



Enhancement of red upconversion emission of cubic phase NaLuF₄: Yb³⁺/Ho³⁺/Ce³⁺ nanocrystals



Wei Gao*, Jun Dong*, Jihong Liu, Xuewen Yan

School of Electronic Engineering, Xi'an University of Post & Telecommunications, Xi'an 710121, PR China

ARTICLE INFO

Article history:

Received 5 January 2016

Received in revised form 17 March 2016

Accepted 21 March 2016

Available online 24 March 2016

Keywords:

A. Optical materials

A. Fluorides

C. transmission electron microscopy (TEM)

D. Optical properties

D. Luminescence

ABSTRACT

The red upconversion emission of lanthanide-doped fluoride nanocrystals have great potential applications in color display and anticounterfeiting applications, especially for biological imaging and biomedical. In this work, a significant enhancement of red upconversion emission of Ho³⁺ ions was successfully obtained in the cubic phase NaLuF₄ nanocrystals through codoping Ce³⁺ ions under NIR 980 nm excitation. The ratio of red-to-green emission of Ho³⁺ ions was enhanced about 10-fold, which is due to two efficient cross relaxation processes derived from Ho³⁺ and Ce³⁺ ions promoted the red emission and quenched the green emission. The upconversion emission and luminescent colors of NaLuF₄: Yb³⁺/Ho³⁺ nanocrystals were carefully investigated by a confocal microscopy setup. The possible upconversion emission mechanism and conversion efficiency of cross relaxation between Ho³⁺ and Ce³⁺ ions were discussed in detail. The current study suggests that strong red emission of NaLuF₄: Yb³⁺/Ho³⁺/Ce³⁺ nanomaterials can be used for color display and anticounterfeiting techniques.

© 2016 Published by Elsevier Ltd.

1. Introduction

In recent years, lanthanide-doped upconversion (UC) fluoride materials have been widely applied in phosphors, color displays, optical storages, solid-state lasers, solar cells and biomedical imaging, which is due to the low phonon energy can effectively suppress nonradiative multiphonon relaxation processes [1–6]. Up to now, many UC fluoride materials (NaYF₄, NaLuF₄, LaF₃, LiYF₄ and NaScF₄) have been successfully prepared by different methods, including hydrothermal method, solvothermal method, high-temperature thermal decomposition of trifluoroacetate precursors and liquid-solid two-phase approaches [7–11]. Among them, NaYF₄ crystal has been considered as one of the most efficient host matrix for UC emission [12,13]. Recently, a new UC host matrix that the NaLuF₄ host matrix with same crystalline plane as NaYF₄ has been reported [14–18]. And Li's group has reported that the Yb³⁺/Er³⁺ and Yb³⁺/Tm³⁺ codoped cubic phase NaLuF₄ nanocrystals (NCs) shown about 10-fold stronger UC emission than that of corresponding hexagonal phase NaYF₄ NCs with same size [19]. As is well known, the hexagonal phase NaYF₄ and NaLuF₄ crystals are evolved from the cubic-phase ones through increasing reaction time or at a high reaction temperature [20–22]. Comparing with

the hexagonal phase NaYF₄ and NaLuF₄ crystals, the cubic phase ones can be more easily synthesized through different method. Meanwhile, their UC emission properties can be anticipated to be adjusted by an appropriate method such as changing their crystal phase, morphology and size, and so on [23]. To date, many researchers have reported that NaLuF₄ is an excellent host matrix for UC luminescence, especially nanoscale NaLuF₄ NCs [24–26].

