Controllable synthesis and upconversion luminescence of

NaYF₄: Yb³⁺, Er³⁺ nanocrystals

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Abstract

NaYF₄ nanorods, and nanoparticles co-doping with Yb³⁺ and Er³⁺ were synthesized by hydrothermal method. The effects of doped ion concentration, the ratio of NaF to Ln(NO₃)₃ and the reactant content on the luminescence properties of the nanocrystals were investigated in detail in this paper. The materials were characterized by powder X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and photoluminescence (PL) spectra. The results indicate that a doping level of 20mol% Yb³⁺ and 2mol% Er³⁺ gives the strongest luminescence, and concentration quenching occurs, when Er³⁺ concentration exceeds 5mol%. Besides, the reaction of temperature and time were also investigated and the results showed that they have an effect on the shape, size, and crystal phase purity of the nanoparticles. The luminescence mechanism for the NaYF₄: Yb³⁺, Er³⁺ was discussed. Under 980 nm excitation, the Er³⁺ ions doped into NaYF₄ samples emitted green fluorescence 520 nm (⁴H_{11/2}→⁴H_{15/2}), 550 nm (⁴S_{3/2}→⁴H_{15/2}) and red fluorescence 650 nm(⁴F_{9/2}→⁴I_{15/2}), which were modified and enhanced by Yb³⁺ ions.

Keywords: Hydrothermal synthesis, Rare-earth ions, Up-conversion luminescence.

1. Introduction

Since the first up-conversion (UC) material $\text{LaF}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ with a practical use was developed in 1968, up-conversion materials containing rare earth (RE) ions have been the focus of much research^[1]. With the development of nano-science and technology, up-conversion nanocrystals have received much attention owing to their wide potential application in such fields as infrared detection, biological recognition, three-dimensional display, and especially luminescent probe in biological labeling and imaging technology^[2, 3]. Up-conversion (UC) phosphors have been investigated extensively because of their potential application in various fields, such as solid-state lasers^[4], light emitting devices^[5], biological labeling^[6, 7] and flatpanel displays. Up-conversion is a process for low energy light, usually near-infrared (NIR) or infrared (IR), converting to higher energies, ultraviolet (UV) or visible, which is based on sequential absorption and energy transfer steps^[8]. And this material is called the up-conversion material.

In the up-conversion material, the amount of the phonon energy of the host material largely affects non-radiative transitions of rare earth ions, and it has been reported that NaYF_4 is one of the most efficient up-conversion host lattices due to its low phonon energy^[9, 10]. Among RE^{3+} ions, Er^{3+} has very rich energy levels, it has a strong absorption for a particular wavelength in the infrared region, and its green fluorescence quenched with a high concentration, so Er^{3+} is an important activator in the process of up-conversion. Yb^{3+} is an excellent sensitizer, because of its special energy level structure, long excited state lifetime and other characteristics, which can improve the conversion efficiency^[11]. So $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ is one of the most efficient 980nm near-infrared (NIR) to visible up-conversion phosphors^[12, 13]. However, low temperature NaYF_4 is a metastable cubic phase and, due to the crystal symmetry, has naturally low up-conversion efficiency. Hence, efforts are usually focused on improving the NaYF_4 up-conversion efficiency through high temperature phase transformation from the cubic phase to hexagonal NaYF_4 , which increases the efficiencies by an order of magnitude^[14]. Among these materials,

hexagonal-phase NaYF₄ is reported as one of the most efficient hosts for performing infrared-to-visible photon conversion when activated by Yb³⁺, Er³⁺ ion pairs, whose green emission is ten-times stronger and overall (green-plus-red) emission are 4.4-times greater than those for cubic-phase NaYF₄ [15, 16].

