



Molten-salt synthesis and upconversion of hexagonal $\text{NaYF}_4:\text{Er}^{3+}:\text{Yb}^{3+}$ micro-/nano-crystals



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ABSTRACT

The NH_4NO_3 molten solution system was developed to synthesize $\text{Er}^{3+}/\text{Yb}^{3+}$ -doped hexagonal NaYF_4 micro-/nano-crystals with different sizes and morphologies. The influences of the reaction temperature, the reaction time, the usage amounts of reaction materials and flux NH_4NO_3 on the structure and morphology were studied and discussed in detail. The effect of the sizes and morphologies on the upconversion properties was also investigated detailedly. The rod-like particles exhibit much stronger UC emission than for those with other shapes. The abnormal characteristics of the strong UC emission for the phosphors with the length of 80–100 nm and the diameter of ca. 50 nm was also observed. This work demonstrates a rational approach to synthesis high-quality fluorides and other types of materials in NH_4NO_3 molten solution system, as well as a possibility to meet the increasing commercial demand.

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1. Introduction

In the past decade, many scientific researchers have paid considerable attention to ongoing research of rare earth doped upconversion (UC) nano-/micro-materials since they exhibit superior chemical and optical properties, such as low toxicity, large Stokes shifts, sharp emission bands, high quantum yield, long lifetime, weak background luminescence, and good resistance to photo-bleaching, blinking and photochemical degradation [1]. These unique properties, involved in size- and shape-independent luminescence phenomena, make rare earth doped UC materials have diverse potential applications in the field of photovoltaic devices, advanced lighting and displays, sensors, and biological labels [2–5].

Among various UC materials, fluoride compounds are one kind of excellent UC hosts because of their low phonon energy and transparency in the visible and ultraviolet range [1,6], which could significantly reduce fluorescence quenching and expand their usability in optical application. $\text{RE}^{3+}/\text{Yb}^{3+}$ -codoped NaYF_4 (RE = Tm, Ho, and Er) phosphors are considered to be the most efficient UC materials for green, blue, and red UC phosphors to date [1,7–9], and hexagonal NaYF_4 phase offers about an order-of-magnitude enhancement of UC efficiency relative to cubic NaYF_4 phase [10]. Therefore, it is necessary to fabricate pure hexagonal NaYF_4 . Recently, rare-earth doped hexagonal NaYF_4 materials were prepared through

hydrothermal method [11–13], thermolysis method [1,14], and molten salt method [17–19]. To the best of our knowledge, most of hexagonal NaYF_4 materials to date have been synthesized by thermolysis method [1,14]. Although this method can be used to fabricate monodisperse nanoparticles with high dispersibility in organic solvents, it suffers from some inherent disadvantages of low yield, large total costs, toxic rare-earth trifluoroacetate precursors and byproducts, and substantial environmental loads, limiting its use for commercial purposes. The molten salt method exhibits several advantages, including simplicity, versatility, low cost, large scale, and environmental friendliness [15,16]. Recently, $\text{RE}^{3+}/\text{Yb}^{3+}$ -doped hexagonal NaYF_4 nanocrystals were prepared in NaF, NaF-KF and NaNO_3 flux by the cooling method [17–19]. Unfortunately, the synthesis temperature (500–800 °C) is still high, and the products are poorly aggregated and contained minute YF_3 and $\text{Y}_7\text{O}_6\text{F}_9$ impurities [18,19]. Consequently, it is necessary to find a new flux with abundance in nature, low melting point, and easy deliquescence in water. With its aforementioned advantages [20], NH_4NO_3 will be selected to be one novel solvent to synthesize the hexagonal NaYF_4 materials. As known, the morphologies can be determined by the intrinsic structure of target compound and the growth surroundings. To obtain high quality nano-/micro-crystals, it is very necessary to fastidiously control some parameters such as the temperature, the time, and the usage amounts of raw materials and flux. Here, we mainly concentrate upon the effects of the usage amount of reaction materials and NH_4NO_3 flux, the temperature and the time on the structure, morphology and size of the as-obtained products. Finally, the influences of morphologies and sizes

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of the hexagonal $\text{Er}^{3+}/\text{Yb}^{3+}:\text{NaYF}_4$ products on fluorescence UC emission are also investigated in detail.

