Influence of annealing temperature on the upconversion luminescence properties of NaYF₄:Er,Yb@SiO₂ particles

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Abstract. Upconversion phosphors are promising materials for a medical application. Investigation of influence of annealing temperature of particles on the upconversion luminescence properties is relevant. The synthesized NaYF₄:Er,Yb@SiO₂ particles were annealed at different temperatures in the range of 300 °C to 550 °C. Dependence of the luminescence intensity on the annealing temperature takes the maximum value at 550 °C and has local maximum at 400 °C.

1. Introduction
Innovative luminescence materials arouse substantial interest due to the extensive perspective, which they open in different areas of science and technology. Particularly, upconversion NaYF₄:Er,Yb phosphors are promising materials for the photodynamic therapy, creation of temperature micro-nanosensors and bioimaging of cells and tissue [1]. The effects of the reagent concentration molar ratio, temperature and time of hydrothermal synthesis on the morphology, size and luminescence properties of the particles is actively investigated [2, 3, 4, 5]. Point out that creation of the heterogeneous core/shell structure promotes the enhancing upconversion luminescence of the particles [6]. In addition, important factor influenced to the effective of upconversion is the annealing temperature of obtained particles. The aim of this work is investigation of influence of annealing temperature of NaYF₄:Er,Yb@SiO₂ particles on the upconversion luminescence properties.

2. Experimental Section
In a typical hydrothermal synthesis, 2 mmol trisodium citrate (Na₃Cit) and 114 mmol sodium chloride (NaCl) were firstly dissolved in 16,7 mL H₂O with magnetic stirring. Solution of YCl₃·6H₂O (0,5 M), Yb(CH₃COO)₃·4H₂O (0,5 M) and ErCl₃·5H₂O (1 M) (molar ratio of rare earth Y/Yb/Er = 0,5/0,33/0,05) was added slowly into the above solution to form the metal-citrate complex. After vigorous stirring for 30 min, 20 mL aqueous solution of NaF (1 M) was introduced. After additional stirring for 60 min, the as-obtained mixing solution was transferred into a teflon bottle held in a stainless steel autoclave and maintained at 200°C for 20 h. After the autoclave was cooled to room temperature naturally, the resulting precipitates were separated by centrifugation and washed with weak sodium citrate solution (5g/L) three times. Obtained NaYF₄:Yb³⁺/Er³⁺ particles were dispersed in 36 mL of isopropanol. Then 1,0 mL of ammonia aqueous solution (12 wt %) and 80 μL of TEOS (99 wt %) were added to the solution. After stirring at room temperature for 1 h, the obtained particles were separated, washed with distilled water three times and dried in air at 75°C for 12 h. The as-prepared NaYF₄:Yb,Er@SiO₂ particles were annealed at different temperatures in the range of 300 °C to 550 °C.
The structure, morphology and size of obtained NaYF$_4$:Er,Yb@SiO$_2$ particles were characterized by XRD, thermogravimetric analysis, scanning electron microscopy (SEM) and method of dynamic light scattering. Upconversion luminescence of Er$^{3+}$ ions under irradiation of the particles by NIR-laser (980 nm, 2.8 W/cm$^2$) was observed using a spectrometer (Ocean Optics QE6500 FL, USA).

3. Results and discussion

The XRD-patterns indicate that the lattice of the synthesized particles is hexagonal with the residual cubic phase. In addition, the half-width of reflexes decreases and the intensity increases with annealing. It is worth noting that the XRD-patterns of the annealed particles demonstrate larger crystallite sizes what causes increasing the luminescence intensity. From the data of dynamic light scattering, the average diameter of the not annealed and annealed particles is about 0.3 μm and 1 μm, respectively. Upon that two phase of the not annealed particles with diameters about 5 μm and 300 nm are observed in the SEM image.

The luminescence spectra of the particles annealed at the different temperature are presented in Figure 1. It should be note that luminescence spectra of NaYF$_4$:Yb,Er@SiO$_2$ particles are sensitive to their temperature. Exciting IR-radiation heats the particles in the absence of an external temperature support system. For example, the particles are heated to 80°C at a power density of 2.8 W/cm$^2$. Figure 1 demonstrates spectra of heated particles by the laser to the equilibrium temperature.

![Figure 1. Luminescence spectra of the particles.](image)

In order to easily compare upconversion between samples, the area under the peaks was calculated over the wavelengths within each of the bands. Integral values of luminescence were obtained for the three emission bands corresponding to the energy transition: $^4$H$_{11/2} \rightarrow ^4$I$_{15/2}$ (525 nm), $^4$S$_{3/2} \rightarrow ^4$I$_{15/2}$ (543 nm) and $^4$F$_{9/2} \rightarrow ^4$I$_{15/2}$ (655 nm). The obtained dependences of luminescence intensity on the annealing temperature are presented in Figure 2 (right ordinate axis). The ratio of the intensities of ‘red’ and ‘green’ emission bands (‘red/green’ ratio) as a function of annealing temperature is also presented in Figure 2 (left ordinate axis). The intensities at 200 °C (the temperature of hydrothermal synthesis) correspond with not annealed particles.

