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OH^- ions-controlled synthesis and upconversion luminescence properties of $NaYF_4:Yb^{3+},Er^{3+}$ nanocrystals via oleic acid-assisted hydrothermal process

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Abstract: Yb^{3+} and Er^{3+} ions co-doped $NaYF_4$ nanocrystals were synthesized with different amounts of NaOH via oleic acid (OA)-assisted hydrothermal process. X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), and photoluminescence spectra were used to characterize the products. The result indicated that the introduction of NaOH into the initial reaction solution effectively promoted the cubic (α-) to hexagonal (β-) phase transition of $NaYF_4:Yb^{3+},Er^{3+}$ nanocrystals, while excessive amount of NaOH favored the formation of α-$NaYF_4:Yb^{3+},Er^{3+}$ nanocrystals. Besides, with the increase of NaOH amount, the morphologies of β-$NaYF_4:Yb^{3+},Er^{3+}$ nanocrystals varied from irregular nanobranch to uniform nanorod. Further investigation revealed that the addition of NaOH could facilitate the deprotonation of OA, leading to the formation of oleate (OA^-), and meanwhile increased the concentration of OH^- ions, inducing consequently the phase transition and morphology evolution of $NaYF_4:Yb^{3+},Er^{3+}$ nanocrystals. Moreover, the upconversion luminescence properties of $NaYF_4:Yb^{3+},Er^{3+}$ nanocrystals were systematically investigated. It was found that the upconversion emissions not only depended on the phase and morphology but also were influenced by the surface groups.

Keywords: $NaYF_4:Yb^{3+},Er^{3+}$ nanocrystals; OH^- ions; phase transition; morphology evolution; upconversion luminescence; rare earths

Rare earth (RE) ions-doped upconversion materials that can emit high energy photons under the excitation of near-infrared light have evoked great research interest due to their potential applications in solar cell, three-dimensional displays, bioimaging and photocatalysis[1–4]. Typically, upconversion materials are composed of an inorganic host and RE dopant ions embedded in the host lattice. Due to the low photon energy, high solubility for RE ions and good thermal stability, the RE fluoride compounds with general formula like $NaREF_4$, especially $NaYF_4$, have been considered as one of the most efficient hosts to realize high efficient upconversion luminescence[5,6]. Besides, it is widely accepted that the upconversion luminescence properties are also dependent of their crystalline phase, morphology, size and surface state[7]. One of the most well known examples is that $NaYF_4$ exists in two polymorphic forms, cubic (α-) and hexagonal (β-) phases, relying on the synthesis conditions and methods. In general, β-$NaYF_4$ offers several orders of magnitude enhancement of upconversion efficiency than α-$NaYF_4$[8,9].

To date, many soft chemical methods have been employed to obtain $NaREF_4$ nanocrystals, such as hydrothermal treatment, thermal decomposition, ionothermal approach, co-precipitation and precipitation transformation method[10–14]. Among these methods, hydrothermal treatment is capable of preparing highly crystalline and pure products under a relatively lower temperature. Moreover, the method has proven to be an effective and convenient process in preparing products with controllable morphologies and architectures. A great number of researches have demonstrated that in the synthesis of $NaREF_4$ crystals with hydrothermal method, the most efficient and straightforward strategy for fine-tuning the morphology and architecture of $NaREF_4$ is to select addition of organic additives[15]. Typical ligands, including ethylenediaminetetraacetic acid (EDTA), polyvinyl pyrrolidone (PVP), citrate (Cit^{3-}), cetyltrimethylammonuim bromide (CTAB), and oleic acid (OA), have been widely used for governing the phase and shape of $NaREF_4$ crystals[16–20]. Unlike other ligands, OA is hydrophobic and also acts as solvent with high boiling point. Besides, oleate (OA^-) anions, the dissociated form of OA molecules, are electron donors and can easily coordinate with RE^{3+} ions. As a result, the obtained products are usually much smaller and ordered.

It is well known that the crystal growth is not only determined by its intrinsic structure but also greatly af-

