Effect of Er$^{3+}$ Concentration on Upconversion in Hexagonal-Phase NaYF$_4$:Er$^{3+}$ Nanocrystals

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Abstract. A facile synthesis method was developed to produce hexagonal-phase of NaYF$_4$ nanocrystals (NCs) doped with Er$^{3+}$ in different concentration, which showed upconversion (UC) emission from infrared to visible spectral region. This proposed method is simple and less toxic compared with generally used method so far. It was found that up-conversion emission spectra of NaYF$_4$:Er$^{3+}$ NCs, excited at 1550 nm, included four peaks at about 980 nm, 800 nm, 660 nm and 540 nm. The effect of Er$^{3+}$ concentration on UC in β-phase NaYF$_4$:Er$^{3+}$ NCs were discussed based on the excitation power dependence. The optimum Er$^{3+}$ concentration for 2-step and 3-step UC was found to be around 10~30%.

1. Introduction

Upconversion (UC) nanocrystals (NCs) have recently attracted significant attentions, due to their potential applications on solar cells, light emitting devices, flat-panel displays, biological assays and medical imaging [1]. One of the promising UC nanomaterial is lanthanide ion doped NaYF$_4$, since the phonon energy of the host is relatively low which suppresses non-radiative relaxation. The phase control of NaYF$_4$ is very important, because the hexagonal (β)-phase NaYF$_4$ has higher UC efficiency than the cubic (α)-phase [2]. However, the synthesis method generally used is relatively complex, sensitive to the condition and with discharging toxic gas like COF$_2$ [2]. Moreover, the chemical product is generally mixture of α- and β-phase of NaYF$_4$ which is sensitive to the synthesis conditions. Therefore, the UC efficiency is not stable and depends on the lot of the production.

In this work, a facile synthesis method for hexagonal NaYF$_4$:Er$^{3+}$ NCs with less toxicity was presented. The NaYF$_4$:Er$^{3+}$ NCs were synthesized in oleic acid (OA) and 1-octadecene (ODE) with Y$_2$(CO$_3$)$_3$·xH$_2$O, Er$_2$(CO$_3$)$_3$·xH$_2$O, Na$_2$CO$_3$ and NH$_4$F as precursors [3]. During the reaction process, small NaYF$_4$:Er$^{3+}$ crystal nucleation was progressed at low temperature and the discharged gas was mainly ammonia. The optimum synthesis conditions were obtained and the properties of the UC were studied.

2. Experimental Details

Er$_2$(CO$_3$)$_3$·xH$_2$O (99.9%) was purchased from ChemPur, Y$_2$(CO$_3$)$_3$·xH$_2$O (99.9%), Na$_2$CO$_3$ (99.5%), NH$_4$F (98%), OA, and ODE were purchased from Aldrich. The NaYF$_4$:10%Er$^{3+}$ NCs were synthesized as follows: Y$_2$(CO$_3$)$_3$·xH$_2$O (0.4 mmol), Er$_2$(CO$_3$)$_3$·xH$_2$O (0.1 mmol), Na$_2$CO$_3$ (0.5 mmol) and NH$_4$F (4 mmol) were mixed with OA (10 mmol) and ODE (30 mmol) and put into 100 ml flask. Then the mixture solution was degassed at 100 °C for 30 min. The temperature was increased to around 310 °C for 0.5 h followed by 330 °C for 0.5 h heating. After cooling down, the NCs were collected by
centrifugation and washed with ethanol for three times. Finally the products were dried at 80℃ for 3 h. The chemical reaction can be expressed as below:

$$\text{Na}_2\text{CO}_3 + \text{RE}_2(\text{CO}_3)_3 + \text{NH}_4\text{F} \rightarrow \text{NaREF}_4 + \text{CO}_2 \uparrow + \text{NH}_3 \uparrow + \text{H}_2\text{O}$$  \hspace{1cm} (1)

In fact, Na₂CO₃ and rare earth carbonates were mixed with NH₄F in OA and ODE, immediately resulting in occurrence of ammonia gas and the formation of nanoscale α–phase NaREF₄. When the reaction temperature was increased to 100 ℃, the formation rate of nanoscale α–phase NaREF₄ was also increased. It was found that the hexagonal-phase of NaYF₄:Er³⁺ NCs were controlled by the reaction temperature during synthesis.

