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Abstract. Water-soluble NdF_3 , $\text{NdF}_3:\text{Li}^+$, and $\text{NdF}_3:\text{Ba}^{2+}$ 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^+ ions 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]

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1 Introduction

In recent years, water-soluble fluorescent nanoparticles have been applied often in biological label applications.^{1,2} 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.³ 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.^{4,5}

NdF_3 nanoparticles have been reported to lack the concentration quenching effect and have very low phonon energy.⁶ NdF_3 nanoparticles coated with silica shells have been used in biological detection for near-infrared (NIR) luminescence.⁷ 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.^{8–10}

In this study, water-soluble NdF_3 , $\text{NdF}_3:\text{Li}^+$, and $\text{NdF}_3:\text{Ba}^{2+}$ 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.⁹ The $\text{NdF}_3:\text{Li}^+/\text{PVP}$ nanoparticles were prepared by adding 0.3 g PVP and 5% LiNO_3 into the solution, and $\text{NdF}_3:\text{Ba}^{2+}/\text{PVP}$ 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 $\text{Cu K}\alpha$ irradiation 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

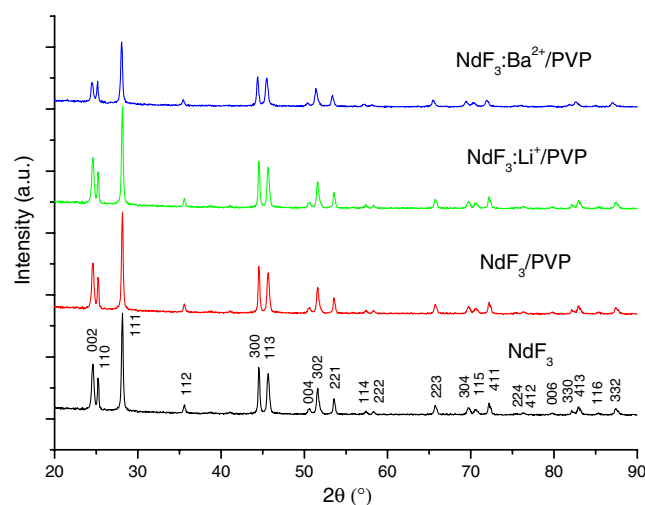


Fig. 1 XRD patterns of NdF_3 , NdF_3/PVP , $\text{NdF}_3:\text{Li}^+/\text{PVP}$, and $\text{NdF}_3:\text{Ba}^{2+}/\text{PVP}$ nanoparticles.

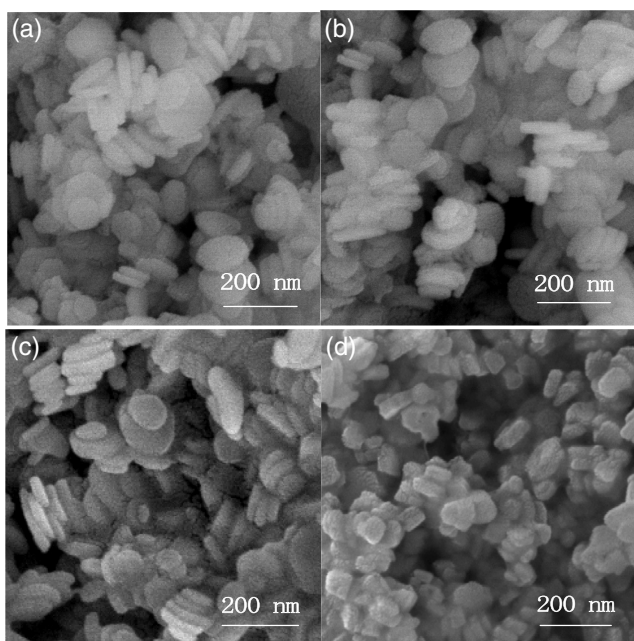


Fig. 2 FE-SEM images of NdF_3 (a), NdF_3/PVP (b), $\text{NdF}_3:\text{Li}^+/\text{PVP}$ (c), and $\text{NdF}_3:\text{Ba}^{2+}/\text{PVP}$ (d) nanoparticles.

host lattice without formation of any additional phase at codoped concentrations.

The FE-SEM images of NdF_3 , NdF_3/PVP , $\text{NdF}_3:\text{Li}^+/\text{PVP}$, and $\text{NdF}_3:\text{Ba}^{2+}/\text{PVP}$ nanoparticles are shown in Fig. 2. The NdF_3 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 Ba^{2+} , 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