The strong red UC emission of lanthanide-doped NCs have great potential applications in color display and anticounterfeiting applications, especially for biomedical. However, it is very difficult to obtain a pure single red UC emission from rare earth ions, which because of abundance radiative and nonradiative transition channels of 4f^N electronic states. Consequently, achieving a high-purity single red UC emission has been an increasing focus and formidable challenge. Up to now, there have many reports about obtaining a single-band UC red emission. For example, the intense red emission of Er³⁺ ions in fluoride materials have been successfully obtained by increasing Yb³⁺ ion concentrations, codoping Mn²⁺ or Pb²⁺ ions and attaching noble metal nanoparticles, etc. [27–30]. Like Er³⁺ ions, Ho³⁺ ion is also an intriguing active ion for UC emission because of its broad fluorescence spectrum ranging from vacuum ultraviolet to infrared. The enhancement of red UC emission of Ho³⁺ ions in fluoride nanomaterials, however, remain few [31–33]. In this work, we attempted to enhance red UC emission in cubic phase NaLuF₄: Yb³⁺/Ho³⁺ NCs through codoping Ce³⁺ ions. The structure and

* Corresponding authors.

E-mail addresses: gaowei@xupt.edu.cn (W. Gao), dongjun@xupt.edu.cn (J. Dong).

morphology of NaLuF₄: Yb³⁺/Ho³⁺ NCs were confirmed by x-ray diffraction (XRD) and transmission electron microscope (TEM), respectively. The spectral properties, UC mechanisms and conversion efficiency between Ho³⁺ and Ce³⁺ ions were systematically studied by a confocal microscopy setup under NIR 980 nm and 532 nm excitation. Studies on enhancing the red UC emission in NaLuF₄ NCs will further extend their applications to the three-dimensional color displays, anticounterfeiting techniques and biological images.

2. Experimental details

2.1. Synthesis of NaLuF₄: Yb³⁺/Ho³⁺/Ce³⁺ NCs

All chemicals used in the current study are analytical graded used without further purification. Ce(NO₃)₃·6H₂O (99.99%), Lu₂O₃ (99.99%), Yb(NO₃)₃·5H₂O (99.99%) and Ho(NO₃)₃·5H₂O (99.99%) are purchased from Sigma-Aldrich Chemicals Co. Lu(NO₃)₃ was prepared by dissolving the Lu₂O₃ in dilute nitric acid at elevated temperature followed by evaporating the superfluous nitric acid. NaF (Sodium fluoride, 98.0%) and EDTA (hylene-diaminraacic acid, 99.0%) with analytical grade are supplied by the Tianjin chemical reagent factory. The NaLuF₄: Yb³⁺/Ho³⁺/Ce³⁺ NCs were synthesized via a facile hydrothermal method [34]. 5.00 ml NaF (0.5 M) and 20.00 ml deionized water were mixed under vigorous stirring. Subsequently, (0.50-x) ml Lu(NO₃)₃ (0.5 M), 0.10 ml Yb(NO₃)₃ (0.50 M), 0.01 ml Ho(NO₃)₃ (0.50 M), x ml (x = 0, 0.02, 0.03, 0.04, 0.05, 0.06) Ce(NO₃)₃ (0.50 M) and 0.0931 g EDTA were slowly added into the solution under vigorous stirring 30 min. Then the mixture was slowly transferred into a 40.00 ml Teflon-lined autoclave and heated at 180 °C for 8 h. The samples were collected by centrifuging and washing with deionized water and ethanol 3–4 times, respectively, and dried at 60 °C for 12 h.

2.2. Sample characterization and spectral measurement

The structure and morphology of the samples were characterized by XRD with Cu Kα (40 kV, 40 mA) irradiation (λ = 0.15406 nm) and TEM (JEM2100, 200 kV). Fourier transform infrared spectroscopy (FTIR) was measured in the spectral range 400–4000 cm⁻¹ with a Bruker EQUINX55 spectrometer. The optical microscope (OLYMPUS-BX51) is used in the confocal setup. Ti sapphire laser (MBR-110, 700–1000 nm) and YAG: Nd³⁺ (Quanta Ray Lab-170, 10 Hz, 532 nm) pulse laser were employed as

excitation sources. The spectrometer (SP2750i, 0.008 nm) with a PIXIS 100 charge coupled device (CCD, ACTON) and a PD471 photomultiplier tube (PMT, ACTON) were used for luminescence collection and detection. All of the spectroscopic measurements were carried out at room temperature.

