

# Chemical Conversion Synthesis and Luminescence Properties of Hexagonal-NaYF<sub>4</sub>:Eu Nanorods

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**Abstract**—Using simple method to synthesize well-shaped and uniform Hexagonal-NaYF<sub>4</sub> is a challenge to modern nano/micro technology. Through a hydrothermal chemical conversion route, a kind of uniform NaYF<sub>4</sub>:Eu Nanorods have been synthesized. The crystal structure, morphology, and luminescence properties were characterized by XRD, FE-SEM, and PL, respectively. The results show that the nanorods have high purity, high crystallinity and high luminescence intensity.

**Index Terms**—NaYF<sub>4</sub>: Eu Nanorods, chemical conversion, luminescence

## I. INTRODUCTION

Hexagonal-NaYF<sub>4</sub> with a high refractive index and low phonon energy, which normally used as host lattices for upconversion (UC) [1] and downconversion (DC) [2] luminescence of rare earth ions for the application in biomedical fields [3] and as active optical components in composites [4]. With the development of nano/micro technology, it is a challenge to use a kind of facile method to synthesize well-shaped and uniform nano/microsized NaYF<sub>4</sub>. A wide range of methods, including co-precipitation [5], ionic liquids based synthesis [6], thermal decomposition [7], hydro (solvo) thermal synthesis [8], chemical conversion route [9], and Polyol-mediated synthesis [10] have been developed. Recently, chemical conversion has been used as an efficient method to synthesize rare earth fluorides nanowires/nanorods/nanotubes [9], [11], [12], with the precursors of rare earth hydroxides [Re(OH)<sub>3</sub>] and Lu<sub>4</sub>O(OH)<sub>9</sub>(NO<sub>3</sub>) respectively. However, to the best of our knowledge, the use of layered rare earth hydroxide as the parent precursor to synthesize NaYF<sub>4</sub> via chemical conversion has not been reported.

Here, we have synthesized the uniform (Y<sub>0.95</sub>Eu<sub>0.05</sub>)<sub>2</sub>(OH)<sub>5</sub>NO<sub>3</sub> • 1.5H<sub>2</sub>O (LYH:Eu) nanoplates, which are a kind of anion type of inorganic layered rare earth hydroxides, through a simple hydrothermal process without any organic solvents or surfactants. In this paper,

the as-obtained precursors have been successfully utilized to fabricate hexagonal-NaYF<sub>4</sub>:Eu nanorods by a facile hydrothermal chemical conversion route. Furthermore, the possible formation processes and luminescence properties of the as-synthesized hexagonal-NaYF<sub>4</sub>:Eu nanorods have been discussed in detail.

## II. EXPERIMENTAL SECTION

### A. Synthesis of Precursor Nanoplates

The yttrium and europium sources for LYH:Eu (5 mol%) nanoplates are Y(NO<sub>3</sub>)<sub>3</sub> • 6H<sub>2</sub>O (99.99%, Kanto Chemical Co., Inc., Tokyo, Japan) and Eu(NO<sub>3</sub>)<sub>3</sub> • 6H<sub>2</sub>O (99.95%, Kanto Chemical Co., Inc.), respectively. Typically, the LYH:Eu nanoplates were synthesized using the reaction between ammonium hydroxide solution (25%, Wako Chemical Co., Inc., Tokyo) and Y(NO<sub>3</sub>)<sub>3</sub> and Eu(NO<sub>3</sub>)<sub>3</sub> following a method described previously [13], with a proper amount of NH<sub>4</sub>NO<sub>3</sub> as a NO<sub>3</sub><sup>-</sup> complement agent.

### B. Synthesis of Hexagonal-NaYF<sub>4</sub>: Eu nanorods

1 mmol of NaF and 0.7 mL of HF (40%) [9] were dissolved in 50 mL of deionized water with stirring, and then 0.03mmol of LYH:Eu (5 mol%) nanoplates were added into the mixture solution. After agitation for 30 min, the mixture was transferred to a 100 mL autoclave and maintained at 120 °C for 24 h. The white precipitate was obtained by centrifugation, and washed with deionized water, and dried at 60 °C for 12 h.

