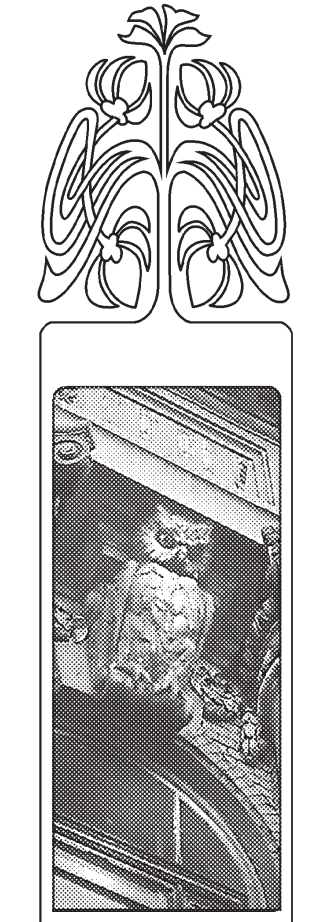

НАУЧНЫЙ ОТДЕЛ

КРАТКИЕ СООБЩЕНИЯ

Effect of the Temperature of $NaYF_4$: Er,Yb Upconversion Particles on the Formation of Luminescence

E. A. Sagaidachnaya, V. I. Kochubey

Elena A. Sagaidachnaya, https://orcid.org/0000-0002-8118-0300, Saratov State University, 83 Astrakhanskaya St., Saratov 410012, Russia, lastovskaia_e@mail.ru

Vyacheslav I. Kochubey, https://orcid.org/0000-0001-7834-9067, Saratov State University, 83 Astrakhanskaya St., Saratov 410012, Russia, saratov_gu@mail.ru

The intensity of upconversion luminescence depends nonlinearly on the excitation intensity. The aim of this work is to study the effect of the temperature of $NaYF_4$:Er,Yb upconversion particles on the dependence of the luminescence intensity on the excitation intensity. The synthesized particles were observed to have the shape of a hexagonal prism with a width of about 440 nm and a height of 445 nm. The upconversion luminescence spectra were obtained in the temperature range of 22–55° C with the excitation intensity in the range of 1.5–9.4 W/cm^2. The obtained results show the green-band luminescence photons can be generated by means of two-step and three-step mechanisms: the contribution of these mechanisms depends on the temperature of the particles. As the temperature increases, the contribution of the three-stage mechanism of green luminescence excitation is enhanced.

Keywords: upconversion particles, upconversion luminescence.

Received: 23.09.2020 / Accepted: 14.10.2020 / Published: 30.11.2020

DOI: https://doi.org/10.18500/1817-3020-2020-20-4-306-310

Introduction

Upconversion particles have great potential for application in various fields due to their luminescent properties [1, 2]. They luminesce in the visible range when excited by near-infrared laser radiation. One of the most promising upconversion particles is $NaYF_4$: Er,Yb [1].

Various mechanisms are involved in the generation of upconversion luminescence (UCL), such as ground-state absorption (GSA), excited-state absorption (ESA), energy transfer upconversion (ETU), cross-relaxation, non-radiative relaxation (NRR), and photon avalanche. Figure 1 shows a diagram of the energy levels of Er^{3+} and Yb^{3+} ions, which demonstrates how the donor-acceptor pair determines the spectral range of luminescence and excitation.

The intensity of upconversion luminescence depends nonlinearly on the excitation intensity [2–4] and can be expressed as follows:

$$I_{UC} \propto {I_P}^n, \quad (1)$$

where I_{UC} is the UCL intensity, I_P is the excitation intensity, n is the number of photons of the exciting radiation required for obtaining one photon of UCL. The n coefficient is determined by the entire set of processes that contribute to the formation of UCL. Representation of the dependence

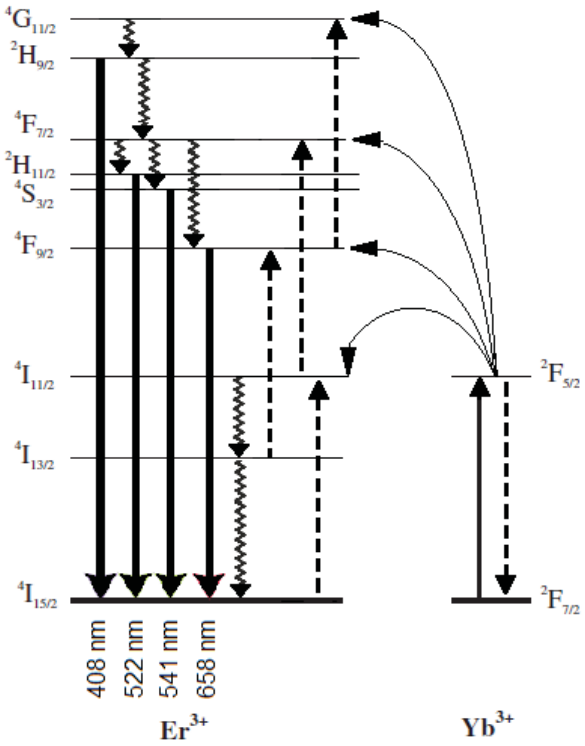

Fig. 1. Diagram of energy transfer from the Yb^{3+} donor ion to the Er^{3+} acceptor ion and the formation of upconversion luminescence

