Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Preparation, upconversion luminescence, and solid-state NMR studies of water-soluble hexagonal NaScF₄:Yb/Er microcrystals



ALLOYS AND COMPOUNDS

霐

Mingshun Yang ^{a, b}, Jinjun Ren ^{a, *}, Ruili Zhang ^{a, b}

^a Key Laboratory of Materials for High Power Laser, Shanghai Institute of Optics and Fine Mechanics, CAS, Shanghai 201800, China ^b University of Chinese Academy of Science, Beijing 100049, China

ARTICLE INFO

Article history: Received 17 January 2017 Received in revised form 14 April 2017 Accepted 19 April 2017 Available online 19 April 2017

Keywords: NaScF4 Upconversion luminescence Solid-state NMR

ABSTRACT

Water-soluble hexagonal NaScF₄:Yb/Er upconversion microcrystals (UCMCs) were synthesized using the hydrothermal method. The upconversion photoluminescence properties of NaScF₄:xYb/2%Er microcrystals (x = 4-20%) were characterized under a 980-nm-wavelength laser excitation. The dependence of red/green (R/G) ratio on the concentration of Yb³⁺ ions was investigated. The local environments of dopant ions (Yb³⁺, Er³⁺) in NaScF₄ were studied using multiple solid-state nuclear magnetic resonance (NMR) techniques. The ¹⁹F single pulse and ¹⁹F{²³Na} and ¹⁹F{⁴⁵Sc} rotational echo double resonance (REDOR) techniques proved that the dopant rare-earth ions (Yb³⁺, Er³⁺) preferred to substitute Na⁺ rather than Sc³⁺ ions. Such solid-state NMR techniques provide a novel approach to study new phosphors.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Lanthanide ions (Ln^{3+}) -doped upconversion nanoparticles (LDUCs) have been of significant interest, owing to their promising use in displays, solar energy devices, bioimaging, photothermal therapy devices, and fluorescent biolabels [1-6]. Unlike traditional fluorescent labels, upconversion (UC) nanomaterials have many advantages, such as low toxicity, narrow emission bandwidths, large anti-Stokes shifts, good chemical stability, and smaller photodamage incurred to biological tissues [7]. Especially, excitation using near infrared (NIR) sources can significantly minimize the auto-fluorescence background associated with biological tissues, reduce light scattering, and increase the penetration depth [8–10].

Among the lanthanide-based host materials observed to date, fluorides have received the most attention owing to their exceptional chemical stability and low phonon energies, which can reduce non-radiative transitions and increase the UC efficiency [11–14]. Compared with bulk materials, nanoparticles (NPs) have low quantum yield and weak emission intensity owing to surface defects or vibrational deactivations caused by ligands [15]. For biolabeling and imaging applications, small UC nanocrystals (NCs) with intensive red emission characteristics are preferred. Therefore, enormous efforts have been devoted to pursuing synthesis methods to control the size and phases of UCNCs, and to increase their red emission. The size and phases are typically adjusted by varying the reaction time, temperature, and the ratio between starting materials [16-21]. The methods to increase the red UC emission have been mainly based on host lattice manipulation by codoping cations [22], surface-plasmon coupling [23], energytransfer modulation [24,25], and UC core-shell nanostructures [15]. Codoped cations can reduce the inter-ionic distance between activators and sensitizers and the distortion of the crystal structure, yielding a stronger UC emission [26,27]. Luminescence concentration quenching has been widely observed in lanthanide-based UC materials, which sets a limit on the amount of lanthanide emitters that can be used to produce luminescence, resulting in a low UC efficiency. Recently, efforts have been made to achieve high dopant concentrations in UCNCs. Prasad et al. [28] used organic dye sensitization to alleviate concentration quenching. The optimal doping concentration of Nd³⁺ in colloidal NaYF₄:Nd UCNCs was increased from 2 mol% to 20 mol%, when an energy harvestor organic dye was anchored onto the nanoparticle's surface, resulting in a nearly tenfold increase in the UC brightness. Almutairi et al. [29] reported that after inert epitaxial shell growth, Er³⁺ concentrations in NaY(Er)F₄/NaLuF₄ core/shell NCs could reach as high as 100 mol%. The NCs exhibited enhanced UC and downshifted luminescence intensity, with negligible concentration quenching effects.



^{*} Corresponding author. E-mail address: renjinjunsiom@163.com (J. Ren).