The luminescence intensity is observed to increase as the annealing temperature is raised up to 400 °C. This is because impurities desorb from the particle surface. According to data of thermogravimetric analysis, the bound water is removed by heating. When the temperature is raised above 400 °C, luminescence intensity decreases. This can be caused by the decomposition of the stabilizing shell of sodium citrate which melts at a temperature above 300 °C and decomposes without evaporation. Recrystallization takes place at a temperature above 500 °C what provides an increase in the luminescence intensity. It should be noted that the sintering of the particles annealed at 550 °C is observed.
According to the obtained data, the ‘red/green’ ratio has peak value at the annealing temperature 300°C. It decreases with increasing the annealing temperature to 550°C. The change of the ‘red/green’ ratio is consistent with the data [7, 8]. This is the results of the rate reducing of thermal relaxation which in turn can be the consequence of reducing the number of defects and increasing the crystallites size.

![Figure 2](image2.png)

**Figure 2.** Luminescence intensity (right ordinate axis) and ‘red/green’ ratio (left ordinate axis) versus annealing temperature.

Upconversion emission of green and red luminescence versus excitation power density is presented in Figure 3. The experimentally observed saturation of the upconversion-induced luminescence with increasing excitation is consistent with the existing model [9]. In the low-power limit an n-photon process will characterized by the slope of n when the luminescence intensity is plotted in a double-logarithmic representation versus absorbed pump power. In the high-power limit slope of all processes is less than or equal to 1 depending on the prevailing mechanism of upconversion (energy transfer.

![Figure 3](image3.png)

**Figure 3.** Log–log plot of upconversion emissions of green and red luminescence versus excitation power density of annealed at different temperatures NaYF₄:Er,Yb@SiO₂ particles.

Upconversion emission of green and red luminescence versus excitation power density is presented in Figure 3. The experimentally observed saturation of the upconversion-induced luminescence with increasing excitation is consistent with the existing model [9]. In the low-power limit an n-photon process will characterized by the slope of n when the luminescence intensity is plotted in a double-logarithmic representation versus absorbed pump power. In the high-power limit slope of all processes is less than or equal to 1 depending on the prevailing mechanism of upconversion (energy transfer.
upconversion or exited-state absorption). It is worth mentioning that the measurements carried out in this research correspond to the low and medium pump power. The slopes of the approximating lines in log-log scale at this pump powers are given in the Table 1.

Table 1. The slope at low and medium pump powers.

| Annealing temperature | Red luminescence (655 nm) | Green luminescence (543 nm) | Green luminescence (525 nm) |
|-----------------------|---------------------------|----------------------------|-----------------------------|
|                       | low pump power medium pump power | low pump power medium pump power | low pump power medium pump power |
| 200°C                 | 0.4 0.9                     | 0.3 0.2                     | 0.8 1.5                     |
| 300°C                 | 1.5 1.1                     | 1.4 0.5                     | 1.8 1.2                     |
| 350°C                 | 1.8 1.1                     | 1.6 0.5                     | 1.7 1.0                     |
| 400°C                 | 1.7 0.8                     | 1.4 0.2                     | 1.6 0.7                     |
| 450°C                 | 1.6 0.8                     | 1.2 0.1                     | 1.5 0.5                     |
| 500°C                 | 1.5 1.2                     | 1.1 0.4                     | 1.4 0.6                     |
| 550°C                 | 1.7 1.1                     | 1.3 0.5                     | 1.6 0.7                     |

Red and green luminescence as known is a result of two-photon excitation. Deviation of the slope from two with increasing the pump power is conditioned by the complex interplay between the relevant energy transfer processes, exited-state absorption, upconversion from the intermediate state, cross-relaxation, radiative and nonradiative decay. The obtained values of slope for the green luminescence at the different pump powers are consistent with simplify model (when only energy transfer upconversion on the acceptor ion is included), whilst slope for the red luminescence correspond to the more complex model described in [9]. However, keeping in mind that the particles were investigated in the range of low and medium pump power, obtained results may indicate different values of the high-power limit for different luminescence bands.

4. Conclusion

In results it can be concluded that complicated changes of luminescence intensity occur due to the existence of several processes such as removing bound water, decomposition of the sodium citrate sell and recrystallization. More effective conversion of NIR excitation to visible light energy occurs at annealing temperatures at 400 °C and 550 °C. However, after annealing at 550 °C in contrast to the annealing at 400 °C the particles are sintered. At the same time, the conversion efficiency of the exciting radiation to green luminescence increases with the increasing of the annealing temperature.

Acknowledgments

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