Colloids and Surfaces A: Physicochem. Eng. Aspects 436 (2013) 386–391

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Enhanced luminescence properties of monodisperse trioctylphosphine oxide-capped Nd^{3+}-doped LaF_3 nanorods without OH groups

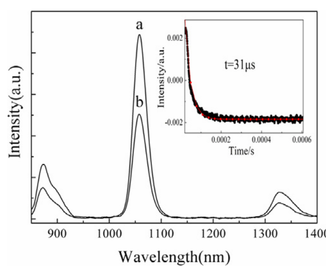
Xiaoxia Cui [a,*], Haitao Guo [a], Chaoqi Hou [a], Fei Gao [a], Zhongyue Wang [b], Wei Wei [a,b], Bo Peng [a,b,**]

[a] State Key Laboratory of Transient Optics and Photonics, Xi'an Institute of Optics and Precision Mechanics, Chinese Academy of Science (CAS), Xi'an, Shaanxi 710119, PR China
[b] Institute of Advanced Materials, Nanjing University of Posts and Telecommunications, Nanjing 210003, PR China

HIGHLIGHTS

- LaF_3:Nd/TOPO nanorods without OH groups were synthesized by thermolysis method.
- The solubility and luminescence intensity of nanorods were effectively enhanced.
- The nanorods grow along the <0 0 0 1> direction due to the special absorption of TOPO.
- The nanorods exhibit higher emission cross-section (3.22×10^{-20} cm^2).

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 23 April 2013
Received in revised form 4 July 2013
Accepted 10 July 2013
Available online 18 July 2013

Keywords:
LaF_3:Nd nanorods
Thermolysis method ;TOPO
Surface modification

ABSTRACT

Nd^{3+}-doped LaF_3 nanorods without –OH groups were synthesized via a simple thermolysis method in trioctylphosphine oxide (TOPO) solvent. FTIR spectrum indicates that TOPO molecules have been coordinated to LaF_3:Nd nanorods surface, which reduce the number of –OH groups on the nanoparticles surface effectively. The structure and morphology of as-synthesized nanorods were characterized. The possible grow mechanism of LaF_3:Nd nanorods has been also discussed in detail. The TOPO capped LaF_3:Nd nanoparticles preferentially grow along the <0 0 0 1> orientation under high temperature. Based on the absorption spectra and Judd–Ofelt theory, higher value of emission cross-section for ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition of Nd^{3+} was calculated to be 3.22×10^{-20} cm^2. The strong fluorescence intensity of LaF_3:Nd nanorods in chloroform demonstrates that these nanorods are promising luminescence materials.

1. Introduction

Nd^{3+}-doped fluorides have attracted infinite interest in recent years because of their potential optical applications in lighting displays [1,2], optical amplifiers [3] and lasers [4]. Among various fluorescent matrixes, LaF_3 with lower phonon energy was often chosen as the host of various phosphors to minimize the quenching of the excited state of rare-earth ions [5]. However, due to the high surface to volume ratio, the contribution of surface states is significant for the optical properties of nanoparticles. The photoluminescence of Nd^{3+} ions are sensitive to the surface defects including the impurities of –OH and –CH groups [6,7]. Besides these groups have similar vibration frequency with the radiative bands of the Nd^{3+} ion, heavy nonradiative-transition and lower luminescence efficiency were occurred in the presence of –OH groups. In order to decrease the number of –OH groups attached on the nanoparticles surface, some efforts

* Corresponding author. Tel.: +86 29 88887505; fax: +86 29 88865829.
** Corresponding author at: State Key Laboratory of Transient Optics and Photonics, Xi'an Institute of Optics and Precision Mechanics, Chinese Academy of Science (CAS), Xi'an, Shaanxi 710119, PR China. Tel.: +86 29 88887505; fax: +86 29 88865829.
E-mail addresses: cuixx@opt.ac.cn (X. Cui), bpeng@opt.ac.cn (B. Peng).

0927-7757/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.colsurfa.2013.07.009

including modifying the nanoparticles surface with organic surfactants [8] or heat-treating [9] have been dedicated to dehydroxylate the nanoparticles. Despite these efforts, some residual hydroxyl groups remain on the nanoparticles surface. Furthermore, it is difficult for the nanoparticles obtained by heat-treating procedures to disperse in solvents. This further limits its application in boilable and liquid laser fields. Therefore, it is necessary to explore a simple method to prepare nanomaterials without –OH groups rapidly and effectively.

TOPO, a coordinating solvent with high boil-point, has been widely used as ligand during the synthesis of quantum dots, which can prevent particle agglomeration and enhance the nanoparticles solubility [10,11]. Recently, Zhuravleva et al. [12] group synthesized Ln (Er, Ho and Tm) doped EuF_3 and $NaYF_4$ upconversion nanocrystals using TOPO as ligand. Up to date, no report has demonstrated the fabrication of low-dimensional Nd^{3+}-doped LnF_3 nanorods without –OH groups, which are expected for optoelectronic and biolable applications.

Herein, we describe a convenient process for synthesis of Nd^{3+}-doped LaF_3 nanorods using $Ln(CF_3COO)_3{\cdot}3H_2O$ as precursors, which have both metal and fluorine elements and can thermally decompose to LnF_3 nanoparticles in TOPO. The samples can be dispersed in non-polar organic solvent to form stable colloid suspension for some specific application. Moreover, –OH groups on the surface of obtained LaF_3:Nd nanorods were effectively reduced. The TOPO molecules separate the emitting Nd^{3+} centers and prevent energy transfer between them effectively. As expected, strong fluorescence intensity and larger emission cross-section were observed for TOPO capped LaF_3: Nd nanorods in $CHCl_3$ solvent. The new process offered a simple effective way to reduce –OH and improve the luminescence properties of lanthanide ions doped nanomaterials.