Currently the method of preparing NaYF₄ include high temperature solid-phase method [17], hydrothermal synthesis method [18], the solution - gel method [19], co-precipitation method [20] and so on. In this paper, NaYF₄:Yb³⁺,Er³⁺ nano-crystals was synthesized by hydrothermal method [21-24], by changing the experimental conditions, prepared with different crystalline phase or morphologies, in order to study the reaction parameters on crystal morphology, crystal phase and influence on luminescence properties and then explore the optional conditions of preparing NaYF₄ nano -crystals.

2. Experimental Method

All the chemicals were of analytical grade and used as received without further purification. deionized water was used throughout. Y₂O₃、Y₂O₃、Er₂O₃(purity>99.9%) were purchased from Sinopharm Chemical Reagent Company. NaF、EDTA、HNO₃、C₂H₅OH、NaOH were supplied by Aladdin Industrial Corporation.

In a typical procedure, lanthanide oxides Y₂O₃, Yb₂O₃ and Er₂O₃ were dissolved in nitric acid to acquire Ln(NO₃)₃. Solvent was evaporated after reaction. Y(NO₃)₃, Yb(NO₃)₃, Er(NO₃)₃ and EDTA were prepared at 0.02 mol/L, sodium fluoride was dissolved in deionized water. Firstly, appropriate amounts of Y(NO₃)₃, Yb(NO₃)₃ and Er(NO₃)₃ solution were added into container, then appropriate amounts ethylenediamine tetraacetic acid (EDTA) was added into the above solution, the molar ratio of EDTA/Ln³⁺ was fixed at 1. After vigorous stirring for 30 min, the above solution was dissolved thoroughly. Then appropriate amounts sodium fluoride (NaF) solution was added drop-wise into the above solution. The as-obtained solution was stirred for another 60 min. The resulting transparent feedstock was transferred to a 50 ml Teflon-lined stainless autoclave and heated 200 °C for 24 h. After naturally cooling to room-temperature, the precipitate washed with ethanol and deionized water several times, and dried in

atmosphere at 60°C for 24 h.

The X-ray powder diffraction (XRD) pattern was recorded using a Japan Regaku D/max ϕ A X-ray diffractometer equipped with graphite monochromatized Cu K α irradiation ($\lambda = 1.5418 \text{ \AA}$) irradiated at a scanning rate of 4° min^{-1} . The field-emission scanning electron microscopy (FESEM) images were obtained using a JEOL JSM-7500F microscope operated at an acceleration voltage of 15 kV. A JEOL JEM-200CX microscope operating at 160 kV in the bright-field mode was used for transmission electron microscopy (TEM). UC spectra were recorded on a JOBIN YVON FL3–21 spectrofluorometer equipped with a R928 photomultiplier tube as the detector and an external power-controllable 980nm semiconductor laser (Beijing Viasho Technology Company, Beijing, China) as the excitation source.

3. Results and Discussion

The up-conversion properties are mainly affected by the following conditions, such as reaction temperature and time, reactant concentration, the doped ion concentration, which has been discussed in detail as follows.

To explore the luminescent properties of rare earth ion-doped NaYF₄, a series of Yb³⁺ and Er³⁺ co-doped NaYF₄ aggregates were also prepared. In the series of Yb³⁺ and Er³⁺ co-doped NaYF₄, the amount of Er³⁺ was fixed at 0.03, and the amount of Yb³⁺ was varied from 0.05 to 0.7. Their up-conversion luminescent spectra are shown in Fig.1. The hydrothermal temperature is 180°C, and the reaction time is 24h. Under 980nm NIR excitation, as can be seen from Fig.1, the NaYF₄:xYb³⁺, 0.03Er³⁺ show green emission at about 525 and 545nm and red emission at about 660nm of the ions. With Yb³⁺ concentration increasing, the intensity of green and red emission and the overall emission intensity of phosphor increase firstly, and then decrease remarkably. The intensity of the green emission shows that 20mol% Yb³⁺ doping gives the strongest luminescence when Er³⁺ is set to 3mol% (Fig.1).