2. Experimental section

Reagent-grade NaNO_3 , NH_4NO_3 , $\text{Y}(\text{NO}_3)_3$, $\text{Yb}(\text{NO}_3)_3$, $\text{Er}(\text{NO}_3)_3$ and NH_4F powders were used to synthesize hexagonal $\text{Er}^{3+}/\text{Yb}^{3+}:\text{NaYF}_4$ crystals. To make Er^{3+} and Yb^{3+} homogeneously distributed, NaNO_3 and $\text{Ln}(\text{NO}_3)_3$ ($\text{Ln} = \text{Y}, \text{Er}, \text{Yb}$) were dissolved in alcohol under heating. After all materials were completely dissolved and stirred for an hour, the alcohol was removed by evaporation. The mixture was used as the raw materials of sodium and Ln sources. The starting materials were thoroughly mixed. The mixtures were put into 15 ml capacity crucibles. After the lids were tightly closed, the crucibles were placed in an oven. The sealed tank was heated to 160–250 °C, and held for different times in an oven, and then cooled to room temperature naturally. After being washed several times with deionized water and ethanol, the precipitates were dried at 70 °C for 12 h in vacuum.

The samples were examined by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS), and photoluminescence (PL). XRD analyses were carried out on a Bruker D8-Advance diffractometer with graphite-monochromatized $\text{Cu K}\alpha$ radiation (40 kV/60 mA, graphite monochromator, $\lambda = 0.1541 \text{ nm}$). The size, morphology and chemical compositions of products were determined by a transmission electron microscopy (TEM, JEOL2010) operating at 200 kV and a JSM 6700F scanning electron microscope (SEM) equipped with the energy dispersive X-ray spectrum (EDS). Structural information was measured by a high-resolution transmission electron microscopy (HRTEM). Emission spectra were recorded on an Edinburgh Instruments FLS920 spectrofluorimeter equipped with both continuous (450 W) and pulsed xenon lamps. The best wavelength resolution is 0.05 nm. The line intensities and positions of the measured spectra were calibrated according to the FLS920 correction curve and standard mercury lamp.

3. Results and discussion

3.1. Crystal structure

Since NH_4F have the same cation with the flux NH_4NO_3 and the excessive F^- acts as a mineralization, decreasing the crystallization temperature [21], NH_4F was selected as a fluoride source to synthesize $\text{Er}^{3+}/\text{Yb}^{3+}$ -codoped hexagonal NaYF_4 crystals. The reaction time, reaction temperature, the usage amount of flux NH_4NO_3 and reaction material NaNO_3 , $\text{Ln}(\text{NO}_3)_3$ (Ln represents the total amount of Y, Yb and Er) and NH_4F , as listed in Tables 1–4, were selected to study the effect on crystal phase, and morphology and size of the products.

When the molar ratio of $\text{NaNO}_3\text{--Ln}(\text{NO}_3)_3\text{--NH}_4\text{F}$ (hereinafter to be referred as Na--Ln--F) is 1:1:2, the diffraction peak of the product (**S1**) matched well with that of the orthorhombic phase YF_3 (JCPDS No. 74-0911) (see Fig. 1a), the product **S1** is made of orthorhombic YF_3 . When the molar ratio of Na--Ln--F increases to 1:1:4, the intensity of the XRD peaks originating from orthorhombic YF_3 becomes very weak in the XRD pattern of the product (**S2**) (see Fig. 1a); however the XRD peaks belonging to hexagonal NaYF_4 appear and take a predominant role, implying that the as-obtained product is made of predominant hexagonal NaYF_4 and minute orthorhombic YF_3 . As the molar ratio of Na--Ln--F further increasing to 1:1:4.5, the diffraction peaks of the product (**S3**) due to the orthorhombic YF_3 disappeared, and all the diffraction peaks are in good agreement with those of pure hexagonal NaYF_4 and no trace of

characteristic peaks for other impurity phases such as cubic NaYF_4 were observed, which implies that the obtained $\text{Er}^{3+}/\text{Yb}^{3+}$ -doped NaYF_4 crystals have the same crystallographic structure as pure hexagonal NaYF_4 crystal. With the further increase of the molar ratio of Na--Ln--F , all diffraction peaks of the samples (**S4–S6**) take on the characteristic peak of pure hexagonal NaYF_4 and have no additional diffractions (see Fig. 1a). This observation (see Table 1) suggests that the hexagonal $\text{Er}^{3+}/\text{Yb}^{3+}:\text{NaYF}_4$ materials can be synthesized at $\text{Ln}/\text{NH}_4\text{F}$ molar ratio of more than 4.5, and the NH_4NO_3 molten solution system can be developed to prepare the hexagonal NaYF_4 materials.

