Optical Materials 48 (2015) 86–91

Contents lists available at ScienceDirect

Optical Materials

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

Synthesis and the luminescent properties of the Nd^{3+} ions doped three kinds of fluoride nanocrystals in organic solvents

Zhuo Chen [a], Changyong Tian [b], Shuhui Bo [a,*], Xinhou Liu [a], Zhen Zhen [a]

[a] Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China
[b] Key Laboratory of Functional Crystals and Laser Technology, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China

ARTICLE INFO

Article history:
Received 19 December 2014
Received in revised form 16 July 2015
Accepted 17 July 2015
Available online 25 July 2015

Keywords:
Luminescence
Nanocrystals
Neodymium
Optical loss

ABSTRACT

Oleic acid (OA)-modified LaF_3:Nd, $NaYF_4$:Nd and CaF_2:Nd nanocrystals (NCs) with the different Nd^{3+} ion concentration (2% and 5%) have been prepared. The structure and morphology of NCs were identified by XRD, TEM, FT-IR and TGA. The size of OA-modified NC is a mean diameter of 5–10 nm and can be dispersed in common organic solvents to form a transparent solution. The optical loss of NCs in organic solvent is the first time to discuss in this work. The luminescence properties of NCs were also characterized and studied by fluorescence spectrometer. The nanoparticles in solid and in the solution all exhibited the strong emission at the 1060 nm when the materials were excited around 800 nm. Compared with the LaF_3 and CaF_2 matrix, $NaYF_4$ as the host can protect the Nd^{3+} ions more efficiently away from the nonradiative transitions. The longest luminescent lifetime of the solid $NaYF_4$:2%Nd NCs was up to 136 μs, and the little difference of the fluorescence lifetime existed between the NCs in solid state and in solution. The low optical loss in organic solvent indicated that the Nd^{3+} ions-doped fluoride NCs are promising materials for optical amplification fields.

1. Introduction

Because the neodymium (Nd^{3+}) ion has abundant pumping levels, a four-level laser operation mode and relatively higher gain cross sections, Nd^{3+} ion doped single crystals and glasses were widely used for the laser medium specifically in some high pump laser and signal source [1–3]. However, in some high-energy laser pumping situation, it was difficult to remove the excessive heat from the inside of the solid laser medium. For this reason, the solid laser medium can be easily damaged in this condition. Thus the Nd^{3+} ion containing liquid laser material which can be cooled more efficiently and had very little thermal shock damage was studied since 1960s [4–6]. One method is Neodymium oxide or chloride dispersing in the inorganic liquid just like $SeOCl_2$ and $POCl_3$ [4,5], but this solution has very strong toxicity and corrosivity, and this property limits its application severely. Another method is Nd^{3+}-doped organic polydentate cage complexes dispersing in the organic solvent [7]. The organic solvent is safer than the inorganic ones, but the C—H and O—H bands from the organic solvent and ligands can quench the luminescence of the Nd^{3+} ions easily, so the lifetime of this kind of material usually is very short and the quantum efficiency is very low [7]. Over the past few years, more and more rare-earth doped nanocrystals (NCs) are emerging with very promising properties for amplification and laser emission in active integrated optical devices [8–10]. Especially, it is worth noting that the rare-earth doped NCs can be used as the liquid laser medium by surface modifying to make the nanoparticles water-soluble or oil-soluble, and also keep the high luminescent efficiency [11,12]. The modified NCs can be dispersed into the common organic solvents or water to form a transparent solution. It has been reported that rare-earth fluoride is a kind of good host for rare-earth ions incorporation because of its low phonon energy which could in principle reduce the luminescent quenching and lead to longer luminescent lifetimes [13–18]. For these advantages, the modified Nd^{3+} ions doped NCs is a promising new kind of liquid laser medium.

In this paper, to get the Nd^{3+} ions-doped NCs in organic solvent with long luminescent lifetime, high concentration of Nd^{3+} ions and low optical loss, a series of oleic acid (OA)-modified Nd^{3+} ions-doped fluoride LaF_3:Nd, $NaYF_4$:Nd and CaF_2:Nd NCs with the different Nd^{3+} ions concentration (2% and 5%) were synthesized by using the coprecipitation synthesis method. Coprecipitation method is a simple method which can carry out at the relative low temperature and ensure the good solution of the nanocrystals. The solid NCs and the NCs in the solution all exhibited strong emission at the 1060 nm when the NCs were excited around 800 nm.

