

# Sol-gel synthesis of $\beta$ -NaYF<sub>4</sub>:Yb<sup>3+</sup>/Nd<sup>3+</sup>/Tm<sup>3+</sup>/Mn<sup>2+</sup> nanophosphors and color-tunable upconversion luminescence



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## ABSTRACT

Highly crystalline  $\beta$ -NaYF<sub>4</sub>:Yb<sup>3+</sup>/Nd<sup>3+</sup>/Tm<sup>3+</sup>/Mn<sup>2+</sup> nanophosphors were prepared by sol-gel methods with isopropyl alcohol as complexing agent. X-ray diffraction analysis data demonstrated that hexagonal phase  $\beta$ -NaYF<sub>4</sub> was successfully synthesized by a calcination process on the as-prepared precursor at 550 °C for 1 h. Under a 980 nm laser diode (LD) excitation, the samples demonstrated bright upconversion luminescence (UCL), which was caused by the energy level transition of Tm<sup>3+</sup> and Nd<sup>3+</sup> ions. With the increase of the doping concentration of Mn<sup>2+</sup> ions, the UCL intensities in the blue light region increased firstly and then decreased, meanwhile, the UCL intensities in the red, yellow and green light region gradually increased. Color-tunable UCL of the sample was generated by the continuous variation of the pumping power of 980 nm LD.

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## 1. Introduction

In recent years, rare earth (RE)-doped upconversion (UC) nanomaterials, which can be excited by the near-infrared (NIR) ray to emit visible light, have attracted increasing attentions due to their potential applications in the fields in solar cells, volumetric displays, UC lasers and biology, etc [1–6]. Among all these UC phosphors,  $\beta$ -NaYF<sub>4</sub> with hexagonal crystal structure has been proven to be one of the most efficient UC host materials under NIR excitation because of its features of low phonon energy, low non-radiative decay rates and excellent chemical stability, so RE-doped  $\beta$ -NaYF<sub>4</sub> become a rising material in many fields, especially in bio-imaging and biological detection [7–9]. Realization of color-tunable UCL in RE-doped  $\beta$ -NaYF<sub>4</sub> nanocrystals is of particular importance for the applications in biological labeling, since this can extend their capabilities for simultaneous imaging and tracking of multiple molecular targets, so as to allow scientists to understand, classify and differentiate complex diseases [5,8,10]. The doping of Mn<sup>2+</sup> can change the electron distribution on the energy levels of Tm<sup>3+</sup> and Nd<sup>3+</sup> ions, so modify the relative luminescent intensity among blue, green, yellow and red light and realize color-tunable emission of the phosphors. Meanwhile, the

doping of Mn<sup>2+</sup> can also decrease the non-radiative transition probability of phonon, so improve the UCL intensity of the sample [11–14].

Until now, several techniques have been reported for the synthesis of NaYF<sub>4</sub> nanocrystals, including co-precipitation [15], hydrothermal and solvothermal [16,17], thermal decomposition method [18], and so on. However, these methods have the features of complicated procedure, high costs and environmental loads, long reaction time, and low crystallinity of the products, etc. Compared with the methods mentioned above, sol-gel method has been a more convenient and widely used method to synthesize nanoparticles because of its characteristics of low-cost, rapid reaction, good control on the chemical composition, crystalline structure, morphology and particle size distribution of the products etc. [19,20], and there have been seldom reports about the synthesis of NaYF<sub>4</sub> nanocrystals by sol-gel method. In this work, we report the synthesis of well-crystalline  $\beta$ -NaYF<sub>4</sub>:Yb<sup>3+</sup>/Nd<sup>3+</sup>/Tm<sup>3+</sup>/Mn<sup>2+</sup> nanophosphors by sol-gel method using isopropyl alcohol as complexing agent, effect of Mn<sup>2+</sup> doping concentration and pumping power of 980 nm LD on the UCL of  $\beta$ -NaYF<sub>4</sub>:Yb<sup>3+</sup>/Nd<sup>3+</sup>/Tm<sup>3+</sup>/Mn<sup>2+</sup> were studied, UCL mechanism of the sample was also discussed.