The prepared NCs powders were characterized by X-ray diffraction (XRD) on a Panalytical X’Pert diffractometer. The UC spectra were measured by using a Seki Technotron spectrometer with the excitation wavelength of 1550 nm with the density of ranging from 0.22 W/cm² to 45.19 W/cm².

3. Results and Discussion

Figure 1 showed the XRD pattern of NaYF₄ NCs doped with 10%, 20%, 30%, 40% and 60% Er³⁺, prepared separately at 310 ℃ for 1 h, or at 310 ℃ for 0.5 h followed by 330 ℃ for 0.5 h heating. The XRD pattern demonstrated that the pure β-phase NaYF₄ (PDF card No. 160334) NCs doped with 10–60% were successfully obtained under the reaction at 310 ℃ for 0.5 h followed by 330 ℃ for 0.5 h heating. In case of NaYF₄:10%Er³⁺ prepared at 310 ℃ for 1 h, both β- and α- phase (PDF card No. 060342) were observed by XRD with comparable intensity. Therefore it was found that the temperature was key factor for the formation of pure β-phase of NaYF₄ NCs. The mean size of NaYF₄:30%Er³⁺ NCs calculated by XRD was about 27 nm and its size obtained from TEM image in figure 2 was about 32 nm.

![Figure 1](image_url)

**Figure 1.** XRD patterns of the NaYF₄:10%, 20%, 30%, 40%, 60% Er³⁺ NCs obtained after heating separately at 310 ℃ for 1 h, or at 310 ℃ for 0.5 h followed by 330 ℃ for 0.5 h heating and the line pattern of cubic (PDF card No. 060342) and hexagonal (PDF card No. 160334) phase of NaYF₄ were presented.

The UC emission spectra of NaYF₄:30%Er³⁺ NCs, excited by the light with 1550 nm, were dominated by four peaks at around 980 nm, 800 nm, 660 nm and 540 nm as shown in figure 3. The
Energy levels diagram and corresponding transitions were demonstrated in figure 4. Two major up-conversion mechanisms, energy transfer up-conversion (ETU) and ground state absorption followed by excited state absorption (GSA+ESA), are commonly accepted [4], and following the accepted model, the optical process for the luminescence observed in figure 3 may be considered as below. The ground state of Er$^{3+}$ ion absorbs the excitation light with 1550 nm, resulting in a generation of excited Er$^{3+}$(I_{13/2}) ion. A subsequent absorption of excitation light gives rise to high excited Er$^{3+}$(I_{02}) ion, from which 800 nm (Er$^{3+}$: $^4S_{3/2}$ $\rightarrow$ $^4I_{15/2}$) peak emission occurs. Green emission, its peak at 540 nm (Er$^{3+}$: $^4S_{3/2}$ $\rightarrow$ $^4I_{15/2}$), occurs via Er$^{3+}$(I_{02})$\rightarrow$Er$^{3+}$(S$^3_2$) transition by another subsequent absorption of excitation light. From Er$^{3+}$(I_{02})$\rightarrow$Er$^{3+}$(I$^{11/2}$) relaxation, 980 nm (Er$^{3+}$: $^4I_{11/2}$ $\rightarrow$ $^4I_{15/2}$) emission can take place. Red emission, its peak at 660 nm (Er$^{3+}$:F$^3_{92}$ $\rightarrow$I$^{15/2}_{15/2}$), occurs via Er$^{3+}$(S$^3_2$)$\rightarrow$Er$^{3+}$(F$^{9/2}$) relaxation or Er$^{3+}$(I$^1_{02}$)$\rightarrow$Er$^{3+}$(I$^{11/2}$) relaxation followed by Er$^{3+}$(I$^{11/2}$)$\rightarrow$Er$^{3+}$(F$^{9/2}$) transition. From the energy transitions process, it was found that emission at 980 nm and 800 nm were generated by 2-step UC and at 660 nm and 540 nm were by 3-step UC.