expressed by Eq. (1) on a double logarithmic scale is linear over a limited range and is useful for determining the value of *n* for individual luminescence bands and analyzing the effectiveness of the upconversion mechanisms [5, 6]. The slope of the approximating lines corresponds to the value *n* of the stepwise excitation process expressed by Eq. (1).

A theoretical justification has been given in report [5] for vary the value of *n* at different excitation intensities, provided that the absorption coefficient does not depend on the laser intensity and the sample is not heated by the exciting radiation. The low-intensity excitation corresponds to $n = 2$ for the red and green regions of the upconversion luminescence spectrum. The value of *n* decreases (and may not be an integer) as the intensity increases due to the competition between the processes of non-radiative deactivation and the subsequent excitation of the intermediate states. Saturation is observed at high intensity, and $n = 1$ for all bands, i.e., the dependence of the luminescence intensity on the excitation intensity becomes linear [2]. This is because the number of ions in the intermediate metastable states approaches equilibrium. The extra energy translates the ions into higher energy states. At intermediate intensities, there is a complex interaction of energy transfer, cross-relaxation, and non-radiative transitions. The proposed model incorporates the predominant mechanisms, namely GSA, ESA, and ETU, involved in the formation of UCL. This explains the possible deviation of the experimental values of *n* from those predicted by the model [6]. For example, the value $n > 2$ (three-step generation of green luminescence) can be explained by the non-radiative relaxation $^2H_{11/2}$, $^4S_{3/2} \rightarrow {}^4F_{9/2}$, leading to the additional population of the $^4F_{9/2}$ state. At a high population level of $^4F_{9/2}$, $^4F_{9/2} \rightarrow {}^4G_{11/2}$ electrons can be excited by energy transfer from the Yb^{3+} ion ($^2F_{5/2} \rightarrow {}^2F_{7/2}$) [7, 8]. Note that in extensive studies of the dependence of the luminescence intensity on the excitation intensity, the effect of temperature on the mechanism of luminescence formation has not been fully investigated.

The study of vary in the *n* value under various conditions is important, since it allows us to analyze the changes in the mechanisms of formation of the upconversion luminescence. Knowledge of these mechanisms makes it possible to purposefully predict the vary the spectral characteristics of the luminescence when the host material of particles, the excitation intensity or the temperature of particles changes. The aim of this work is to study the effect of the temperature of $NaYF_4$:Er,Yb upconversion particles on the dependence of the luminescence intensity on the intensity of the exciting radiation.

Materials and methods

We have synthesized the $NaYF_4$:Er,Yb upconversion particles using the standard hydrothermal method [9]. For the synthesis sodium citrate for restricting the crystal growth, aqueous solution of sodium fluoride as a fluorinating agent, aqueous solution of rare earth metal chlorides (Y/Yb/Er = 80/17/3) were used.

The synthesis was performed at a temperature of 160° C. The obtained particles were coated with SiO_2 shell and then subjected to additional heating.

The structure of the crystal lattice of the particles was determined using the ARLX'TRA X-ray phase analysis device (Thermo Fisher Scientific, USA) and the Jana2006 program. The diffractograms of the samples demonstrated the hexagonal β-phase of $NaYF_4$: Er,Yb particles.

The size and shape of the particles were determined using scanning electron microscopy by employing a MIRA 2 LMU microscope (Tescan, Czech

Republic). The synthesized particles demonstrated the shape of a hexagonal prism with a width of about 440 nm and a height of 445 nm.

In order to study the effect of the particle temperature on the intensity and shape of the luminescence spectrum, a 12-μm-thick cellulose acetate film containing the particles was prepared. This ensured a uniform distribution of the particles in a thin layer and minimized the effect of radiation scattering on the particles. For obtaining the upconversion luminescence spectrum of the synthesized $NaYF_4$:Er,Yb particles, the setup and method described in our previous work [10] were used. This helped in minimizing the data distortion, including that occurring due to heating by the exciting radiation. The UCL spectra were obtained in the temperature range of 22–55 °C with the excitation intensity in the range of 1.5–9.4 W/cm^2.