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## 2. Experimental

### 2.1. Synthesis of $\beta$ -NaYF<sub>4</sub>:Yb<sup>3+</sup>/Nd<sup>3+</sup>/Tm<sup>3+</sup>/Mn<sup>2+</sup> nanophosphors

Stoichiometric amounts of rare earth oxide Y<sub>2</sub>O<sub>3</sub> (99.99%), Yb<sub>2</sub>O<sub>3</sub> (99.99%), Nd<sub>2</sub>O<sub>3</sub> (99.99%) and Tm<sub>2</sub>O<sub>3</sub> (99.99%) were weighed according to the chemical formula of NaY<sub>0.765-x</sub>F<sub>4</sub>:Yb<sub>0.2</sub>, Nd<sub>0.03</sub>, Tm<sub>0.005</sub>, Mn<sub>x</sub> (x = 0.04, 0.08, 0.10, and 0.15), the oxides were then dissolved in nitric acid and diluted with deionized water to form the nitrate solution with a concentration of 0.125 mol/L. Stoichiometric amounts of NaOH and manganese acetate (C<sub>4</sub>H<sub>6</sub>MnO<sub>4</sub>·4H<sub>2</sub>O) were added into the solution and mixed thoroughly, then moderate amounts of isopropyl alcohol ((CH<sub>3</sub>)<sub>2</sub>CHOH) and trifluoroacetic acid (CF<sub>3</sub>COOH) were added into the solution. The solution was heated and stirred slowly on a magnetic stirrer at 50 °C for 2 h to form transparent gels. The obtained gels were dried at 100 °C for 12 h and then calcined at different temperatures for 1 h with excess amount of sodium hexafluorosilicate (Na<sub>2</sub>SiF<sub>6</sub>) as a protective material to obtain the crystalline NaYF<sub>4</sub>:Yb<sup>3+</sup>/Nd<sup>3+</sup>/Tm<sup>3+</sup>/Mn<sup>2+</sup> nanophosphors. Na<sub>2</sub>SiF<sub>6</sub> can be decomposed and released gas state of SiF<sub>4</sub> when the calcining temperature was higher than 300 °C. SiF<sub>4</sub> gas can exclude the air presented in the crucible and protect the sample from oxidation during the calcining process.

### 2.2. Characterization

Thermo-gravimetry and differential scanning calorimetry (TG-DSC) analysis on the precursor was carried out on a NETZSCH-STA409PC thermal analyzer with a heating rate of 10 °C/min. Phase identification and crystallite size of the sample were analyzed by X-ray diffraction (XRD) measurement on a Rigaku Ultima IV diffractometer with CuK $\alpha$  radiation source. The morphology of the samples was characterized with a JSM-6701F high resolution field-emission scanning electron microscope (FE-SEM). UCL spectra of the samples were obtained by using a spectrofluorometer (Model RF-5301PC, Shimadzu) with a fiber-coupled 980 nm LD as an excitation source. All the characterizations were performed at room temperature.

## 3. Results and discussion

### 3.1. TG-DSC analysis and structural characterization

Fig. 1 shows the TG-DSC curves of the as-prepared precursor. The weight loss of the sample can be divided into three stages. The

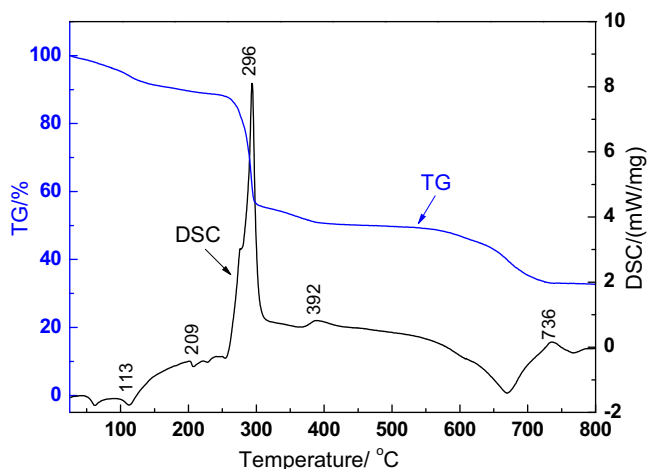


Fig. 1. TG-DSC curves of the as-prepared precursor.

