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Controllable synthesis of β-$NaLuF_4$:Yb^{3+}, Er^{3+} nanocrystals and their application in polymer-based optical waveguide amplifiers

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ABSTRACT

Hexagonal structured $NaLuF_4$ (β-type) nanocrystals (NCs) with controllable particle size were prepared by thermal decomposition approach. The as-prepared NCs possessed good dispersibility in organic solvents. Under a 980 nm laser excited, these Er^{3+} and Yb^{3+} co-doped β-$NaLuF_4$ NCs demonstrated emission around 1530 nm. These β-$NaLuF_4$:Yb^{3+}, Er^{3+} NCs were dispersed into SU-8 polymer to fabricate polymer waveguides, and the results showed that their crystal size influenced greatly on the performance of polymer waveguides. The relative optical gain of 2.413 dB, 1.653 dB and 0.481 dB at 1530 nm was achieved when the particle size was about 8 nm, 15 nm, and 23 nm, respectively. These results show that β-$NaLuF_4$:Yb^{3+}, Er^{3+} NCs with small particle size were promising materials for building Er^{3+}-doped polymer-based optical waveguide amplifiers.

1. Introduction

Erbium (Er^{3+}) doped waveguide amplifier has been investigated widely due to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition (~1530 nm) of Er^{3+} ions, which matches one of the low loss windows of optical fibers in optical communication networks [1–3]. Compared to traditional Er^{3+} doped waveguide amplifier based on silicon substrate, Er^{3+}-doped polymer-based optical waveguide amplifiers could afford high gain in a much smaller device size [3–6]. Recently, Er^{3+} doped inorganic nanocrystals (NCs) dispersed into polymer matrices to fabricate polymer-based optical waveguide amplifiers have been attracting more and more attentions because of their relatively low phonon energy of crystal lattice of inorganic NCs, which dramatically decreases the negative effect to luminescence coming from high-energy vibrations of organic host, such as –OH and C–H. In addition, the compatibility between inorganic NCs and polymer matrices can be simply solved by the surface modification of NCs.

For real applications in polymer-based optical waveguide amplifiers, Er^{3+} doped NCs should possess several features like, small crystalline size, good dispersibility in polymer matrices and highly efficient emission at 1530 nm. The lowing of particle size can decrease the loss caused by scatters [7]. The good dispersibility in polymer matrices can increase the doping percentage of NCs in the polymer matrix and reduce their transmission loss [8]. The high emission efficiency around 1530 nm would cause high optical gain for polymer-based optical waveguide amplifiers [7]. To meet the above requirements, the synthesis method, surface modified ligands and host materials of NCs need to be carefully designed. Among the NCs host materials, fluorides are considered to be the best for rare earth doping due to their low phonon energy [6,7,9]. Thermal decomposition method has been used to synthesize Er^{3+} doped fluoride NCs with small sizes [10–12]. Meanwhile, by using oleic acid (OA) as the surfatant, the prepared Er^{3+} doped fluoride NCs could be easily dispersed in nonpolar solvents such as cyclohexane [13–16]. In recent years, β-$NaLuF_4$ has been found to be more efficient host lattice than β-$NaYF_4$ for Er^{3+} doped up-conversion luminescence materials, especially for high-order photon up-conversion [16–20]. So far, optical gains have been obtained from several Er^{3+}-doped NCs, such as LaF_3:Yb^{3+}, Er^{3+} [6,21–24], $NaYF_4$:Yb^{3+}, Er^{3+} [7,25], $BaYF_5$:Yb^{3+}, Er^{3+} [10,11] and $LiYF_4$:Yb^{3+}, Er^{3+} [12], doped polymeric optical waveguide amplifiers. To our knowledge, optical gains have not been obtained from polymer waveguide including Er^{3+}-doped $NaLuF_4$ NCs.

In this work, Er^{3+} and Yb^{3+} co-doped β-$NaLuF_4$ NCs with different size were synthesized via thermal decomposition using OA as the surfatant. Optical polymer waveguides were fabricated

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by doping these NCs into SU-8 polymer as the core layer and PMMA as the coating layer. The maximum relative optical gain of 2.413 dB at 1530 nm was achieved in 8-nm $NaLuF_4$:Yb^{3+}, Er^{3+} NCs doped polymer waveguides with 12 mm long for a pump power of 150 mW.

2. Experimental

2.1. Chemicals

All chemicals were of analytical grade and used without further purification. $LuCl_3{\cdot}6H_2O$ (99.999%), $YbCl_3{\cdot}6H_2O$ (99.999%), $ErCl_3{\cdot}6H_2O$ (99.999%), NH_4F (98%) were supplied by Shanghai Chemical Reagent Company. 1-Octadecene (ODE, 90%), oleylamine (OM), sodium oleate and oleic acid (OA, 90%) were supplied by Alfa Aesar.