UC core-shell nanostructures exhibit enhanced luminescence because the shells can shield dopant ions and inhibit defect sites on the particle surfaces from luminescence quenching. Ansari et al. [15] designed and synthesized aqueous dispersible NaYF₄:Yb/ Er@NaYF₄ core/shell NPs using the hydrothermal approach. The UC luminescence intensity was remarkably improved (~10 times) after the formation of a NaYF₄ layer. Zhang et al. [30] reported a novel mechanistic strategy for controlling and modifying the photon emission of lanthanides in a core-shell nanostructure using interfacial energy transfer, and realized efficient UC emissions from a series of lanthanide emitters (Eu³⁺, Tb³⁺, Dy³⁺, and Sm³⁺) in these core-shell NPs. Alivisatos et al. [31] unraveled the relationship between quantum yield and shell thickness, and quantified surface quenching rates for the relevant Er^{3+} and Yb^{3+} energy levels by tuning the shell thickness of β -NaLuF₄ around β -NaYF₄ NCs.

Besides increasing the UC emission, core-shell structures were also used to construct devices with specialized characteristics. Feng et al. [32] prepared a carbon-coated core-shell UC nanocomposite NaLuF₄:Yb/Er@NaLuF₄@Carbon and used the material for real-time monitoring of microscopic temperature in photothermal therapy. Boyer et al. [33] synthesized core/shell NaYF₄:Yb/Tm@NaYF₄@dendrons NCs and used them for fluorescence medical imaging applications. Haase et al. [34] synthesized 10-nm-diameter β -NaYF₄:Yb/Er@NaYF₄ core/shell UCNCs with 5-nm-diameter particle cores by controlling the ratio of sodium ions to rare-earth ions. The UCNCs appear to be promising for biolabeling and imaging.

Scandium (Sc) is a unique rare-earth element with a distinct electron configuration and smallest ionic radius. Thus, optical properties of Sc-based UCNCs differ from those of other rare-earth (Y, La-Lu) based NCs [16,25,35-37]. However, Sc-based hosts have got some attention just in the last five years. Er^{3+}/Yb^{3+} co-doped NaYF₄ were found to be one of the most efficient UCNCs, with luminescence in the green region (520-550 nm) [35,38,39], while $\mbox{Er}^{3+}/\mbox{Yb}^{3+}$ co-doped \mbox{NaScF}_4 NCs usually exhibit strong red UC luminescence at 660 nm [17,36,40]. Huang et al. [17,18,41] synthesized Na_xScF_{3+x} NCs using the thermal co-precipitation method, using oleic acid (OA) and 1-octadecene (ODE) as solvent. They adjusted the morphology, sizes and phases of Na_xScF_{3+x} NCs by varying the Na⁺/Sc³⁺ or OA/ODE ratio. Zhang et al. [19] synthesized monodisperse Na_xScF_{3+x} NCs via the co-thermolysis of trifluoroacetates. They tuned monoclinic-phase Na₃ScF₆ to hexagonal phase NaScF₄ by varying the Na⁺/Sc³⁺ ratio. Yang et al. [20] prepared monodisperse ScF₃ and NaScF₄ NCs/MCs employing a simple solvothermal method. The phase, morphology, and sizes of ScF₃ or NaScF₄ NCs/MCs were manipulated by the reaction conditions, including the Na/F/Sc ratio and Ln^{3+} doping. Zhao et al. [21] synthesized tetragonal LiScF₄ NCs employing a modified solvothermal method. The phase and morphology of the obtained samples were adjusted by varying the reaction time and temperature. Yang et al. [42] synthesized Sr₂ScF₇:Ln³⁺ NCs via a one-step hydrothermal route without employing any surfactants. Multiform Sr₂ScF₇ NCs/ MCs were obtained by varying the pH values, F⁻ sources, and surfactants. Chen et al. [43] determined for the first time the crystal structure of NaScF₄ crystals using single-crystal X-ray diffraction. Singh et al. [44] obtained intensive red UC emission by codoping Gd³⁺ ions at Sc³⁺ sites and attaching gold (Au) NPs to the surface of NaSc_{0.8}Er_{0.02}Yb_{0.18}F₄ UCNPs. Huang et al. [45] systematically studied the morphology and UC luminescence evolution of KSc₂F₇:Yb/Er NCs via Li⁺ doping and characterized the morphology evolution and the mechanism of UC emission enhancement.