### C. Characterization Techniques

Phase identification was performed by X-ray diffractometry (XRD, Model RINF 2200 V/PC, Rigaku, Tokyo) operating at 40 kV/40 mA using nickel-filtered Cu KR radiation and a scanning speed of 1.0 °2θ/min. Morphologies of the precursors and the fluoride products were observed by field-emission scanning electron microscopy (FE-SEM, Model S-5000, Hitachi, Tokyo) under an acceleration voltage of 10 kV. Fluorescent spectra of the products were measured using an FP-6500 fluorescence spectrophotometer (JASCO, Tokyo, excitation source: 150-W Xe lamp).

### III. RESULTS AND DISCUSSION

#### A. Phase Identification and Morphology

As can be seen from the XRD patterns shown in Fig. 1a, the precursor has the structure of  $(Y_{0.95}Eu_{0.05})_2(OH)_5NO_3 \cdot 1.5H_2O$  [13]. After reacted with the HF and NaF, the precursor can be converted to the pure phase of hexagonal- $NaYF_4:Eu$  (JCPDS No. 16-0334, Fig. 1b). The sharp diffraction peaks and the absence of impurity peaks indicate high crystallinity and high purity of the products.

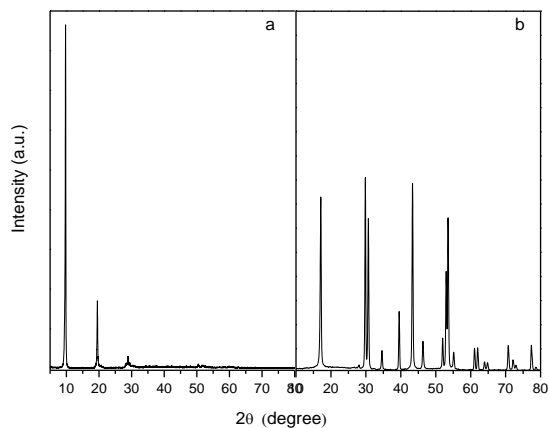


Figure 1. XRD patterns of the LYH:Eu (5 mol%) nanoplates (a) and hexagonal- $NaYF_4:Eu$  (5 mol%) products (b).

FE-SEM observation of the products is shown in Fig. 2. From Fig. 2a, it can be seen that the precursor has uniform nanoplate morphology and the lateral sizes of the nanoplates are about 0.5  $\mu m$ . Fig. 2b revealed that the conversion product consists of nanorods having very smooth surfaces and uniform diameters.

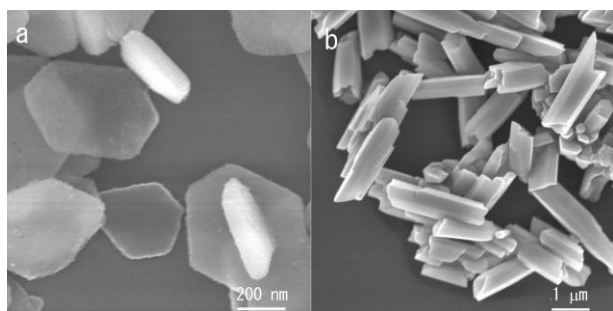


Figure 2. FE-SEM images of the LYH:Eu (5 mol%) nanoplates (a) and hexagonal- $NaYF_4:Eu$  (5 mol%) nanorods (b).

#### B. Possible Formation Processes

The fluoride products were prepared by the chemical conversion route. There are two kind of possible mechanism to explain the formation process. One is *in situ* conversion reaction; another is dissolution and recrystallization [12]. In the recent reaction, a possible explanation of the formation process is later one, which is acid corrosion dissolution followed by re-nucleation. HF first corrodes LYH:Eu nanoplates and the nanoplates begin to dissolve gradually in solution, and then the  $F^-$  ions react with  $Y^{3+}$  and  $Eu^{3+}$  to form a  $YF_3:Eu$  phase. In

the structure of  $\beta-NaYF_4$ , one-fold out of three of the cation sites is randomly occupied by  $1/2Na^+$  and the other sites randomly occupied by  $Na^+$  and vacancies, so the  $Na^+$  ions are easily trapped into the crystals to form a more stable hexagonal- $NaYF_4:Eu$  phase [14].

