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Original Article

Influences of Growth Durations on Characteristics of $NaYF_4$:(Yb,Tm) Upconversion Materials

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Abstract: $NaYF_4$:(Yb,Tm) upconversion materials were synthesized by the simple hydrothermal method. Growth duration was varied from 4h to 12h under a growth temperature of 150°C. The structural, optical and surface morphology characteristics of the $NaYF_4$:(Yb,Tm) UC materials were investigated. The XRD and SEM results illustrated that the $NaYF_4$:(Yb,Tm) materials were transformed from the multiple phases (hexagonal and cubic) to the single-phase (hexagonal prism) as growth duration being longer than 8h with the average diameter and length of these prisms being about 0.5 µm and 2 µm, respectively. Under 980 nm laser excitation, the $NaYF_4$:(Yb,Tm) emits at peaks of 450 nm ($^1D_2 \rightarrow {}^3F_4$), 475 nm ($^1G_4 \rightarrow {}^3H_6$), 647 nm ($^1G_4 \rightarrow {}^3F_4$) and 697 nm ($^3F_3 \rightarrow {}^3H_6$), with the highest emission belonging to $NaYF_4$:(Yb,Tm) grown for 8h.

Keywords: $NaYF_4$:(Yb,Tm), upconversion materials, photoluminescence, growth duration, hydrothermal method.

1. Introduction

Recently, Lanthanide-doped upconversion nanocrystals (UCNCs) have captured special attention of scientists over the world because of their particular properties [1, 2]. These UCNCs materials enable to produce strong anti-stokes luminescence, efficiently converting NIR light to UV/VIS emissions, by absorbing several low energy photons and afterward emitting higher energy photons via intermediate long-lived electronic states of lanthanides [3]. The lanthanide - doped upconversion nanocrystals have been used in different areas such as solar cells [4], water treatment [4], lasers [5], sensors [6, 7], bio-imaping [8, 9] because of its chemical stability, low toxicity, large anti-stock shift sharp, and emission bandwidths [10].

The efficiency of the up-conversion process significantly depends on the rate of non-radiative transitions within the RE^{3+} ion. Among

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upconverting host materials such as LaF_3, PbF_2, CaF_2, SrF_2, BaF_2, sodium yttrium fluoride ($NaYF_4$) has been proven to be an ideal host material because of its low photon cutoff energy so that it effectively reduces non-radiative energy losses at the intermediate states of RE^{3+} ions. $NaYF_4$ can exist in two different crystalline phases which are cubic and hexagonal structure. Recent studies have shown that the hexagonal phase of UCNCs offers a higher magnitude of up-conversion luminescence intensity than the cubic phase does [11, 12]. Hence the hexagonal phase becomes an interesting target in preparation of $NaYF_4$ UCNCs. The two crystal forms can be mutually converted by heat treatment [13]. However, the hexagonal $NaYF_4$ (β-$NaYF_4$) is thermodynamically less stable than the cubic $NaYF_4$ (α-$NaYF_4$) which attribute to the mixture of crystallographic phases in synthesized samples. In order to solve this problem, lanthanide ions, having higher ionic radii than that of Y^{3+}, such as europium (Eu) and terbium (Tm), can be added into $NaYF_4$ UCNCs to stabilize its hexagonal phase. There are some studies about the phase transformation of $NaYF_4$ depending on the temperature and concentration of lanthanide ions [12, 14]. Besides, the methods of synthesis β-$NaYF_4$ upconversion materials from a simple method (solid-state reaction) to complexity (co-thermolysis) have been well documented [13]. However, the effect of growth duration on β-$NaYF_4$ formation in the hydrothermal process at 150℃ is not reported.

In this study, a simple hydrothermal method has been utilized for the synthesis of $NaYF_4$:(Yb,Tm) and then investigated the influence of growth duration on the structure of materials and photoluminescence intensities.