Results and discussion

From experimental data, the luminescence intensity of was calculated as an integral of the intensity by wavelengths for a corresponding band in range of this band (for the green 510–560 nm) and for the red 630–680 nm). Figure 2 shows an example of the dependence of the intensity of the green and red luminescence bands on the excitation intensity at a particle temperature of 22° C. As excitation intensity increases, the luminescence intensity grows non-linearly when represented on a double logarithmic scale. This dependence is consistent with the theoretical models on the mechanisms of the formation of UCL described in well-known works [3, 4].

Figure 3 shows the dependence of the obtained slope of the approximating lines on the particle temperature in the region of low and high excitation intensity of the luminescence bands. At low intensity, the value $n > 2$ can be explained by an increase in the probability of the non-radiative relaxation $^2H_{11/2}$, $^4S_{3/2} \rightarrow {}^4F_{9/2}$, leading to an additional population of the $^4F_{9/2}$ state and the requirement for three photons to excite the UCL of the green radiation range. In other words, the green-band luminescence photons can be generated by two-step and three-step mechanisms, and the ratio of the contributions of these mechanisms depends on conditions such as the temperature of the particles. Two- and three-step mechanisms for generating green luminescence represent a corresponding series of transitions:

$$n = 2: {}^4I_{15/2}\ (\text{GSA}) \rightarrow {}^4I_{11/2}\ (\text{ESA}) \rightarrow$$
$$\rightarrow {}^4F_{7/2}\ (\text{NRR}) \rightarrow {}^2H_{11/2}, {}^4S_{3/2}\ (\text{UCL}) \rightarrow {}^4I_{15/2};$$

$$n = 3: {}^4I_{15/2}\ (\text{GSA}) \rightarrow {}^4I_{11/2}\ (\text{NRR}) \rightarrow$$
$$\rightarrow {}^4I_{13/2}\ (\text{ESA}) \rightarrow {}^4F_{9/2}\ (\text{ESA}) \rightarrow {}^4G_{11/2}\ (\text{NRR}) \rightarrow$$
$$\rightarrow {}^4F_{7/2}\ (\text{NRR}) \rightarrow {}^2H_{11/2}, {}^4S_{3/2}\ (\text{UCL}) \rightarrow {}^4I_{15/2}.$$

It is worth noting that all the ways of red luminescence formation are two-step, so a possible change in the mechanism of luminescence formation is not accompanied by a change in the value of n:

$$n = 2: {}^4I_{15/2}\ (\text{GSA}) \rightarrow {}^4I_{11/2}\ (\text{ESA}) \rightarrow$$
$$\rightarrow {}^4F_{7/2}\ (\text{NRR}) \rightarrow {}^4F_{9/2}\ (\text{UCL}) \rightarrow {}^4I_{15/2};$$

$$n = 2: {}^4I_{15/2}\ (\text{GSA}) \rightarrow {}^4I_{11/2}\ (\text{NRR}) \rightarrow$$
$$\rightarrow {}^4I_{13/2}(\text{ESA}) \rightarrow {}^4F_{9/2}\ (\text{UCL}) \rightarrow {}^4I_{15/2}.$$

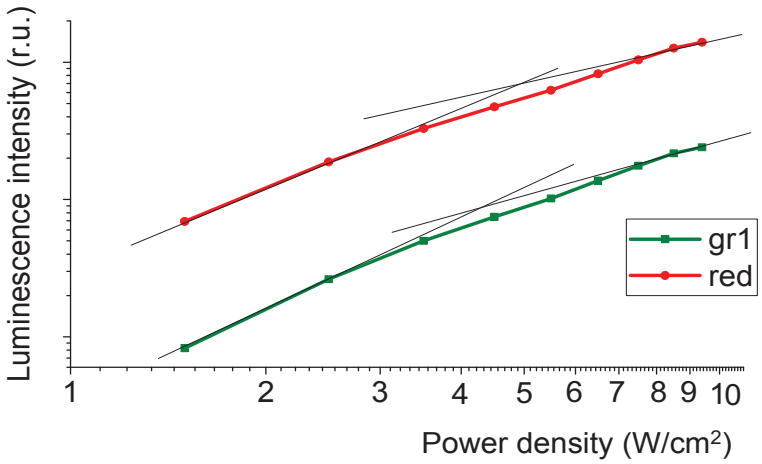

Fig. 2. The dependence of the integral luminescence intensity on the excitation intensity at a temperature of 22°C, presented in a double logarithmic scale (color online)

