Photoluminescence of water-soluble NdF$_3$ nanoparticles by codoping Li$^+$ or Ba$^{2+}$ ions

Ting Fan
Jiantao Lü
Na Li
Dingan Han
Photoluminescence of water-soluble NdF$_3$ nanoparticles by codoping Li$^+$ or Ba$^{2+}$ ions

Ting Fan, a Jiantao Lü, b Na Li, b and Dingan Han a

a Foshan University, School of Electronics and Information Engineering, Foshan, 528000, China
b Foshan University, School of Science, Foshan, 528000, China
E-mail: keentle@gmail.com

Abstract. Water-soluble NdF$_3$, NdF$_3$:Li$^+$, and NdF$_3$:Ba$^{2+}$ nanoparticles coated with polyvinylpyrrolidone were synthesized by a simple hydrothermal method. The products were characterized by x-ray diffraction, field-emission scanning electron microscopy, and photoluminescence spectra at room temperature. Codoping with Li$^+$ does not change the emission intensity of water-soluble NdF$_3$ nanoparticles, whereas codoping with Ba$^{2+}$ ions improves the near-infrared emissions. © 2013 Society of Photo-Optical Instrumentation Engineers (SPIE) [DOI: 10.1117/1.OE.52.2.020503]

Subject terms: luminescence; optical materials; lanthanide; nanoparticle.

Paper 121781L received Dec. 4, 2012; revised manuscript received Jan. 14, 2013; accepted for publication Jan. 18, 2013; published online Feb. 4, 2013.

1 Introduction

In recent years, water-soluble fluorescent nanoparticles have been applied often in biological label applications. Among the fluorescent nanoparticles, rare-earth ion–doped nanoparticles have played an important role. They show superior chemical and optical properties, including low toxicity, large effective Stokes shifts, sharp emission band widths of 10–20 nm, and high resistance to photobleaching, blinking, and photochemical degradation. The problem with rare-earth ion-doped nanoparticles is their weak luminescence efficiency. Consequently, a great deal of research work has been devoted to improving luminescence efficiency of rare-earth ion–doped nanoparticles.

NdF$_3$ nanoparticles have been reported to lack the concentration quenching effect and have very low photon energy. NdF$_3$ nanoparticles coated with silica shells have been used in biological detection for near-infrared (NIR) luminescence. When NdF$_3$ nanoparticles disperse in water, the luminescence intensity is weakened. Improving the photoluminescence (PL) of water-soluble NdF$_3$ nanoparticles is urgent.

It is possible to tune the emission intensity of rare-earth ions by modifying neighboring network environment by introducing other atoms into the host lattice. Commonly, incorporation of metal atoms into host lattice can distort the lattice and modify the energy absorption and transfer behaviors, resulting in increased emission intensity of rare-earth ions. The reason is that the doped metal atoms distort the local symmetry around rare-earth ions and modify the selection rules of rare earth ions.

In this study, water-soluble NdF$_3$, NdF$_3$:Li$^+$, and NdF$_3$:Ba$^{2+}$ nanoparticles coated with polyvinylpyrrolidone (PVP) were synthesized by a facile hydrothermal method. Morphology and luminescence properties were studied. In comparison with NdF$_3$ nanoparticles, codoping with Ba$^{2+}$ ions improves the NIR emissions of NdF$_3$, whereas codoping with Li$^+$ ions does not appreciably change the emission intensity. The reason for the phenomena is discussed below.

2 Methods

NdF$_3$ and NdF$_3$/PVP nanoparticles were prepared via a hydrothermal method previously described. The NdF$_3$:Li$^+$/PVP nanoparticles were prepared by adding 0.3 g PVP and 5% LiNO$_3$ into the solution, and NdF$_3$:Ba$^{2+}$/PVP nanoparticles were prepared by adding 0.3 g PVP and 5% BaCl$_2$ into the solution.

The powder x-ray diffraction (XRD) patterns were tested by Philips PW1830 diffractometer using Cu K$_\alpha$ radiation at 40 kV and 40 mA. The morphologies were imaged with field-emission scanning electron microscopy (FE-SEM) (Nova NanoSEM 430) operating at 10 kV. The PL spectra were measured at room temperature through a spectrometer (Jobin-Yvon Triax320) with an 808-nm laser diode as excitation source recorded with a liquid nitrogen–cooled InGaAs detector.