3. Results and discussion

3.1. Phase identification and morphology characterization

The typical XRD patterns of NaLuF₄: 20 mol%Yb³⁺/2 mol%Ho³⁺ NCs with codoping different Ce³⁺ concentrations are given in Fig. 1. All the diffraction peaks from NaLuF₄ NCs coincide well with the standard pattern of JCPDS 77-2042, which indexes to the pure cubic phase NaLuF₄ (α-NaLuF₄). In addition, it is noticed that the diffraction peaks shifted slightly to the low angle side after Ce³⁺ ions doping, which indicates the unit cell of α-NaLuF₄ expanded because Lu³⁺ (r = 0.085 nm) ions are substituted by bigger Ce³⁺ (r = 0.128 nm) ions in the host lattice [35,36].

The TEM images and EDX spectra of α-NaLuF₄: Yb³⁺/Ho³⁺ NCs with codoping different Ce³⁺ ions, as shown in Fig. 2. A series of Ce³⁺ codoped NaLuF₄:Yb³⁺/Ho³⁺ NCs are nearly monodisperse nanosphere with an average diameter of about 100 nm. With increasing Ce³⁺ ion concentrations, the morphology and size of α-NaLuF₄:Yb³⁺/Ho³⁺ NCs have no obvious effect because of the low dopant concentrations and similar ionic radius. Fig. 2(a1–c1) shows the EDX spectra of α-NaLuF₄: Yb³⁺/Ho³⁺ NCs with doping different Ce³⁺ ions, the elemental components of the samples are Lu, Na, Yb, F, Ho and Ce are clearly presented. It is noted that the peak intensity of the Lu elemental is reduced when the introduction of Ce elemental in α-NaLuF₄: Yb³⁺/Ho³⁺ NCs host lattice, which demonstrates Lu³⁺ ions occupy the lattice sites by the substitution of the Ce³⁺ ions.

3.2. FTIR spectra

The functional groups attached on the α-NaLuF₄: Yb³⁺/Ho³⁺ NCs can be identified by FTIR spectroscopy, as shown in Fig. 3. The strong absorption band around 3400 cm⁻¹ is found, which is attributed to –OH stretching vibration of adsorbed EDTA [33]. In addition, the weak bands at 1400 cm⁻¹, 1091 cm⁻¹ and 1640 cm⁻¹ can be assigned to the stretching vibration of –CH₂–, C–O and –COO– group, that originates from the EDTA, respectively [37]. These results prove the existence of EDTA on the surface of the

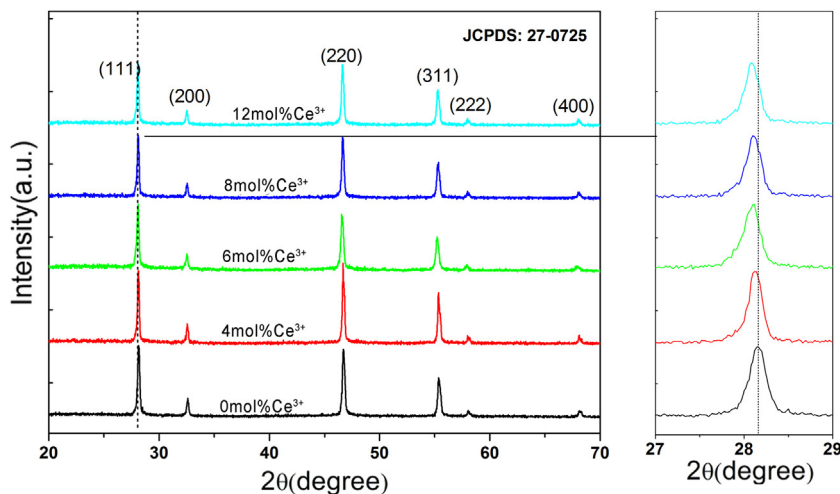


Fig. 1. XRD patterns of α-NaLuF₄: 20%Yb³⁺/2%Ho³⁺/x%Ce³⁺ NCs (x = 0%, 4%, 6%, 8% and 12%).

Download English Version:

<https://daneshyari.com/en/article/1486952>

Download Persian Version:

<https://daneshyari.com/article/1486952>

[Daneshyari.com](https://daneshyari.com)