. 17 075901
[8] Liu H, Xu C T, Lindgren D, Xie H, Thomas D, Gundlach C, Andersson-Engels S 2013 Nanoscale 5 4770
[9] Shyichuk A, Câmara S S, Weber I T, Carneiro Neto A N, Nunes L A O, Lis S, Longo R L, Malta O L 2016 J. Lumin. 170 560
[10] Zhao J, Lu Z, Yin Y, McRae C, Piper J A, Dawes J M, Jin D, Goldys E M 2013 Nanoscale 5 944
[11] Erneneux F, Goutaudier C, Moncorgé R, Sun Y, Cone R, Zannoni E, Cavalli E, Bettinelli M 2000 Phys. Rev. B 61 3915
[12] Golab S, Solarz P, Dominiak-Dzik G, Lukasiewicz T, Ryba-Roma W 2002 J. Alloys Compd. 341 165
[13] Golab S, Dominiak-Dzik G, Solarz P, Lukasiewicz T, Swirkowicz M, Sokolska I, Ryba-Roma W 2001 Proceedings of SPIE 4412 380

[14] Lüthi S R, Pollnau M, Güdel H U, Hehlen MP 1999 Phys. Rev. B 60 162