2. Materials and methods

$NaYF_4$:(47%Yb, 2%Tm) - mol% was prepared from $YbCl_3.6H_2O$, $YCl_3.6H_2O$, $TmCl_3.6H_2O$, NaOH, NH_4F, and ethanol. All chemicals are analytic grade and used as received without further purification. The synthesis of β-$NaYF_4$: :(47%Yb,2%Tm)- mol% UCNCs was carried out by the following steps. Firstly, 0.6g NaOH was added to a mixture of 4 ml acetic acid and 16 ml ethanol. A fixed ratio of $YbCl_3.6H_2O$, $YCl_3.6H_2O$, $TmCl_3.6H_2O$ of 51:47:2 in mol % and 0.29 g NH_4F were then dissolved in the above solution and stirred till to generate the homogeneous growth solution. Afterward, the growth solution was put in the autoclave and undergone the hydrothermal process at 150℃ for the various growth durations of 4, 5, 6, 7, 8, and 12h. Finally, the autoclave was slowly cooled down to room temperature. The white precipitate $NaYF_4$:(Yb,Tm) was then washed with a mixture of DI water and ethanol by centrifuge process and dried for 12h at 80℃.

The surface morphologies of $NaYF_4$:(Yb,Tm) UCNCs were characterized by field emission scanning electron microscopy (FESEM, Hitachi, S-4800) while the crystal phases were determined using an X-ray diffractometer (XRD) with Cu K_α radiation (λ= 1.5406 Å) over the 2θ range 10-70^o at room temperature. The upconversions photoluminescence (UPL) spectra were studied by a spectrometer under excitation at 980 nm using laser diode.

3. Results and discussions

3.1. XRD analysis

$NaYF_4$:(Yb,Tm) crystals are formed under two stages of nucleation and crystal growth. The growth duration plays a significant role in the crystal growth where the size of the crystals was defined, after shaped in the nucleation process [14-16]. To investigate the growth duration effect to the crystal phases, the different growth duration of the hydrothermal process was carried out. XRD patterns of various samples synthesized at different growth durations were illustrated in Figure 1(a). The crystal structures of $NaYF_4$:(Yb,Tm) exits in two phases (the cubic and the hexagonal phases). For the growth duration between 4h and 7h, the diffraction peaks of $NaYF_4$ crystals appear to be in the coexistence of β-$NaYF_4$:(Yb,Tm) and α-

$NaYF_4$:(Yb,Tm). The result indicates that with the longer growth duration, the more percentage of hexagonal phase crystals are favored while the percentage of cubic phase is decreased. With growth duration being longer than 8h, the single hexagonal phase is achieved, which is illustrated in Fig.1 (b) [13].

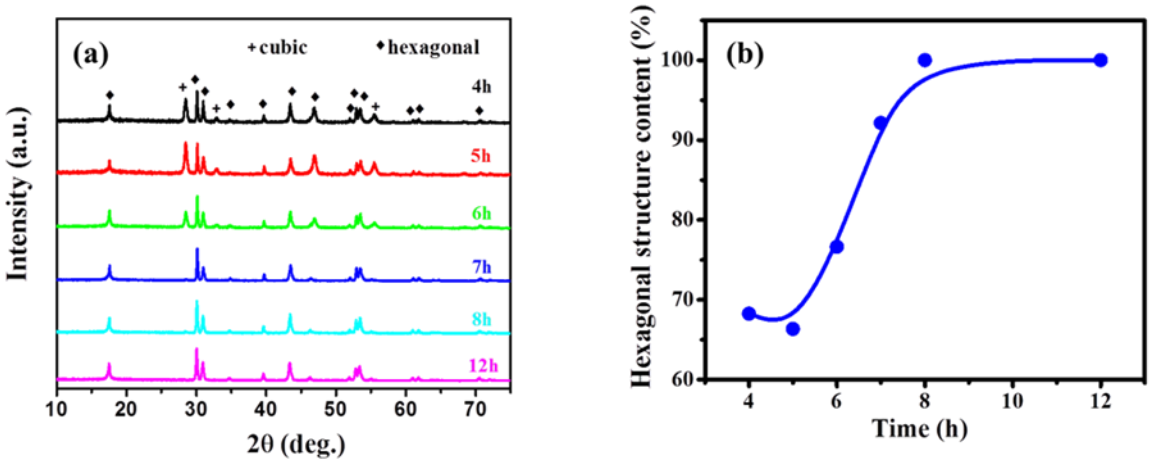

Figure 1. (a) XRD patterns for NaYF4: (Yb,Tm) samples prepared at different growth durations. (b) The percentage of the hexagonal phase in synthesized NaYF4: (Yb,Tm) samples versus various growth durations.

