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Synthesis of novel branched β-$NaLuF_4$: Yb/Er upconversion luminescence material and investigation of its optical properties

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ABSTRACT

Branched β-$NaLuF_4$: Yb/Er was synthesized using a simple hydrothermal method by controlling the NaF/Ln molar ratio. In contrast to the β-$NaYF_4$: Yb/Er hexagonal disks, the branched β-$NaLuF_4$: Yb/Er has stronger emission intensity. The integrated intensities of green and red emission bands were as 6.2 and 3.3 times as that of $NaYF_4$, respectively. The branched β-$NaLuF_4$: Yb/Er has the smaller unit cell volume, the higher absorption intensity around 980 nm and the lower crystal field symmetry than $NaYF_4$, which made a significant contribution to the stronger upconversion (UC) fluorescence emissions. The results indicate that the branched β-$NaLuF_4$: Yb/Er is an excellent UC luminescence material. The current research has a great potential in improving near-infrared conversion efficiency of solar cells.

1. Introduction

The upconversion luminescent materials have a wide range of technological applications in lasers [1], three-dimensional color displays [2], fluorescent biolabels [3], especially in solar cell applications because of their ability to convert two or more low energy photons to one high energy photon [4–6]. Among all the UC materials, the hexagonal β-$NaYF_4$ crystals, with various dimensions and morphology, have been investigated extensively. Compared to the $NaYF_4$ host, $NaLuF_4$ might be a better host lattice for UC luminescence materials. P. Rambaldi and C. Maunier compared the emission properties of Y- and Lu-containing oxide and fluoride crystals, and found that the Lu crystals emit more intense UC emission due to the intensity-borrowing mechanism mixing the 4f and 5d orbital of the Ln^{3+} ions via the lattice valence band level [7]. In 2012, Tianshe Yang [8] reported that 20 nm α-$NaLuF_4$ nanocrystals shown about 10 times stronger UC emission than 20 nm β-$NaYF_4$ in cyclohexane solution. Enjie He demonstrated that the local crystal field symmetry was lower in $NaLuF_4$ than that for $NaYF_4$, which lead to the stronger fluorescence emissions [9]. So, lutetium could be a more favorable cation than yttrium for trivalent lanthanide dopant emission.

β-$NaLuF_4$: Yb/Er upconversion materials with excellent optical properties, have attracted more and more attention of researchers [10–12]. In 2013, Wang et al. systemically compared the variation of size, structure and the overall UC intensity of $NaYF_4$: Yb/Er and $NaLuF_4$: Yb/Er nanoparticles (NPs) samples prepared at different temperatures. The results shown that the emission intensity of $NaREF_4$: Yb/Er NPs depend strongly on particle size of samples [11]. Many methods have been used to synthesis different morphology $NaLuF_4$-based crystals. For instance, β-$NaLuF_4$: Yb, Tm nanoplates are synthesized by a thermal decomposition method using oleic acid as a chelating agent and shape modifier [13]. β-$NaLuF_4$ nanorod bundles have been prepared by a urea-assisted precipitation process [14]. Different morphologies of upconversion material have different optical properties because the bonding, surface energy and chemical reactivity are directly related to their surface morphology [15,16]. So, the rational control of the crystal size and morphology is crucially important to obtain the efficient upconversion materials. For photovoltaic (PV) applications, microcrystals should be favored due to the strong UC luminescence. In addition, phase control is also crucially important, as the properties of materials are determined first by their phases.

In this work, the branched β-$NaLuF_4$: Yb/Er was synthesized by a simple hydrothermal method using sodium citrate as a stabilizing agent. Stronger UC fluorescence emissions are observed when the morphology is branched. The effects of the NaF/Ln molar ratio on the crystal structures, morphology, and luminescence properties of the products are discussed. A possible growth mechanism was proposed for the formation of branched β-$NaLuF_4$: Yb/Er.

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2. Experimental section

2.1. Materials

All the chemical reagents used in this experiment are analytical grade without further purification. Lu_2O_3 (99.99%) (99.99%), Yb_2O_3 (99.99%), Er_2O_3 (99.99%), NaF and sodium citrate were purchased from Tianjin Guangfu Fine Chemical Research Institute. Water used in the experiment was purified to a resistivity of 18.2 MΩ.

2.2. Preparation of branched β-$NaLuF_4$: Yb/Er microcrystals

The branched β-$NaLuF_4$: 18%Yb/2%Er, microcrystals were synthesized by a simple hydrothermal procedure [17]. In a typical process, Lu_2O_3, Er_2O_3 and Yb_2O_3 were dissolved in 38% HCl to yield (0.2 M) $LuCl_3$, $ErCl_3$ and $YbCl_3$ respectively. $LnCl_3$ (Ln = Lu^{3+}, Yb^{3+}, Er^{3+}) solutions was mixed with Sodium citrate at the molar ratio of 1:1, and then added anhydrous ethanol under vigorous stirring. Subsequently, different amounts of NaF were added into the above solution. The resulting mixture was transferred into a 100 ml stainless Teflon-lined autoclave, which was sealed and heated at 200 °C for 24 h in an electric drying oven. The reaction mixture was centrifuged for 10 min at a speed of 4000 rpm, the precipitate was washed with deionized water and ethanol three times respectively and vacuum dried at 80 °C for 8h. To investigate the fluorescence emission properties of $NaLuF_4$-based and compare the difference between $NaLuF_4$-based and $NaYF_4$-based samples, $NaYF_4$: 18%Yb/2%Er hexagonal disks samples were synthesized with the same method using ethylenediamine tetraacetic acid disodium salt (EDTA) as a chelating agent.