2. Experimental

2.1. Reagents

Trioctylphosphine oxide (TOPO) (90%), 1-octadecene (ODE) and oleic acid (OA) were purchased from Sigma–Aldrich. All of the chemicals were used as received without further purification. $Ln(CF_3COO)_3{\cdot}3H_2O$ precursors were prepared by dissolving the corresponding lanthanide oxides in trifluoroacetic acid and heating at the reflux temperature. After clear solutions were obtained, the solvent was removed under vacuum. The resulting solids were dried under vacuum at room temperature overnight and used without further purification.

2.2. Synthesis of LaF_3:Nd nanorods

The decomposition of Nd/La $(CF_3COO)_3{\cdot}3H_2O$ complex (Nd/La = 1:9) was studied by thermal analysis in N_2 atmosphere (Fig. 1). The first effect at 80–120 °C corresponds to the loss of crystal water while the second at 150–220 °C corresponds to the loss of water from the first coordination sphere, and the decomposition and evaporation of complex occurs at 285 °C. Besides, TOPO was expected to reduce the –OH groups on the nanoparticles surface and enhance the luminescence intensity of nanoparticles, which has been successfully used as both the solvent and ligand to synthesize Nd^{3+}-doped LaF_3 nanomaterials. On the basis of DTA-TG data, the subsequent decomposition of complex in TOPO melt was carried out at 310 °C.

Nd^{3+} ions-doped LaF_3 nanorods without crystal water were prepared according to Ref. [12]. In brief, a mixture of 0.8 mmol La $(CF_3COO)_3{\cdot}3H_2O$ and 0.2 mmol Nd $(CF_3COO)_3{\cdot}3H_2O$ were subjected to the drying procedure at 0.1 Pa for 2 h. Then it was transferred to a three-necked flask with liquid 5.0 g TOPO at 250 °C. To avoid

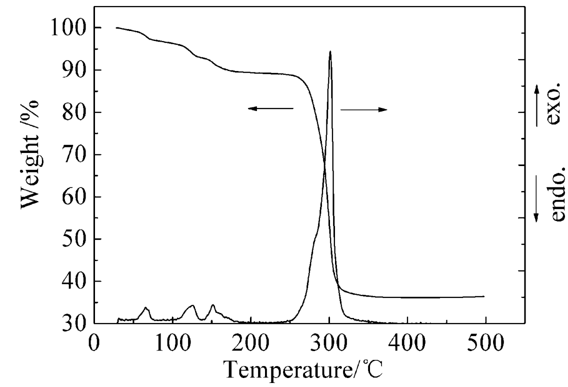


Fig. 1. Thermo gravimetric analysis study of decomposition of Nd/La $(CF_3COO)_3{\cdot}3H_2O$ in N_2 atmosphere.

the oxidation of intermediate products, all steps of synthesis were carried out in N_2 atmosphere. The solution was then heated to 310 °C with a heating rate of 5–25 °C/min to promote the decomposition of complex. With nucleation and growth of the new phase occurring in spatially constrained zone of TOPO micelles, the reaction stopped after 30 min by removing the heating and the system was cooled down to 70 °C. Subsequently, 30.0 mL methanol was added to prevent TOPO agglomeration and yield in precipitation of TOPO-capped fluoride nanorods. Finally, the precipitates were separated by centrifugation and washed with ethanol for three times. After separation by centrifugation, the nanoparticles were dried in a vacuum over P_2O_5 for 2 days. The purified nanorods capped with organic species can be dispersed in organic solvents such as hexane, chloroform and toluene.

The contrast experiment was done in another high boiling point solvent of ODE without TOPO. The OA capped LaF_3:Nd nanoparticles were prepared by co-precipitation reported in our previous work [13]. Briefly, OA (4.5 mL), NaOH (5.0 mg), 40 mL ethanol and 8.0 mL water were mixed together under stirring. Then, KF (6.0 mmol) in 4.0 mL water was added; after 30 min, La $(NO_3)_3{\cdot}6H_2O$ and $Nd(NO_3)_3{\cdot}6H_2O$ (2.0 mmol total) in 4.0 mL water was added dropwise. Finally, the solution was stirred at 75 °C for 3 h. The precipitate was separated by centrifugation and washed subsequently with water and ethanol for three times. After separation by centrifugation, the nanoparticles were dried in a vacuum over P_2O_5 for 2 days.

2.3. Instrument

The morphology of the samples was characterized by JEOL JEM-3010 transmission electron microscope under a working voltage of 300 kV. Photoluminescence (PL) emission spectra were performed by using 800 nm laser diode, a Zolix Omini-λ 300 fluorescence spectrophotometer and InGaAs1700 detector. Fourier transform infrared spectroscopy (FTIR) measurements were carried out using Perkin-Elmer FT-IR system. Thermal gravimetric analysis (TGA) was performed under N_2 atmosphere at a heating rate of 10 °C/min with a Shimadzu DTG-60H thermal analyzer. Phase identification of the samples was carried out using Rigaku D/max-2400 X-ray powder diffractometer (XRD) instrument with Cu Kα radiation λ = 1.5406 Å.

3. Results and discussion

3.1. Structures and morphologies of LaF_3:Nd/TOPO nanorods

Figs. 2a–c represent the transmission electron micrographs (TEM) of LaF_3:Nd/TOPO nanorods under different magnification.