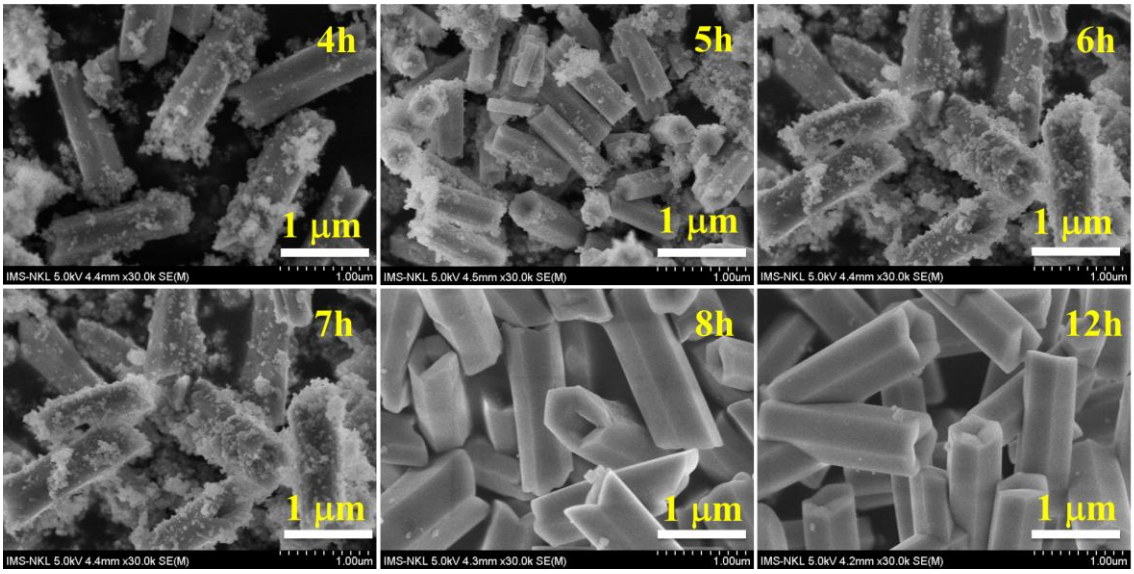

Figure 2. SEM images of $NaYF_4$:(Yb,Tm) crystals at different growth durations.

3.2. SEM analysis

Fig. 3 shows SEM images of $NaYF_4$: (Yb,Tm) crystals which were synthesized at different growth durations. It shows that the samples are in the coexistence of the prism, which is identified as hexagonal prism phase, and the nanoparticles, which is determined as the cubic phase of $NaYF_4$:(Yb,Tm) UCNCs. When growth duration is prolonged, the percentage of the nanoparticles in the samples decreases. After

the growth durations being longer than 8h, the samples are a purely hexagonal prism. The results from SEM images are consistent with the XRD results. The average length and diameter of these β-$NaYF_4$:(Yb,Tm) are about 0.5 µm and 2 µm, respectively and the size of the product is well uniformed while the size of α-$NaYF_4$:(Yb,Tm) is about 25 nm.

3.3. Up-conversion luminescence (UCL) property

The growth duration defines the crystal phase of $NaYF_4$:(Yb,Tm). The more hexagonal phase is given at a longer growth duration. The up-conversion luminescence process can undergo different mechanisms and the energy level structure, which can be easily found [17, 18]. Fig. 3 shows that after being excited at 980 nm, $NaYF_4$:(Yb,Tm) emits UCL at peaks of 450 nm and 475 nm (blue emission), 645 nm and 795 nm (red emission), which correspond to the $^1D_2 \rightarrow {}^3F_4$, $^1G_4 \rightarrow {}^3H_6$, $^1G_4 \rightarrow {}^3F_4$, and $^3F_3 \rightarrow {}^3H_6$ transitions of Tm^{3+} ions, respectively. As can be seen in Fig. 3, UCL intensity increases with an increase in growth duration and reaches the highest value with the growth duration of 8h. Hence, the optimization of growth duration is 8h. The UCL intensity of $NaYF_4$: (Yb,Tm) grown for 8h is about fivefold higher than that for 5h. The intensity of UCL gradually increases when the growth duration raises. The XRD results illustrate that the relative content of the β-$NaYF_4$:(Yb,Tm) increases as the growth duration raise, and so does the UCL intensity. Therefore, the high efficiency of UCL emission of β-$NaYF_4$:(Yb,Tm) is due to the higher percentage of β -$NaYF_4$:(Yb,Tm) in synthesized samples. The decrease of UCL intensity of samples which are grown beyond 8h of growth duration can be ascribed to the effect of longterm heating to luminophores [19].