* Corresponding author.
E-mail address: boshuhui@mail.ipc.ac.cn (S. Bo).

http://dx.doi.org/10.1016/j.optmat.2015.07.025
0925-3467/

The longest luminescent lifetime of the solid $NaYF_4$:2%Nd NCs was up to 136 μs, and the lifetime of the $NaYF_4$:2%Nd NCs in hexane solution was also up to 122 μs indicating that the nanocrystals can protect the Nd^{3+} ions well from the luminescent quenching. These fluoride NCs all showed excellent dispersion ability in many common solvents, such as hexane, chloroform and toluene. As a liquid laser medium, the optical loss is also an important property, but there are few literatures reported the optical loss of this kind of materials. In this paper, the optical loss of the $NaYF_4$:2%Nd NCs hexane solutions were tested by the equipment built by ourselves, and the optical loss with different content was about 0.0446 and 0.0453 cm^{-1}, respectively. This optical loss value can meet the demand of the applications.

2. Experimental

2.1. Materials and instrumentation

Lanthanum chloride heptahydrate ($LaCl_3{\cdot}7H_2O$, 99.99%), neodymium chloride hexahydrate ($NdCl_3{\cdot}6H_2O$, 99.99%), yttrium chloride hexahydrate ($YCl_3{\cdot}6H_2O$, 99.99%), 1-octadecene ($C_{18}H_{36}$, 90%) were obtained from Sigma–Aldrich (St. Louis, USA). Sodium fluoride (NaF, 99%), sodium hydroxide (NaOH, 99%), hexane (C_6H_{14}, 99%), ethanol (C_2H_5OH, 99%), oleic acid (AR), calcium nitrate ($Ca(NO_3)_2{\cdot}4H_2O$) and hydrochloric acid (HCl, 36–38%) were obtained from Beijing Chemical Works (Beijing, China). The powder X-ray diffraction (XRD) patterns were obtained with a Bruker D8-Advance X-ray powder diffractometer, with Cu Ka radiation (λ = 1.5418 Å). The shape, size and lattice structure were characterized by transmission electron micro-scopy (TEM, JEM-2100F, JEOL). The thermal behavior of the (OA)-modified fluoride NCs were investigated using a SDT Q600 thermogravimetric analyzer with a heating rate of 10 °C min^{-1} under nitrogen atmosphere. Infrared spectra for the prepared nanocrystals were recorded in the range between 400 and 4000 cm^{-1} on a Fourier-transform spectrometer (Excalibur 3100, Varian). The photoluminescence measurements were recorded with an Edinburgh Instruments LFS920 instrument with a 450 W Xe arc lamp as the excitation source and a liquid nitrogen-cooled NIR PMT as the detector. The nanoparticle samples were excited at around 800 nm and the samples' emission were monitored at about 1060 nm. The excitation and emission spectrometer gratings are 1200 grooves mm^{-1}, and are blazed at 330 nm and 500 nm, respectively. The luminescence lifetimes were measured by the method of time-correlated single photon counting (SPC) and the data was obtained using a single-exponential decay fit.

2.2. Synthesis of the oleic acid (OA)-modified LaF_3:Nd NCs

2.2.1. Synthesis of the oleic acid OA-modified LaF_3:5%Nd NCs

NaF (1.008 g, 24 mmol) was dissolved in 80 mL of de-ionized water and 120 mL ethanol. The resulting mixture was stirred and heated to 80 °C under N_2 atmosphere. When the NaF was solved, 20 mL oleic acid was added into this mixture. When the mixture became transparent, a solution of $LaCl_3{\cdot}7H_2O$ (3.7531 g, 10.11 mmol) and $NdCl_3{\cdot}6H_2O$ (0.1908 g, 0.53 mmol) in 20 mL de-ionized water was added dropwise into the NaF solution. The mixture solution was stirred at 80 °C for 8 h and then cooled down to room temperature. 200 mL ethanol was add to the mixture, then settled through night, and collected the precipitation using the centrifugation. To remove the inorganic salt, the collected precipitation was solved into the hexane and was separated by centrifugation and the precipitation was removed. The solution was precipitated by ethanol to remove the residual oleic acid and inorganic salt, and the solution was separated by centrifugation, the precipitation of LaF_3:Nd NCs were collected. Finally, the NCs were dried in vacuum over. The final NCS can be dispersed in some common organic solvents.