![Figure 2](image1.png)  
**Figure 2.** TEM image of NaYF$_4$:30%Er$^{3+}$ NCs.

![Figure 3](image2.png)  
**Figure 3.** Emission spectra of NaYF$_4$:30%Er$^{3+}$ NCs prepared at 310 °C for 0.5 h followed by 330 °C for 0.5 h heating, excited by the light with 1550 nm.

![Figure 4](image3.png)  
**Figure 4.** Energy level diagram showing the optical process of UC in NaYF$_4$:Er$^{3+}$.

![Figure 5](image4.png)  
**Figure 5.** Pump-power dependence for (a) 980 nm, (b) 800 nm, (c) 660 nm and (d) 540 nm UC emission intensity of NaYF$_4$:10%, 20%, 30%, 40%, 60% Er$^{3+}$ NCs with 1550 nm laser excitation.
The excitation power dependence of UC plotted by a double-logarithmic representation was illustrated in figure 5. The slope n shown in figure 5 decreased at high laser powers, which indicated a saturation effect in high excitation energy [5]. The NaYF₄ NCs with the Er³⁺ concentration of around 10~30% had relatively high intensity of UC emission. In higher doped Er³⁺ concentration, the loss process, such as cross relaxation, may be increased [6].

Table 1 showed the values of the slope n for 980 nm, 800 nm, 660 nm and 540 nm emissions of NaYF₄:10%, 20%, 30%, 40%, 60% Er³⁺ NCs. The n values for 980 nm and 800 nm emissions were about 1.7, and for 660 nm and 540 nm emissions were about 2.2, respectively. Such n values showed that the emission at 980 nm and 800 nm were generated by 2-step UC (n≈2) and at 660 nm and 540 nm were 3-step UC (n≈3). Compared to the n value of the 2-step UC and 3-step UC, it was found that higher excitation density preferred to increase 3-step UC rather than 2-step UC. Table 1 also demonstrated that the n value was strongly affected by the Er³⁺ concentration. The n value in higher Er³⁺ concentration was basically larger value than those in lower Er³⁺ concentration.

Table 1. The slope n for 980 nm, 800 nm, 660 nm and 540 nm emission.

| Concentration (%) | 980 nm | 800 nm | 660 nm | 540 nm |
|-------------------|--------|--------|--------|--------|
| 10% Er³⁺         | 1.7    | 1.7    | 2.0    | 2.1    |
| 20% Er³⁺         | 1.6    | 1.7    | 2.0    | 2.1    |
| 30% Er³⁺         | 1.7    | 1.8    | 2.1    | 2.2    |
| 40% Er³⁺         | 1.7    | 1.7    | 2.3    | 2.2    |
| 60% Er³⁺         | 1.8    | 1.9    | 2.5    | 2.3    |

4. Conclusion

A simple and less toxicity synthesis method was developed for pure hexagonal-phase of NaYF₄ NCs doped with 10%, 20%, 30%, 40% and 60% Er³⁺. The hexagonal of NaYF₄:Er³⁺ can be fabricated by controlling the temperature during synthesis. UC emission spectra of NaYF₄:Er³⁺ NCs, excited at 1550 nm, showed four peaks at about 980 nm, 800 nm, 660 nm and 540 nm. The values of the slope n in pump-power dependence of UC emission intensity confirmed that 980 nm, 800 nm emission were 2-step UC, and 660 nm, 540 nm emission were 3-step UC. It is found the optimum Er³⁺ concentration for 2-step and 3-step UC was around 10~30%.

References

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