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Controlled synthesis of β-$NaYF_4$:Yb, Er microphosphors and upconversion luminescence property

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HIGHLIGHTS

- Effect of EDTA and citrate on upconversion luminescence was investigated.
- EDTA & citrate can promote phase transition from cubic to hexagonal.
- EDTA can improve the emission intensity at low reaction temperatures.
- EDTA & citrate play a role in changing crystals' growth direction.

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ABSTRACT

$NaYF_4$:Yb^{3+}/Er^{3+} with different phases, morphologies, and luminescent properties were synthesized using a facial hydrothermal method. The as-obtained samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED) pattern, and photoluminescence (PL). The XRD results indicated that ethylene diamine tetraacetic acid (EDTA) and citrate play an important role in phase transition at low reaction temperatures. SEM images revealed that samples morphologies can be changed from irregular shapes to regular microprisms by EDTA and citrate. TEM images showed that the diameter of samples synthesized at 120 °C without any chelating agents is ~50 nm. HRTEM indicated that the crystal grows along the [111] plane. The selected area electron diffraction (SAED) pattern showed that the nanoparticles have a good single-crystalline structure. FL spectra revealed that citrate can reduce the luminescence intensity at any reaction temperature. However, EDTA can improve optical properties at low reaction temperatures.

1. Introduction

$NaYF_4$:Yb^{3+}, Er^{3+} has been widely investigated for its potential functions in many fields, such as bioimaging, high-density optical storage, and lighting [1–7]. $NaYF_4$ is regarded as the most efficient host for the upconversion of Ln ions, because it has unique advantages, such as low lattice phonon energy, ultraviolet range, and transparency in the visible range [8–11]. Two phases are known for the crystallization of $NaYF_4$: cubic (α-) and hexagonal (β-) phases. Compared with α-$NaYF_4$, β-$NaYF_4$ was reported as the material with the highest upconversion efficiencies. $NaYF_4$ crystals have low phonon energies (<400 cm^{-1}) and low non-radiative decay rate [12,13]. So, phase-controlled synthesis to obtain the pure hexagonal phase of $NaYF_4$ is the key for enhanced material luminescent performance.

To date, $NaYF_4$ nanocrystals have been synthesized through different methods. Yi et al. [14] and Wei et al. [15] have prepared $NaYF_4$ upconversion nanoparticles using the coprecipitation method; the diameter of the as-obtained products is approximately 30 nm–150 nm. Although the synthetic process is simple and safe, the sizes of the products are not uniform, and they tend to have low luminous efficiency. The pyrolytic process is another efficient method used to prepare nanocrystals. Boyer et al. [16] have synthesized α-$NaYF_4$:Yb,Er/Tm upconversion nanoparticles with a diameter of approximately 30 nm. Mai et al. [17] has focused on controlling the as-obtained products' phase, morphologies, and sizes by adjusting the ratio of Na/Re (Rare earth), reaction time, and reaction temperature. Using a pyrolytic process, researchers can obtain a good crystallization and control the size of crystals.

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However, the steps of the process are complex, and samples prepared using this method tend to have high toxicity because there are some poisonous leftovers. The solvothermal method is a more convenient and safe way to prepare samples compared with the methods mentioned above. Many attempts have been made to prepare $NaYF_4$ crystals with various morphologies and luminescent properties [18–24]. The as-obtained products with good crystallization, high purity, good dispersion, and high luminescent property have been hydrothermally constructed. EDTA and citrate with different coordination constants were used usually to control the sizes of products [25]. For example, some researchers prepared β-$NaYF_4$ crystals by increasing reaction temperature, extending time, or adding PO_4^{3-} [13]. Also Xu et al. [26] and Wang et al. [27] synthesized samples by rare earth stearates. However, the effect of the EDTA and citrate on the phase transition of the $NaYF_4$ crystals rarely reported.

In the present study, we found that the phase transition temperatures can be reduced by the addition of chelating agents. The effect of EDTA and citrate on phase transition, morphology, and upconversion luminescence were investigated. Samples with hexagonal phase, uniform morphology and excellent luminescent property were synthesized at 120 °C by EDTA.

2. Experimental

2.1. Chemicals

All reagents were of analytical grade. Yttrium oxide (Y_2O_3), ytterbium oxide (Yb_2O_3), and erbium oxide (Er_2O_3) were purchased from Shanghai Yuelong Non-Ferrous Metals Ltd. Oleic Acid (OA) (A.R., 99%) was purchased from Tianjin Hengxing Chemical Reagent Co., Ltd. NaF (A.R., 98%) was purchased from Sinopharm Chemical Reagent Co., Ltd. EDTA (A.R., 99%) was purchased from Tianjin Ruijinte Chemical Co., Ltd. Citrate (A.R., 99.5%) was purchased from Tianjin Yongda Chemical Reagent Co., Ltd. NaOH (A.R., 96%) was purchased from Yantai Tieta Chemical Co., Ltd.