2.2.2. Synthesis of the OA-modified LaF_3:2%Nd NCs

The methods of synthesis and purification of the oleic acid (OA)-modified $Nd_{0.02}La_{0.98}F_3$ NCs were just like that of $Nd_{0.05}La_{0.95}F_3$ NCs, using NaF (1.008 g, 24 mmol), $LaCl_3{\cdot}7H_2O$ (3.8716 g, 10.43 mmol) and $NdCl_3{\cdot}6H_2O$ (0.0763 g, 0.21 mmol).

2.3. Synthesis of the OA-modified $NaYF_4$:Nd NCs

2.3.1. Synthesis of OA-modified $NaYF_4$:5%Nd NCs

200 mL oleic acid was mixed with 100 mL ethanol and heated to 75 °C under a N_2 atmosphere, and NaOH (20 g, 0.5 mol) was solved into 30 mL de-ionized water, then the solution was added into the mixture. NaF (2.94 g, 0.07 mol), $NdCl_3{\cdot}6H_2O$ (0.1793 g, 0.5 mmol), and $YCl_3{\cdot}6H_2O$ (2.88 g, 9.5 mmol) were solved into 90 mL de-ionized water, and add into the mixture after 15 min. The resulting solution was stirred at 75 °C for 5 h and then cooled to the room temperature. The purification of resulting $NaYF_4$: Nd NCs was just like that of $Nd_{0.05}La_{0.95}F_3$ NCs.

2.3.2. Synthesis of the OA-modified $NaYF_4$:2%Nd NCs

The synthesis and purification of OA-modified $NaNd_{0.02}Y_{0.98}F_4$ NCs were just like that of $NaNd_{0.05}Y_{0.95}F_4$ NCs, using NaF (2.94 g, 0.07 mol), $NdCl_3{\cdot}6H_2O$ (0.0717 g, 0.2 mmol), $YCl_3{\cdot}6H_2O$ (2.97 g, 9.8 mmol).

2.4. Synthesis of the OA-modified CaF_2:Nd NCs

2.4.1. Synthesis of the OA-modified CaF_2:5%Nd NCs

NaF (1.008 g, 24 mmol) was dissolved in 180 mL of de-ionized water and 120 mL ethanol. The resulting mixture was stirred and heated to 80 °C under N_2 atmosphere. When the NaF was solved, 20 mL oield acid was added into this mixture. When the mixture became transparent, a solution of $Ca(NO_3)_2{\cdot}4H_2O$ (2.24 g, 9.5 mmol) and $NdCl_3{\cdot}6H_2O$ (0.1908 g, 0.53 mmol) in 20 mL de-ionized water was added dropwise into the NaF solution. The mixture solution was stirred at 80 °C for 8 h and then cooled down to room temperature. 200 mL ethanol was add to the mixture, then settled through night, and collected the precipitation.

2.4.2. Synthesis of OA-modified CaF_2: 2%Nd NCs

The synthesis and purification of the OA-modified $Nd_{0.02}Ca_{0.98}F_2$ NCs were just like that of $Nd_{0.05}Ca_{0.95}F_2$ NCs, using NaF (1.008 g, 24 mmol), $Ca(NO_3)_2{\cdot}4H_2O$ (2.24 g, 9.8 mmol) and $NdCl_3{\cdot}6H_2O$ (0.0763 g, 0.21 mmol).

3. Results and discussion

3.1. Structure, morphology and composition of the NCs

The XRD patterns of the NCs were shown in Fig. 1. Indexed with the standard data of LaF_3 (JCPDS card 32-0483), $NaYF_4$ (JCPDS card 39-0724) and CaF_2 (JCPDS card 65-0535), the peak station of the LaF_3:Nd NCs were consistent well with the hexagonal LaF_3 structure [19], all the reflections of the $NaYF_4$:Nd NCs were very closely with the cubic $NaYF_4$ (α-phase) structure [20], and the reflections of the CaF_2:Nd NCs were very closely with the cubic CaF_2 structure [21]. These XRD results indicated that the pure different phase structure of the small fluoride NCs were obtained. The broadening