first stage was from room temperature to 256 °C, the weight loss of this stage was about 11.7%, which was caused by the removal of crystallized water and decomposition of nitrate anions in the precursor, corresponding to the endothermic peaks of 113 °C and 209 °C, respectively. The weight loss of the second stage, which ranged from 256 to 378 °C, was about 36.5%, and the weight loss was caused mainly by the decomposition of lanthanide trifluoroacetates ((CF<sub>3</sub>COO)<sub>3</sub>Ln), the exothermic peak centered at 296 °C indicated the formation of YF<sub>3</sub>. The third stage ranged from 378 to 763 °C, the weight loss of this stage was about 18.3%, which was caused mainly by the release of CO<sub>2</sub> and the organic remains, two exothermic peaks of 392 and 736 °C indicated the crystallization of  $\beta$ -NaYF<sub>4</sub> and the completion of phase transformation from  $\beta$ -NaYF<sub>4</sub> to  $\alpha$ -NaYF<sub>4</sub>. No weight loss was observed when the calcining temperature was higher than 736 °C, indicating the completion of crystallization of the precursor.

Fig. 2 shows the XRD patterns of the as-prepared precursor and phosphors calcined at different temperatures for 1 h. It can be seen that the precursor was almost amorphous. When calcined at 300 °C, the precursor began to crystallize, the crystalline phase was YF<sub>3</sub> (JCPDS card no. 70-1935). The phase of  $\beta$ -NaYF<sub>4</sub> (JCPDS no. 16-0334) began to appear when the sample was calcined at 400 °C, the sample had a mixed phase of YF<sub>3</sub> and  $\beta$ -NaYF<sub>4</sub> at this temperature. With the increase of calcining temperature, the sample transformed to pure hexagonal  $\beta$ -NaYF<sub>4</sub> when the calcining temperature reached 500 °C, and fully crystallized to the phase of  $\beta$ -NaYF<sub>4</sub> at 550 °C. From Fig. 2, it can also be seen that  $\alpha$ -NaYF<sub>4</sub> (cubic phase, JCPDS no. 77-2042) began to appear with the continuous increase of calcining temperature to 650 °C. So, calcining temperature of 550 °C was ideal for the crystallization of pure hexagonal  $\beta$ -NaYF<sub>4</sub>. The crystallite size of the phosphors can be estimated by the Scherrer's formula  $D = 0.89\lambda / \beta \cos \theta$ , where  $D$  is the average grain size,  $\lambda$  is the X-ray wavelength,  $\theta$  and  $\beta$  is the bragg angle and the corrected full-width at half-maximum (FWHM) of an observed peak, respectively. The calculated crystallite sizes of phosphors calcined from 300 to 750 °C ranged from 23.8 to 31.1 nm, all were in a nanometer scale. The SEM images of the phosphors calcined at 550 and 650 °C for 1 h are shown in Fig. 3. It can be seen that the particle size increased with the rise of calcining temperatures. Phosphors calcined at 550 °C

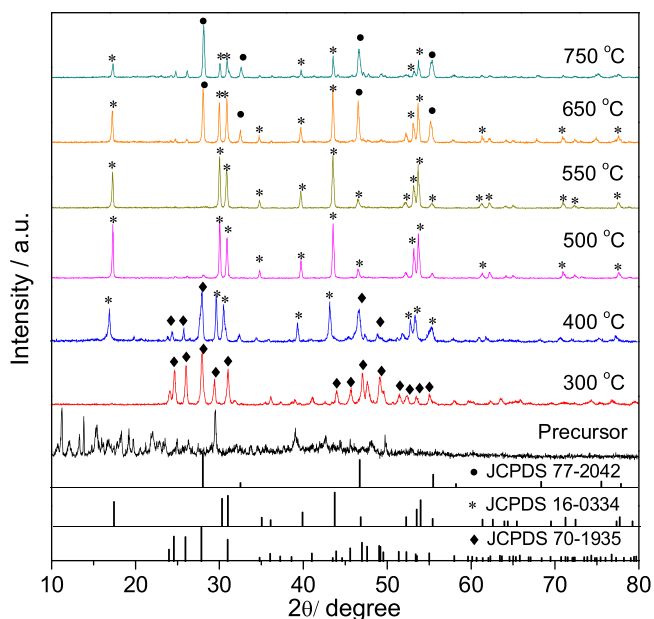


Fig. 2. XRD patterns of the as-prepared precursor and phosphors calcined at different temperatures.

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