Adding a small amount of Yb^{3+} can improve the intensity of green emission, but as the sensitizer, too high concentration of Yb^{3+} will make green emission concentration quenching. There may be two reasons, one is that in the host lattice, with a small amount sensitization Yb^{3+} , the energy absorbed by Yb^{3+} , can be effectively transmitted to the activator Er^{3+} . The introduction of an elevated amount of Yb^{3+} dopants into the NaYF_4 host lattice would decrease the inter-atomic distance between Yb^{3+} and Er^{3+} and thus facilitates the back-energy-transfer process from the Er^{3+} to Yb^{3+} : ${}^4\text{G}_{11/2}(\text{Er}^{3+}) + {}^2\text{F}_{7/2}(\text{Yb}^{3+}) \rightarrow {}^4\text{F}_{9/2}(\text{Er}^{3+}) + {}^2\text{F}_{5/2}(\text{Yb}^{3+})$. The back-energy-transfer should subsequently suppress the population in excited levels of the ${}^4\text{S}_{3/2}({}^2\text{H}_{11/2})$, resulting in a decrease of the green-light emission (${}^2\text{H}_{11/2}$, ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$). Meanwhile, the back-energy-transfer directly populates the ${}^4\text{F}_{9/2}(\text{Er}^{3+})$ level, producing the enhancement of the red (${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$) emission.²⁷ The other reason is that when the content of Yb^{3+} ions is relatively large, the distance between ions (Yb^{3+} ions and Er^{3+} ions, Yb^{3+} ions and Yb^{3+} ions) will be reduced, greatly increasing the probability of energy transferring to the quenching centers by resonance transmission. In this situation, the energy of Yb^{3+} will dissipate quickly in the form of non-radiative transition, so the energy cannot be effectively transferred to Er^{3+} , and resulting in concentration quenching.

When the hydrothermal temperature is 180°C , and the reaction time is 3h, their up-conversion fluorescence spectra are shown in Fig 2. Under 980nm excitation, the $\text{NaYF}_4:0.2\text{Yb}^{3+}, x\text{Er}^{3+}$ show green emission at about 525 and 545nm and red emission at about 660nm of the ions, which can be assigned to the transitions of ${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{15/2}$, ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$ and ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$, respectively^[25,26]. The nanocrystals give the greatest luminescence at 650nm, so they show red emission. The intensity of the overall luminescence shows that 2mol% Er^{3+} doping gives the strongest luminescence when Yb^{3+} is set to 20mol% (Fig.2). When Er^{3+} concentration exceeds 2mol%, the luminous intensity gradually decreases, and the concentration quenching occurs at 5mol%.

When reaction time is 24h, the up-conversion fluorescence spectra can be seen from Fig 3. In the series of Yb³⁺ and Er³⁺ co-doped NaYF₄, the amount of Yb³⁺ was fixed at 0.2, and the amount of Er³⁺ was varied from 1 mol% to 5 mol%. With the increase of Er³⁺ ions concentration, the green emission intensity increase firstly, then decreases remarkably. The intensity of the green emission shows that 2 mol% Er³⁺ doping gives the strongest luminescence when Yb³⁺ is set to 20 mol% (Fig.3). This result is similar to 18 mol% Yb³⁺, 2mol% Er³⁺ prepared via the high-temperature route at 590 °C [27].

Similar changes in luminescence properties can be seen from the up-conversion fluorescence spectra (Fig.2 and Fig.3) when the reaction time are 3 h and 24 h, respectively. With a small increase in the content of activator Er³⁺, the intensity of luminescence increase remarkably. But the Er³⁺ concentration is too high, the luminescent intensity will decrease gradually, or even concentration quenching occurs. The possible reason is that when Er³⁺ ions doping levels are too high, the interaction between Er³⁺ ions and Er³⁺ ion become large, cross-relaxation(CR): Er³⁺ (⁴I_{11/2}) + Er³⁺ (⁴I_{11/2}) → Er³⁺ (⁴F_{7/2}) + Er³⁺ (⁴I_{15/2}) happens, which decrease the green-to-red luminescent ratio and the intensity. So the configuration for the best green UC should occur when an Er³⁺ ion is surrounded by several Yb³⁺ neighbors and no Er³⁺ ions, and a sufficient number of optically inactive Y³⁺ ions to avoid energy migration from the active ions to killer traps. So the Er³⁺ ion concentration should be not too high, should be between 2 mol%-3 mol%.