2.3. Characterization

The crystal structures of the products were determined using X-ray diffraction (XRD, Rikaku, ATX-XRD) with Cu K (alfa) radiation (λ = 1.5405 Å) in a θ −2 θ mode. Scanning electron microscopy (SEM) images were recorded on a Jeol JSM-6700F to investigate the morphology of the material. Combined with an integrating sphere diffuse reflection in a single beam system, ultraviolet–visible–near-infrared (UV–Vis–NIR) absorption spectra were recorded using a shimadzu UV–Vis–NIR spectrophotometer model NO. UV-3600 PV. The UC emission spectra of the powder samples were measured on a Fluorolog-3 luminescence spectrometer under a 980 nm laser excitation with a power density of 0.03 W/mm^2. All the measurements were performed at room temperature.

3. Results and discussion

The crystal structures and the phase purity of the as-prepared products were examined by XRD, as shown in Fig. 1. The samples of $NaLuF_4$:18%Yb/2%Er were prepared at the molar ratio of NaF/Ln = 6 and 12 respectively. From the XRD pattern, we can see that at NaF/Ln = 6, the as-prepared product is a mixture of the minor cubic (α) phase (JCPDS card 27–0725) and the predominant hexagonal (β) phase (JCPDS card 27–0726). Among them, the diffraction peaks corresponding to the stars in the graph belong to the cubic phase. When the molar ratio of NaF/Ln is increased to 12, the α-phase transfers completely to the β-phase, the corresponding products are pure hexagonal $NaLuF_4$. The sharp diffraction peaks indicate the good crystallization of the products. As reported in the literature 14, the excessive fluoride source in a hydrothermal process is beneficial to the formation of β-phase $NaLuF_4$.

To confirm the result, the morphology of the as-synthesized samples were further characterized by SEM and shown in Fig. 2. It can be seen that the NaF/Ln molar ratio has a significant influence on the morphology of the $NaLuF_4$ crystals. At NaF/Ln = 6, the sample shows two distinct particle morphology that include small nanoparticles and large

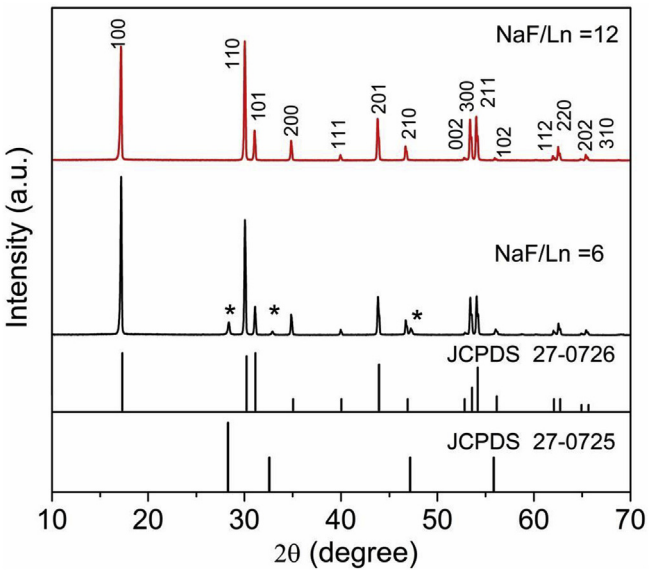

Fig. 1. The XRD pattern of the $NaLuF_4$: Yb/Er as-prepared at different NaF/Ln molar ratio.

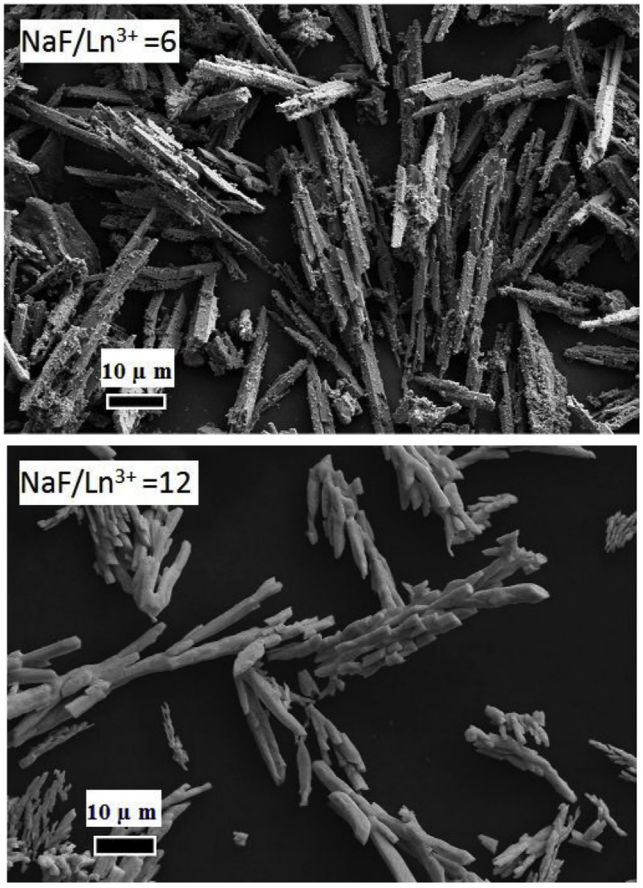

Fig. 2. The SEM images of the as-synthesized samples $NaLuF_4$: Yb/Er with different NaF/Ln molar ratio.

microtube with open ends, the outer surfaces of the tube form a hexagonal prism, well consistent with the presence of two phases observed by X-ray powder diffraction. However, when other experimental conditions are identical and the NaF/Ln molar ratio is 12, the crystal structures and shapes of the products are quite different from the former, as prepared sample presented a novel branched shape.