However, most of the reported synthesis methods of Sc^{3+} -based fluoride NCs were conducted in inert atmosphere and the assynthesized NCs cannot be used directly in biological applications, owing to their low aqueous solubility due to the hydrophobic capping ligands. Zhang et al. [40] first synthesized water-soluble

hexagonal NaScF₄:Yb/Er NCs with intensive red emission employing a facile hydrothermal method and using EG as solvent. Zhao et al. [36] synthesized water-soluble hexagonal NaScF₄:Yb/Er NCs using the hydrothermal method, and tuned the emission from green to red in NaScF₄:Yb/Er NCs by adjusting the reaction time. Wang et al. [46] synthesized water-soluble cubic K₂NaScF₆ NCs using the classic hydrothermal method, using PVP as a chelating agent. The crystalline phase transformation from KSc₂F₇ to K₂NaScF₆ NCs can be achieved by changing the NH₄F/RE³⁺ ratio.

UC luminescence can be affected by many factors, such as the particles' size [38,47], morphology [18–20], doping concentration [15,30,31], and substrate properties [24,26,27]. The crystal structure of the substrate is especially important in determining the luminescence characteristics, because the structure determines the strength of the crystal field around the dopant ions [13,26]. Hosts with lower symmetry typically generate crystal fields containing more uneven components around the dopant rare-earth ions than higher-symmetry hosts, which increases the f-f transition probability and subsequently the luminescence [11]. Therefore, hexagonal-phase materials usually exhibit much stronger luminescence compared with cubic-phase materials. Size matching conditions between host cations and dopant ions also affect UC luminescence efficiency. Host lattices consisting of cations with closer ionic radii to dopant ions can prevent the formation of crystal defects and lattice stress, thus reducing luminescence quenching [27]. A reduction in the cation size (or unit-cell volume) of the host can cause an increase in the strength of the crystal field around the dopant ions and lead to enhanced UC efficiency [11]. For example, the UC luminescence of bulk NaYF₄:Yb/Er is twofold stronger than that of NaLaF₄:Yb/Er [48]. Numerous studies indicate that the local environment of doped rare earth ions in the substrate crystal can significantly affect their luminescence. However, only a few reports have addressed the local structure of dopant ions.

In this work, we synthesized water-soluble hexagonal NaSc- F_4 :Yb/Er crystals employing a facile hydrothermal method. The effect of low Yb³⁺ doping concentration on the system's photoluminescence was investigated. The local environments of Yb³⁺ (Er³⁺) ions, doped in NaScF₄, were first characterized using ¹⁹F single pulse, ²³Na Triple-quantum (TQ)-MAS, ¹⁹F{²³Na} and ¹⁹F {⁴⁵Sc}REDOR double resonance techniques.

2. Experimental

2.1. Chemicals and material synthesis

The starting reagents were $Yb(NO_3)_3 \cdot 6H_2O$ (Aladdin), Er(NO₃)₃ $\cdot 6H_2O$ (Aladdin), Sc(NO₃)₃ $\cdot 6H_2O$ (Aladdin), branched polyethylenimine (PEI, 25 kDa) (Shanghai Chemical Reagent Co. Ltd.), NH₄F (Shanghai Chemical Reagent Co. Ltd.), and Ethylene glycol (EG) (Sinopharm Chemical Reagent Co. Ltd.). All of the chemicals were of analytical grade, and were used as received without further purification.

A modified hydrothermal method was used for the synthesis of NaScF₄:Yb/Er crystals [40]. In the typical procedure, 0.45 g PEI was added into 18 ml EG containing 1.5 mmol Sc(NO₃)₃·6H₂O, Yb(NO₃)₃·6H₂O and Er(NO₃)₃·6H₂O with the molar ratio of 88: 10: 2 under vigorous stirring. Then, 1.5 mmol NaCl was added into the above solution. The mixture was stirred for 30 min to form a homogeneous solution. 7.2 mmol NH₄F was added into 12 ml EG under stirring to form a transparent solution. Thereafter, the NH₄F solution was added to the mixed solution and stirred for another 20 min. Finally, the resulting solution was transferred into a 50 ml Teflon-lined autoclave, which was subsequently heated up to 200 °C and kept for 2 h, and then let to naturally cool to room temperature. The obtained precipitates were collected by

Download English Version:

https://daneshyari.com/en/article/5459084

Download Persian Version:

https://daneshyari.com/article/5459084

Daneshyari.com