3 Results

Figure 1 shows the typical XRD patterns of the synthesized nanoparticles. All the diffraction peaks are well matched with theoretical data for hexagonal-phase structure of NdF$_3$, with lattice constants $a = 0.7030$ nm and $c = 0.7199$ nm (Joint Committee on Powder Diffraction Standards no. 9-416). No other impurity peaks were detected. These results indicate that the coating of PVP does not change the hexagonal phase of NdF$_3$ nanoparticles and the codoping Li$^+$ and Ba$^{2+}$ ions completely entered the

---

Fig. 1 XRD patterns of NdF$_3$, NdF$_3$/PVP, NdF$_3$:Li$^+$/PVP, and NdF$_3$:Ba$^{2+}$/PVP nanoparticles.
host lattice without formation of any additional phase at codoped concentrations.

The FE-SEM images of NdF₃, NdF₃/PVP, NdF₃:Li⁺/PVP, and NdF₃:Ba²⁺/PVP nanoparticles are shown in Fig. 2. The NdF₃ particles are monodisperse nanoplates, as shown in Fig. 2(a). The diameter of the plates is estimated to be in the range of 80–120 nm, whereas the thickness is about 30 nm. When coating with water-soluble PVP, the morphology of the nanoplates is nearly the same as that of the former particles, as shown in Fig. 2(b). Then codoped with Li⁺ ions, as shown in Fig. 2(c), the morphology does not have any distinct change compared to Fig. 2(b). When codoped with Ba²⁺, the morphology has changed, as shown in Fig. 2(d): the diameter of the nanoparticles became more uniform and decreased to about 60 nm, while the thickness has not changed, indicating that Ba²⁺ ions inhibit the growing of nanoplates in the direction of the plane. The smaller size of NdF₃:Ba²⁺/PVP nanoparticles is of benefit for the use of biological labels.

The PL spectra of the nanoparticles under 808-nm laser excitation at room temperature are shown in Fig. 3. The spectra represent the main transition of Nd³⁺ ions at 1060 nm corresponding to ⁴F₃/₂ → ⁴I₁₁/₂ channel. The coating of PVP layer increases the PL intensity of NdF₃ at 1060 nm by 16%. The increase is perhaps due to the PVP layer, which prevents the energy losses from surface quenching of NdF₃ nanoparticles.¹¹

4 Discussion

When codoping with Li⁺ ions into NdF₃/PVP nanoparticles, the NIR emission intensity does not have any appreciable change, unlike the PL enhancement we reported in Y₂O₃ nanocrystals codoped with Li⁺ ions. But when divalent ions Ba²⁺ are codoped into NdF₃/PVP nanoparticles, the NIR emission intensity increases further by 25% at 1060 nm.

Codoping of Li⁺ ions (5%) did not change the emission intensity of NdF₃/PVP nanoparticles, whereas codoping of Ba²⁺ ions (5%) enhanced the NIR emission. The results could be due to the different ionic radius. The ionic radius for Li⁺, Ba²⁺, and Nd³⁺ ions are 76, 135, and 98.3 pm, respectively. Ba²⁺ ions have large ionic radii which might distort the lattice network of Nd³⁺ ions in NdF₃, resulting in the enhanced PL intensity. The smaller Li⁺ ions might be unable to distort the lattice network of Nd³⁺ ions in NdF₃ enough to influence the PL intensity.

5 Conclusions

We have presented a simple synthesis method of water-soluble NdF₃/PVP, NdF₃:Li⁺/PVP, and NdF₃:Ba²⁺/PVP nanoparticles by coating with a layer of hydrophilic polymer PVP via hydrothermal method. Codoping with Li⁺ ions does not change the emission intensity of water-soluble NdF₃ nanoparticles, whereas codoping with Ba²⁺ ions improves the NIR emissions.

Acknowledgments

This work was supported by Foundation for Distinguished Young Talents in Higher Education of Guangdong Province, China (No. 2012LYM_0131) and National Natural Science Foundation of China (No. 61008063).

References


Fig. 2 FE-SEM images of NdF₃ (a), NdF₃/PVP (b), NdF₃:Li⁺/PVP (c), and NdF₃:Ba²⁺/PVP (d) nanoparticles.

Fig. 3 Fluorescence spectra of NdF₃, NdF₃/PVP, NdF₃:Li⁺/PVP, and NdF₃:Ba²⁺/PVP nanoparticles under 808-nm laser excitation.