2.2. Synthesis of $NaLuF_4$:Yb^{3+}, Er^{3+} NCs

$NaLuF_4$:Yb^{3+}, Er^{3+} NCs were synthesized via thermal decomposition method. Briefly, 6 mL OA, 9 mL ODE and 1 mmol $RECl_3{\cdot}H_2O$ (RE = Lu, Yb, Er) with a molar ratio of Lu/Yb/Er = 80:18:2 were added into 100 mL four-neck round-bottom flask. The solution was stirred magnetically and heated to 150 °C for 60 min under argon atmosphere. The heating was stoped and the solution was cooled to room temperature. 8.5 mL OM and 0.76 g sodium oleate were added into the flask and the resulting mixture was stirred for 20 min at 90 °C under argon. After the solution cooled to room temperature, 0.1382 g NH_4F was added into the flash. The solution was heated to 320 °C quickly and kept for 60 min. Subsequently, the mixture was cooled to room temperature, and the NCs were centrifugated, washed, and dried. The obtained powder could be redispersed in toluene, chloroform, or cyclohexane. Furthermore, the size of $NaLuF_4$ NCs was controlled by tunning the volume ratio of OM:OA:ODE (8:6:9, 7:6:10, 6:6:11).

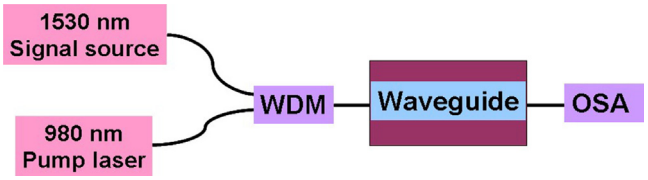

Fig. 1. Schematics of the experimental system for the optical gain measurement.

2.3. Fabrication of optical waveguide amplifiers

By dispersing β-$NaLuF_4$:Yb^{3+}, Er^{3+} NCs into SU-8 polymer matrix, polymer-based optical waveguide amplifiers were fabricated and their performances were studied. Firstly, SU-8 polymer was diluted into toluene. Then, β-$NaLuF_4$:Yb^{3+}, Er^{3+} (0.5 wt%) were added into the above solution, and it was dissolved at room temperature by ultrasonic treatment for 24 h. Waveguides were fabricated by standard photolithography and wet etching technology. Silicon wafer with a thin silicon dioxide layer was used as substrate. The SU-8 polymer dispersed with β-$NaLuF_4$:Yb^{3+}, Er^{3+} NCs was spin coated on the silicon dioxide layer. Then, the waveguide channels were cured by the photo mask using UV light at a 365 nm for 5 s and then baked at 90 °C for 20 min. Finally, a thin PMMA was used as the top cladding.

2.4. Characterizations

The phase identification of the as-prepared products were analyzed via X-ray diffraction (XRD) (Model Rigaku RU-200b) using nickel-filtered Cu-*K*a radiation (λ = 1.5406 Å). The size and morphology were characterized by transmission electron microscopy (TEM) (JEOL 600) with an acceleration voltage of 100 kV. The sample was prepared by placing a drop of dilute cyclohexane dispersion of NCs on a carbon film supported on a copper grid. These $NaLuF_4$:Yb^{3+}, Er^{3+} NCs were excited by using a power-adjustable laser diode

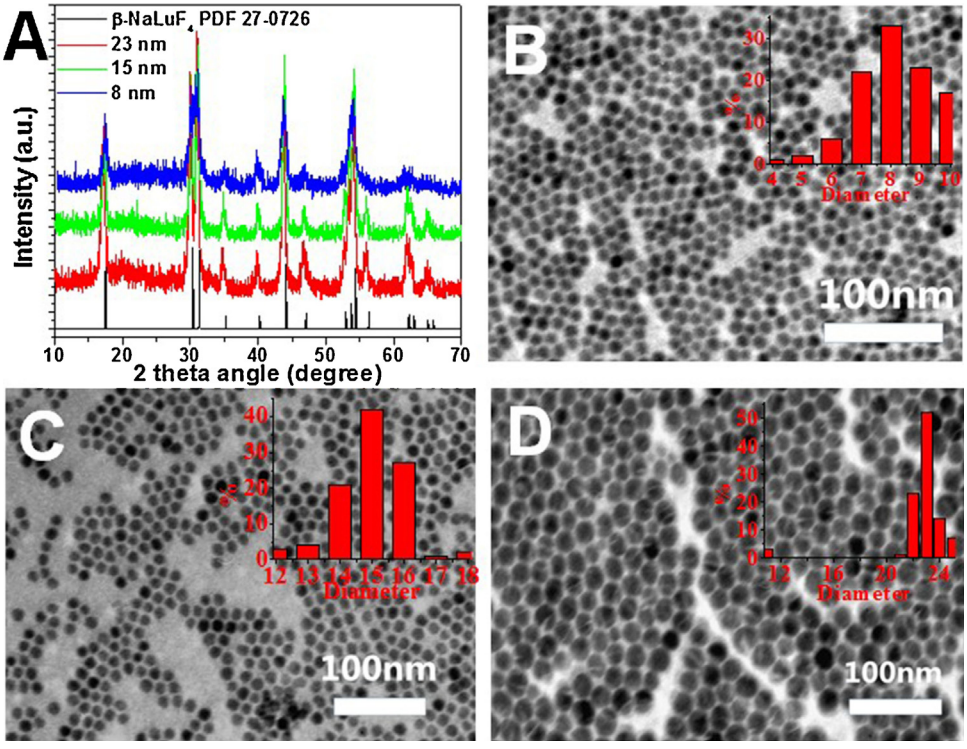

Fig. 2. Powder XRD patterns (A) and TEM images of β-$NaLuF_4$ NCs: 8 nm (B), 15 nm (C), and 23 nm (D). The size distribution plots were shown in insets of B, C, D.