To study the effects of different reaction conditions on the up-conversion fluorescent properties of the material, we prepare a series of Yb³⁺ and Er³⁺ co-doped NaY_{0.98-x}F₄: x mol% Yb³⁺, 2mol% Er³⁺ (x = 0,0.05,0.1,0.2, 0.3 and 0.5) phosphors. And the hydrothermal temperature is 230 °C, the reaction time is 24 h. As showed in fig.4., the FESEM results indicate that the nanoparticles have good dispersibility. This is because when the growth rate in the (001) direction is slower than that of (100) direction, it will cause the formation of hexagonal nanorods. And If the growth rate of (100) direction is faster than growth of (001) direction, nanoparticles form. And we can also see from the images, the reaction temperature affect the

morphology and size of the nanocrystals.

The phase structures of nanoparticles were investigated by X-ray diffraction (XRD). As showed in Fig.5, the XRD results indicate that sample (a) is indexed to hexagonal phase NaYF_4 (JCPDS card 16-0334), in the sample b, hexagonal phase coexists with cubic phases, and sample c is assigned to cubic phase NaYF_4 (JCPDS card 77-2042). XRD patterns of samples a, b and c show relatively sharp diffraction peaks, indicating that the samples a, b and c are well crystallized.

NaYF_4 nanocrystals with hexagonal phase emit green fluorescent, and cubic NaYF_4 nanocrystals give strong red light emission. Because different crystal field splitting was caused by different crystalline structure, affecting the energy transmission between sensitizer ions (Yb^{3+}) and activator ions (Er^{3+}), that different crystal phase have an effect on upconversion efficiency. In general, in the highly symmetrical crystal phase, the interaction between Er^{3+} and F^- is strong, leading to fluorescence color changing from green through yellow to red.

Generally speaking, Yb^{3+} ion has a big atomic radius, so we can interfere that the distance between the ions in the $\text{NaYF}_4\cdot\text{Yb}^{3+}$, Er^{3+} is bigger than the pure NaYF_4 phase. Lattice constant of Yb^{3+} and Er^{3+} co-doped NaYF_4 become bigger than usual, and strengthen of bonds is related to the lattice constant, so the forbidden bandwidth become smaller. The minimum required energy of valence band electron transition, relying on excitation of the conduction band, become small, leading to the energy transferring from Yb^{3+} to Er^{3+} more easily, so the intensity of the emission increase.

Upconversion is an effective avenue for the generation of visible emission with near-infrared (NIR) excitation, which is based on sequential photon absorption and energy transfer steps. Fig.8 shows the possible luminescence mechanism in the system of Yb^{3+} and Er^{3+} ions. Under the excitation of 980 nm light, which can be absorbed by Yb^{3+} , the electrons of Er^{3+} are first excited from the $^4\text{I}_{15/2}$ to the $^4\text{I}_{11/2}$ level ($^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2}$, Er^{3+}) via excitation energy transfer from Yb^{3+} to Er^{3+} and then to the $^4\text{F}_{7/2}$ level ($^4\text{I}_{11/2} \rightarrow ^4\text{F}_{7/2}$,

Er³⁺) by absorbing the energy of another electron from Yb³⁺ (²F_{5/2}). The excited electrons of the ⁴F_{7/2} (Er³⁺) level then decay to the emitting ²H_{11/2}, ⁴S_{3/2}, and ⁴F_{9/2} levels, mainly through nonradiative process. Here, the ⁴S_{3/2} level is predominantly excited in this material, observed for the high green emission intensity of the ⁴S_{3/2}→⁴I_{15/2} transition. Meanwhile green emission of ²H_{11/2}→⁴I_{15/2} transition and red emission of ⁴F_{9/2}→⁴I_{15/2} transition are observed.