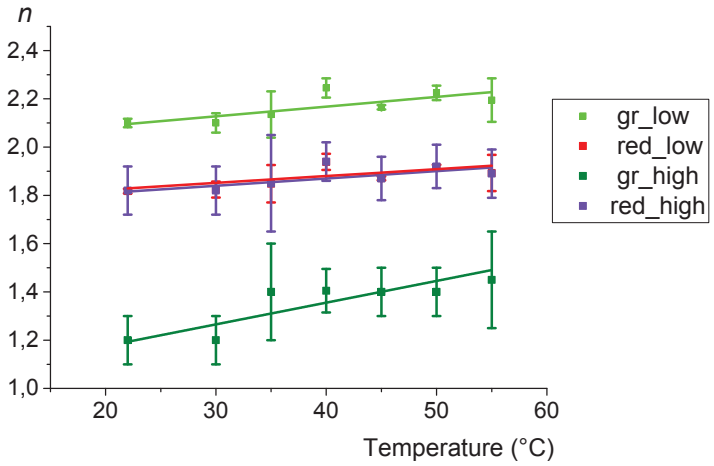

Fig. 3. Dependences of the slope of the approximating lines (n values) on the temperature of the particles in the low and high excitation intensity (color online)

From the results obtained, it is observed that as the particle temperature increases, the value of *n* enhances for the green luminescence bands. At high excitation intensity, a stronger change in the value of *n* is observed, up to 16% (with an increase in temperature from 30° C to 50° C), whereas at low intensity, it is up to 6%. As the temperature increases, the probability of the non-radiative relaxations grows. An increase in the transition probability $^4I_{11/2}$ (NRR) → $^4I_{13/2}$ leads to an enhance in the contribution of the three-stage mechanism of luminescence excitation. The value of *n* for the red luminescence band varies within the error range and does not depend on the particle temperature.

Acknowledgements: *This work was supported by the Russian Science Foundation (project No. 19-12-00118).*

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Cite this article as:
Sagaidachnaya E. A., Kochubey V. I. Effect of the Temperature of $NaYF_4$: Er,Yb Upconversion Particles on the Formation of Luminescence. *Izv. Saratov Univ. (N. S.), Ser. Physics*, 2020, vol. 20, iss. 4, pp. 306–310 (in Russian). DOI: https://doi.org/10.18500/1817-3020-2020-20-4-306-310

УДК 535.372:535.373.2

Влияние температуры апконверсионных частиц $NaYF_4$:Er,Yb на формирование люминесценции

Е. А. Сагайдачная, В. И. Кочубей

Сагайдачная Елена Александровна, аспирант кафедры оптики и биофотоники, Саратовский национальный исследовательский государственный университет имени Н. Г. Чернышевского, lastovskaia_e@mail.ru

Кочубей Вячеслав Иванович, доктор физико-математических наук, профессор кафедры оптики и биофотоники, Саратовский национальный исследовательский государственный университет имени Н. Г. Чернышевского, saratov_gu@mail.ru

Интенсивность апконверсионной люминесценции нелинейно зависит от интенсивности возбуждающего излучения. Целью данной работы является исследование влияния температуры апконверсионных частиц $NaYF_4$:Er,Yb на зависимость интенсивности люминесценции от интенсивности возбуждающего излучения. Синтезированные нами частицы имели форму шестигранной призмы шириной около 440 нм и высотой 445 нм. Регистрацию спектров апконверсионной люминесценции проводили в диапазоне температур 22–55° С при интенсивности возбуждающего излучения в диапазоне 1.5–9.4 Вт/см^2. Согласно полученным данным фотоны зеленой люминесценции могут формироваться в результате двух- и трехступенчатых механизмов, причем соотношение вкладов этих механизмов зависит от температура частиц. С повышением температуры увеличивается вклад трехступенчатого механизма возбуждения зеленой люминесценции.

Ключевые слова: апконверсионные частицы, апконверсионная люминесценция.

Поступила в редакцию: 23.09.2020 / Принята: 14.10.2020 / Опубликована: 30.11.2020

Благодарности

Работа выполнена при финансовой поддержке Российского научного фонда (проект № 19-12-00118).

Образец для цитирования:

Sagaidachnaya E. A., Kochubey V. I. Effect of the Temperature of $NaYF_4$: Er,Yb Upconversion Particles on the Formation of Luminescence [*Сагайдачная Е. А., Кочубей В. И.* Влияние температуры апконверсионных частиц $NaYF_4$: Er,Yb на формирование люминесценции] // Изв. Сарат. ун-та. Нов. сер. Сер. Физика. 2020. Т. 20, вып. 4. С. 306–310. DOI: https://doi.org/10.18500/1817-3020-2020-20-4-306-310