Although the variation of NaNO_3 and the amount of NH_4NO_3 do not transform the pure hexagonal NaYF_4 crystal structure of the products (see Tables 2 and 3), the decrease of the reaction temperature varying from 250 °C to 200 and to 160 °C leads to the appearance of cubic $\text{NH}_4\text{Y}_2\text{F}_7$ (JCPDS No. 01-074-0911) and the cubic $\text{NH}_4\text{Y}_2\text{F}_7$ becomes more and more with the decrease of the reaction temperature (see Table 4). As known, the thermodynamic growth regime is driven by a sufficient supply of thermal energy, and the most stable crystal structure is preferred [9,22]. Since the hexagonal NaYF_4 is more thermodynamically than the cubic $\text{NH}_4\text{Y}_2\text{F}_7$, the cubic $\text{NH}_4\text{Y}_2\text{F}_7$ is susceptible to transform to hexagonal NaYF_4 . Since the energy barrier hinders the formation of the hexagonal NaYF_4 , a sufficient supply of thermal energy must be required to overcome the energy barrier in order to modify the environment of Y^{3+} and Na^+ occupation sites, including coordination number [23]. The high temperature is favorable to this transformation. The chemical compositions of the above samples were tabulated in Tables 1–4 with the following experimental conditions.

3.2. Morphology

Fig. 2 illustrates some representative SEM images of hexagonal $\text{Er}^{3+}/\text{Yb}^{3+}:\text{NaYF}_4$ prepared under different $\text{Ln}/\text{NH}_4\text{F}$ molar ratios. The particle diameter (D) and length (L) are counted by averaging the corner-to-corner distance of the hexagonal surface and the distance between the top and bottom, respectively. The product **S2** prepared at the NH_4F -to- $\text{Ln}(\text{NO}_3)_3$ (hereinafter to be referred as F/Ln) molar ratio of 4.0 is mainly composed of hexagonal rods with the length L of ca. 3.0 μm and the diameter D of 100–200 nm and some irregular particles (Figs. 2a and 3a). As disclosed by the corresponding HRTEM image of the rods, the spacing between the adjacent lattice fringes was determined as 0.360 nm, as shown in Fig. 3b. This plane is well indexed as the d -spacing value of (0001) plane of hexagonal NaYF_4 crystal, confirming that the preferred growth direction is the c -axis, namely the [0001] direction. When the F/Ln molar ratio increases to 4.5, the product (**S3**) maintains hexagonal rod-like morphology, but its length sharply decreases to ca. 1.0 μm and the diameter slightly grows to 200–400 nm. Further increasing the F/Ln molar ratio to 6.0, the morphology of the product **S4** changes to bipyramid capped hexagonal prisms with the mean length of about 500 nm and the mean diameter of 400–500 nm. When F/Ln molar ratio is 8.0, the morphology of the products (**S5**) still keeps the bicapped hexagonal prisms (see

Table 1
Effect of NH_4F amount on the crystal.

Sample	Molar ratio $\text{Na}:\text{Ln}:\text{F}$	Crystal phase	Figure, morphology
S1	1:1:2	Orthorhombic YF_3	/
S2	1:1:4	Hexagonal NaYF_4 + little orthorhombic YF_3	Fig. 2a rods ($D \approx 0.1\text{--}0.2 \mu\text{m}$, $L \approx 2\text{--}3 \mu\text{m}$) + irregular shapes
S3	1:1:4.5	Hexagonal NaYF_4	Fig. 2b rods ($D \approx 0.3 \mu\text{m}$, $L \approx 1.0 \mu\text{m}$)
S4	1:1:6	Hexagonal NaYF_4	Fig. 2c bicapped hexagonal prisms ($D \approx 0.4\text{--}0.5 \mu\text{m}$, $L \approx 0.8 \mu\text{m}$)
S5	1:1:8	Hexagonal NaYF_4	Fig. 2d bicapped hexagonal prisms ($D \approx 0.7 \mu\text{m}$, $L \approx 0.7 \mu\text{m}$)
S6	1:1:12	Hexagonal NaYF_4	Fig. 2e hexagonal plates ($D \approx 0.8 \mu\text{m}$, $L \approx 0.2 \mu\text{m}$)

Reaction temperature: 250 °C; reaction time: 24 h; the molar ratio of $\text{Ln}(\text{NO}_3)_3$ to NH_4NO_3 : 5:1; molar ratio $\text{Na}:\text{Ln}:\text{F}$: the molar ratio of NH_4NO_3 , $\text{Ln}(\text{NO}_3)_3$ to NH_4F .

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