4. Conclusion

In conclusion, hexagonal-phase and cubic-phase NaYF₄:Yb³⁺, Er³⁺ phosphors with controllable size and morphology were synthesized in selected solvents aided by EDTA. Intense UC emission of the nanometer-sized phosphors suggests good crystallinity, which is in good agreement with the results of XRD and TEM. A doping level of 20% mol Yb³⁺ and 2 mol% Er³⁺ gives the strongest luminescence. The host morphology and crystallinity is very important to luminescent properties of the nanocrystals. Yb³⁺/Er³⁺ co-doped NaYF₄ with pure hexagonal phase emits strong green fluorescence, but the intensity of green emission decrease if there is impurity phase or the second phase in the host. And Cubic NaYF₄ emits strong red fluorescence. This is because different crystal field splitting was caused by different crystalline structure, affecting the energy transition between the Yb³⁺ ions and Er³⁺ ions, namely different crystal phases lead to different up-conversion luminescent efficiency. Under the excitation of 980 nm, the red emission (⁴F_{9/2}→⁴I_{15/2}) of the NaYF₄:Yb³⁺, Er³⁺ increases with increasing the Yb³⁺ concentration, while that of the green emission (⁴S_{3/2}/²H_{11/2}→⁴I_{15/2}) decreases. The red emission enhancement is attributed to the enhanced population of the ⁴F_{9/2} level via the energy transfer (⁴G_{11/2} (Er³⁺) + ²F_{7/2} (Yb³⁺) → ⁴F_{9/2} (Er³⁺) + ²F_{5/2} (Yb³⁺)), while green emission diminishment is attributed to ⁴S_{3/2}+ ²F_{5/2} → ²K_{15/2}+ ²F_{7/2}, which depopulates the excited ⁴S_{3/2} level at higher Yb³⁺ concentration. So the emission color can be tuned from green to yellow only by changing the Yb³⁺ concentration.

Acknowledgements

The authors would like to thank the National Science Foundation of China (60807036), the

Science and Technology Commission of Shanghai Municipality (14ZR1430400, 13ZR1430200), the ONR and the Key Laboratory of Rare Earth Functional Materials of Shanghai for supporting the research.

Conflict of Interest

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

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Fig.1. The PL spectra of NaYF₄:xYb³⁺, 0.03Er³⁺ samples with x=0.05, 0.1, 0.2, 0.3, 0.5 and 0.7, excited at 980nm

Fig.2.The PL spectra of NaY_{0.8-x}F₄:Yb_{0.2}, Er_x samples with x=0.01, 0.02, 0.03, 0.04 and 0.05, excited at 980nm. The reaction time is 3h.

Fig.3. The PL spectra of NaY_{0.8-x}F₄: Yb_{0.2}, Er_x samples with 0.01, 0.02, 0.03, 0.04, and 0.05, excited at 980nm. The reaction time is 24h.

Fig.4. FESEM images of $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ samples with different reaction temperature, (a) for 180°C , (b) for 230°C

Fig.5. XRD patterns of $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$.

Fig.6. FESEM images of NaYF₄: Yb³⁺, Er³⁺ with different structure, (a) for nanorods, (b) for nanorods and nanoparticles, (c) for nanoparticles

Fig.7. The PL spectra of NaYF₄: Yb³⁺, Er³⁺ samples with different phase,(a) for hexagonal phase, (b) for hexagonal and cubic phase, (c) for cubic phase

Fig.8. Schematic energy-level diagrams, upconversion excitation, and visible emission schemes for the $\text{Yb}^{3+}/\text{Er}^{3+}$ systems

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8