#### C. Luminescence Properties

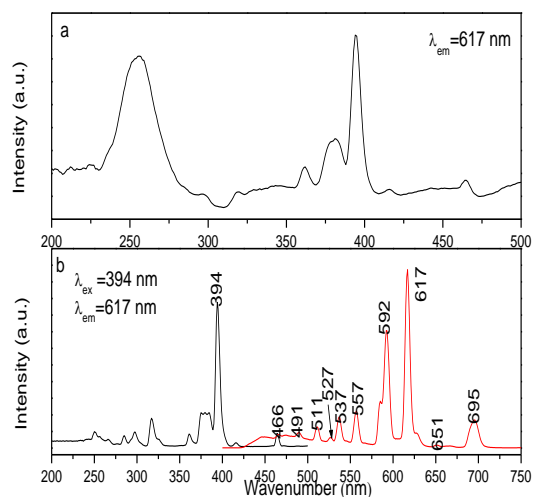


Figure 3. a. PL excitation ( $\lambda_{em}=617$  nm) of LYH:Eu (5 mol%) nanoplates; b. PL excitation ( $\lambda_{em}=617$  nm) (black line) and emission ( $\lambda_{ex}=394$  nm) (red line) spectra of hexagonal- $NaYF_4:Eu$  (5 mol%).

Fig. 3b shows the excitation and emission spectra for hexagonal- $NaYF_4:Eu$ . The excitation spectrum (black line) consists of the characteristic excitation lines of  $Eu^{3+}$ . To be specific, 317 nm for  ${}^7F_0 \rightarrow {}^5H_6$ , 361 nm for  ${}^7F_0 \rightarrow {}^5D_4$ , 379 nm for  ${}^7F_0 \rightarrow {}^5G_2$ , 394 nm for  ${}^7F_0 \rightarrow {}^5L_6$ , 416 nm for  ${}^7F_0 \rightarrow {}^5D_3$ , and 464 nm for  ${}^7F_0 \rightarrow {}^5D_2$ . The strongest  ${}^7F_0 \rightarrow {}^5L_6$  transition of  $Eu^{3+}$  is at 394 nm, which has been used as the excitation wavelength. There is a charge-transfer band (CTB) of  $Eu^{3+}-O^{2-}$  observed between 200 and 300 nm in  $Eu^{3+}$  doped LYH:Eu (5 mol%) nanoplates (Fig. 3a). However, the CTB of  $Eu^{3+}-F^-$  generally located below 200 nm. There is no CTB of  $Eu^{3+}-O^{2-}$  in the reaction product further demonstrates that no LYH:Eu (5 mol%) nanoplates are left after conversion, and the result is coincide the XRD analysis results. The emission spectrum (red line) of the sample consists of all of the  $Eu^{3+}$  transitions from the excited  ${}^5D_{0,1,2}$  levels to the  ${}^7F_j$  level. To be specific, 466 nm for  ${}^5D_2 \rightarrow {}^7F_0$ , 491 nm for  ${}^5D_2 \rightarrow {}^7F_2$ , 511 nm for  ${}^5D_2 \rightarrow {}^7F_3$ , 537 nm for  ${}^5D_1 \rightarrow {}^7F_1$ , 557 nm for  ${}^5D_1 \rightarrow {}^7F_2$ , 592 nm for  ${}^5D_0 \rightarrow {}^7F_1$ , 617 nm for  ${}^5D_0 \rightarrow {}^7F_2$ , 651 nm for  ${}^5D_0 \rightarrow {}^7F_3$ , and 695 nm for  ${}^5D_0 \rightarrow {}^7F_4$ .

### IV. CONCLUSIONS

In summary, the hydrothermal chemical conversion method is very facile and environment friendly to fabricate uniform hexagonal- $NaYF_4:Eu$  nanorods. The possible mechanisms of the conversion process for the products may be the acid corrosion dissolution and re-nucleation approach. Under ultraviolet excitation, the  $Eu^{3+}$  doped hexagonal- $NaYF_4$  shows strong emission with red colors. Furthermore, this facile route may also be of

significance in synthesizing many other lanthanide compounds.

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