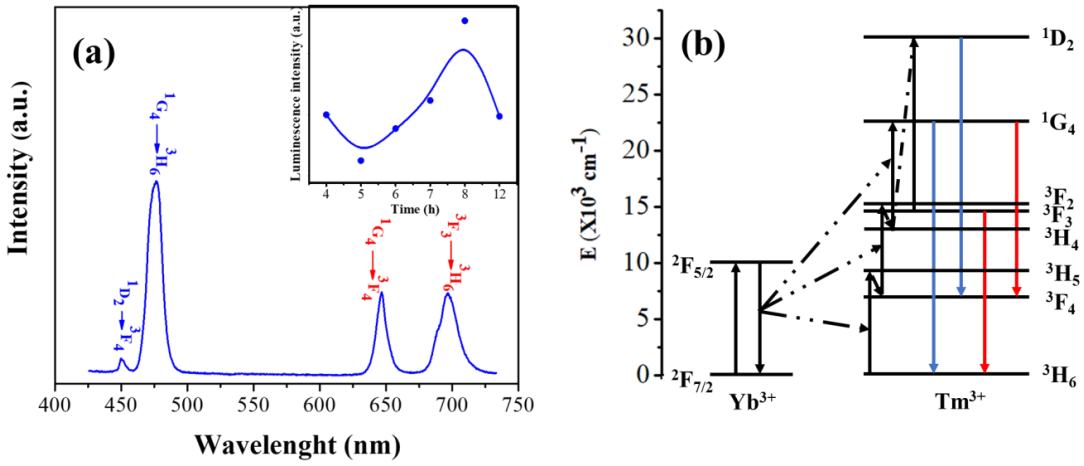

Figure 3. (a) UCL spectrum was measured for NaYF4: (Yb,Tm) UCNCs under excitation at 980 nm. In the inset: The dependence of the blue luminescence intensity (475 nm) on growth durations. (b) The energy-level diagram of up-conversion excitation and visible emission of Yb^{3+} and Tm^{3+} ions in $NaYF_4$:(Yb,Tm) UCNCs.

The energy-level diagram in Fig. 3(b) shows up-conversion emission mechanism of Yb^{3+}/Tm^{3+} in $NaYF_4$:(Yb,Tm) UCNCs. Firstly, Yb^{3+} can be excited by absorbing 980 nm light and then transfer such excitation energy to Tm^{3+}. The electrons of Tm^{3+} are then excited from the $^3H_6$ level to the $^3H_5$ level by receiving excitation energy transferred from Yb^{3+} and then excited to the $^1D_2$ level and $^1G_4$ level by absorbing the energy of other excited electrons from Yb^{3+}. Finally, the transition between $^1D_2 \rightarrow {}^3F_4$ and $^1G_4 \rightarrow {}^3H_6$ produced to up-conversion luminous in 450 nm and 475 nm, respectively. Similarly, the peak of 647 nm and 695 nm come from

energy transition of $^1G_4$ and $^3F_3$ level, respectively. It is obvious that the co-doped materials demonstrate high up-conversion efficiency, which is due to the well uniformed hexagonal prism structure.

4. Conclusions

$NaYF_4$:(Yb,Tm) with the single hexagonal prism structure was synthesized by a simple hydrothermal method. It was illustrated that the structure of materials depends on the various growth durations, which transformed from the multiple phases (hexagonal and cubic phases) to the single hexagonal prism phase as growth duration being longer than 8h. These hexagonal prisms have an average length and diameter of about 2 µm and 0.5 µm, respectively. Under 980 nm laser excitation, $NaYF_4$:(Yb,Tm) emits at peak of 450 nm ($^1D_2 \rightarrow {}^3F_4$), 475 nm ($^1G_4 \rightarrow {}^3H_6$), 647 nm ($^1G_4 \rightarrow {}^3F_4$) and 700 nm ($^3F_3 \rightarrow {}^3H_6$). The UC luminescence intensity reached the maximum value when the $NaYF_4$:(Yb,Tm) was grown for 8h, which contribute by the high efficiency of UCL of the purely hexagonal phase of $NaYF_4$:(Yb,Tm).

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