2.2. Preparation

Y_2O_3 (3.9 mmol), Yb_2O_3 (1.0 mmol), and Er_2O_3 (0.1 mmol) were dissolved in concentrated nitric acid (20 mL), then heated and stirred constantly until all the acid evaporated, and placed in a three-necked flask (500 mL). Then, 80 mL absolute ethanol and 30 mmol stearic acid were added. The solution was stirred continuously at 60 °C until all components were dissolved. The temperature was increased to 78 °C. Subsequently, 20 mL of absolute ethanol was added along with 30 mmol NaOH. This solution was refluxed for 1 h. Rare earth stearates were synthesized after drying the solution at 60 °C for 12 h.

The following were added to a beaker containing 1 mmol rare earth stearates and 5 mmol NaF, 10 mL H_2O, 15 mL absolute ethanol, different amounts of EDTA (molar ratio EDTA to Ln^{3+} is 1:1; 2:1; 3:1, respectively) or citrate (molar ratio citrate to Ln^{3+} is1:1; 2:1; 3:1, respectively), and 5 mL OA. The solution was transferred to a 50 mL Teflon bottle and heated at 120 °C, 150 °C, 180 °C, respectively for 24 h. Products were obtained after washing by trichloromethane/ethanol (V_t:V_e = 1:6) mixed solution for the first time and water/ethanol (V_w:V_e = 1:2) mixed solution for 3 times, and drying at 60 °C for 12 h finally.

2.3. Characterization

The crystal structure of the sample was investigated by XRD (Cu Kα = 1.5406 Å). Size and morphology were characterized by SEM (JSM-6700F; JEOL, Tokyo, Japan). TEM, HR-TEM, and SAED were performed on a JEOL JEM-2010 instrument at an accelerating voltage of 200 kV. Upconversion spectra were recorded by Hitachi F-4600 spectrophotometer (Tokyo, Japan); the excitation source was a 980 nm laser diode. All measurements were taken at room temperature.

3. Results and discussion

3.1. Characterization, morphology, and growth mechanism of $NaYF_4$:Yb^{3+}/Er^{3+} products

Fig. 1 shows the structure of samples prepared without any chelating agent. When the reaction temperature was relatively low (120 °C), only a small amount of β-$NaYF_4$ (PDF file no. 28-1192) was obtained together with α-$NaYF_4$ (PDF file no. 77-2042), as shown in Fig. 1(a). Most of the products were in hexagonal phase when the temperature is increased to 150 °C [Fig. 1(b)]. The diffraction peaks of the sample synthesized at 180 °C [Fig. 1(c)] can be indexed as a pure hexagonal (β-) phase; this result coincides well with the literature (PDF file no. 28-1192).

Fig. 2 shows that when EDTA was added to the reaction system with 1:1 M ratio for EDTA:Ln^{3+}, the three samples prepared at 120, 150, and 180 °C relatively exhibit the peaks of pure crystalline hexagonal β-$NaYF_4$; this result is consistent with the literature data (PDF file no. 28-1192).

The phenomenon of phase transition was also observed, when only citrate with 1:1 M ratio for citrate:Ln^{3+} was added to the reaction system, as shown in Fig. 3.

Based on XRD patterns, the following conclusion can be made: EDTA and citrate can translate the phase from cubic (α-) to hexagonal (β-), particularly at a relatively low temperature. Without chelating agents, Ln^{3+} is released from the precursor and reacts with Na^+ and F^- at the interface between alcohol/water and OA. However, if EDTA or citrate is added, Ln^{3+} reacts with EDTA before

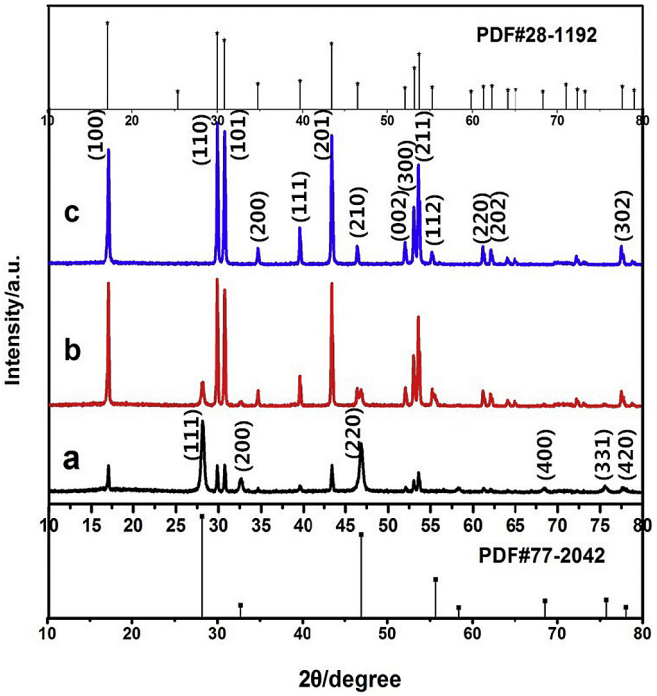

Fig. 1. X-ray diffraction (XRD) patterns of $NaYF_4$:Yb^{3+}/Er^{3+} prepared at temperatures of (a) 120 °C, (b) 150 °C, and (c) 180 °C. The standard cards of α-$NaYF_4$ (PDF file no. 77-2042) and β-$NaYF_4$ (PDF file no. 28-1192) are provided as references.