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fected by the external factors, such as organic addictive, hydrothermal temperature, reaction time, pH value, and so on. In particular, the pH value, or in other words, the concentration of OH^- ions, usually can influence the existent form of ligands and their selective adsorption on different crystal facets, thus indirectly affecting the phase and shape of final product. For example, in acidic condition, Cit^{3+} can combine H^+ and exists as H_xCit^{x-3}, directly decreasing its complexing ability with RE^{3+} to a great degree[21]. Besides, it was reported that the pH value in the initial reaction solution has significant effects on selective adsorption of the organic additive EDTA on different crystal facets, thus controlling the final size and geometry of particles[22]. As for the organic addictive OA, the presence of OH^- ions can deprotonate OA, generating OA^- ions. Different complexing abilities with RE^{3+} ions and selective adsorptions on crystal facets of $NaYF_4$ between OA and OA^- favor morphology control. Zhang et al.[23] reported that different shapes of $NaYF_4$ from disk, tube to elongated rod were obtained with the increase of NaOH amount. Liu et al.[24] used different amounts of NaOH to tune the concentration ratio of OA^- to OA and found that $NaYF_4$ nanocrystals with different aspect ratios were obtained. However, most of the previous studies only focused on the effect of OH^- ions on the morphology evolution of $NaYF_4$ nanocrystals. There is still lack of an investigation on their phase transition induced by OH^- ions through which may give us a deep insight into the role of OH^- ions in governing their growth. Moreover, understanding how the upconversion luminescence properties change with phase and morphology is of great importance in the design of highly efficient upconversion materials.

Recently, our group reported the effect of the mother solution pH value on the phase transition, microstructure evolution and upconversion luminescence properties of Yb^{3+} and Er^{3+} ions co-doped $LiYF_4/YF_3$ nanoparticles under OA-assisted hydrothermal condition, in which the pH value was adjusted by adding diluted nitric acid[25]. As a continuous and extended work, here we prepared Yb^{3+} and Er^{3+} ions co-doped $NaYF_4$ nanocrystals using different amounts of NaOH. The roles of OH^- ions in controlling the phases and morphologies of final products were demonstrated and discussed. In addition, the upconversion luminescence properties as well as mechanisms of $NaYF_4:Yb^{3+},Er^{3+}$ nanocrystals were also demonstrated and systematically investigated.

1 Experimental

1.1 Materials

All materials were used as received without further purification. $Ln(NO_3)_3·6H_2O$ (Ln=Y, Yb and Er, 99.99%) were supplied by A&C Rare Earth Materials Center. Oleic acid (OA, 90%), sodium oleate (NaOA, 98%), sodium hydroxide (NaOH, 97%), sodium nitrate ($NaNO_3$, 99%) and ammonium fluoride (NH_4F, 98%) were purchased from Aladdin Chemistry Co., Ltd. Ethanol (≥99.7%) and cyclohexane (≥99.5%) were bought from Sinopharm Chemical Reagent Co., Ltd.

1.2 Synthesis of $NaYF_4:Yb^{3+},Er^{3+}$ nanocrystals

The $NaYF_4:Yb^{3+},Er^{3+}$ nanocrystals were synthesized via a modified hydrothermal process. In a typical procedure, NaOH (2.00 g) was firstly dissolved into 10 mL of double distilled water, followed by the addition of ethanol (25 mL) and OA (25 mL) under stirring. Secondly, 5 mL aqueous solution containing $RE(NO_3)_3$ (78:20:2 molar ratio for $Y^{3+}:Yb^{3+}:Er^{3+}$, 0.4 mol/L) was added to the resulting mixture. Thirdly, an aqueous solution of NH_4F (5 mL, 2 mol/L) was dropped into the above solution. With additional agitation for 30 min, the solution was transferred into a 90 mL Teflon-lined autoclave and heated at 230 ºC for 2 h. Lastly, after the autoclave was naturally cooled to the room temperature, the precipitates at the bottom were collected by centrifugation, washed with ethanol-cyclohexane three times, and then washed with ethanol-water once more. The products were dried in an air oven at 60 ºC for 24 h. Other samples were prepared by the similar procedure, except for different amounts of NaOH. For all samples, additional $NaNO_3$ was added to keep the amount of Na^+ ions constant at 50 mmol.

1.3 Characterization

The X-ray-powder diffraction (XRD) measurement was carried out using a RigakuD/maxrB 12kW X-ray diffractometer at a scan speed of 5 degrees per second. The microstructure of the synthesized nanoparticles was characterized using a JEM-2100F transmission electron microscope (TEM) and a Hitachi S4800 scan electron microscope (SEM). The photoluminescence spectra were acquired using an Edinburgh FLS920 with an external 980 nm laser and a xenon lamp as an excitation source. The infrared spectra were recorded on BRUKER EQUINOX55 Fourier transform infrared spectrometer (FTIR). All the measurements were carried out at room temperature.

2 Results and discussion

2.1 Crystal structure and morphology

The composition and phase purity of the products prepared with different amounts of NaOH from 0 to 2.00 g were first examined by XRD, as shown in Fig. 1. It can be clearly seen that in absence of NaOH during the synthesis process, the diffraction peaks of the as-obtained product can be indexed as a mixture of the α-phase