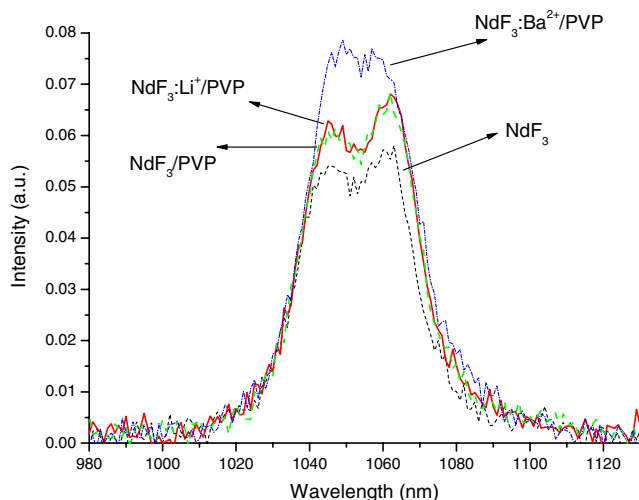


Fig. 3 Fluorescence spectra of NdF_3 , NdF_3/PVP , $\text{NdF}_3:\text{Li}^+/\text{PVP}$, and $\text{NdF}_3:\text{Ba}^{2+}/\text{PVP}$ nanoparticles under 808-nm laser excitation.

thickness has not changed, indicating that Ba^{2+} ions inhibit the growing of nanoplates in the direction of the plane. The smaller size of $\text{NdF}_3:\text{Ba}^{2+}/\text{PVP}$ 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 Nd^{3+} ions at 1060 nm corresponding to ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ channel. The coating of PVP layer increases the PL intensity of NdF_3 at 1060 nm by 16%. The increase is perhaps due to the PVP layer, which prevents the energy losses from surface quenching of NdF_3 nanoparticles.¹¹

4 Discussion

When codoping with Li^+ ions into NdF_3/PVP nanoparticles, the NIR emission intensity does not have any appreciable change, unlike the PL enhancement we reported in Y_2O_3 nanocrystals codoped with Li^+ ions. But when divalent ions Ba^{2+} are codoped into NdF_3/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 NdF_3/PVP nanoparticles, whereas codoping of Ba^{2+} ions (5%) enhanced the NIR emission. The results could be due to the different ionic radius. The ionic radius for Li^+ , Ba^{2+} , and Nd^{3+} ions are 76, 135, and 98.3 pm, respectively. Ba^{2+} ions have large ionic radii, which might distort the lattice network of Nd^{3+} ions in NdF_3 , resulting in the enhanced PL intensity. The smaller Li^+ ions might be unable to distort the lattice network of Nd^{3+} ions in NdF_3 enough to influence the PL intensity.

5 Conclusions

We have presented a simple synthesis method of water-soluble NdF_3/PVP , $\text{NdF}_3:\text{Li}^+/\text{PVP}$, and $\text{NdF}_3:\text{Ba}^{2+}/\text{PVP}$ 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 NdF_3 nanoparticles, whereas codoping with Ba^{2+} ions improves the NIR emissions.

Acknowledgments

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References

1. E. Schröck et al., "Multicolor spectral karyotyping of human chromosomes," *Science* **273**(5274), 494–497 (1996).
2. J. Kim, Y. Piao, and T. Hyeon, "Multifunctional nanostructured materials for multimodal imaging, and simultaneous imaging and therapy," *Chem. Soc. Rev.* **38**(2), 372–390 (2009).
3. F. Wang, X. J. Xue, and X. G. Liu, "Multicolor tuning of (Ln, P)-doped YVO_4 nanoparticles by single-wavelength excitation," *Angew. Chem. Int. Ed.* **47**(2), 906–909 (2008).
4. G. Wang et al., "Enhanced photoluminescence of water soluble $\text{YVO}_4:\text{Ln}^{3+}$ (Ln = Eu, Dy, Sm, and Ce) nanocrystals by Ba^{2+} doping," *J. Phys. Chem. C* **112**(44), 17042–17045 (2008).
5. R. Balakrishnaiah et al., "Effect of Al^{3+} ions on fluorescence properties of $\text{YPO}_4:\text{Eu}^{3+}$ phosphors," *Mater. Lett.* **63**(23), 2063–2066 (2009).
6. F. Bao et al., "Self-assembly of mono-crystalline NdF_3 nanostructures during hydrothermal process," *Mater. Lett.* **60**(3), 389–392 (2006).
7. X. Yu et al., "Highly efficient fluorescence of $\text{NdF}_3/\text{SiO}_2$ core/shell nanoparticles and the applications for *in vivo* NIR detection," *Adv. Mater.* **20**(21), 4118–4123 (2008).

8. T. Fan, Q. Zhang, and Z. Jiang, "Enhancement of the 1.5 μm emission in $\text{Y}_2\text{O}_3:\text{Er}^{3+}$ nanocrystals by codoping with Li^+ ions," *J. Opt.* **13**(1), 015001 (2011).
9. T. Fan, Q. Zhang, and Z. Jiang, "Enhanced near infrared emission in water-soluble NdF_3 nanocrystals by Ba^{2+} doping," *Chin. Opt. Lett.* **10**(2), 021602 (2012).
10. Y. Bai et al., "The effect of Li on the spectrum of Er^{3+} in Li- and Er-codoped ZnO nanocrystals," *J. Phys. Chem. C* **112**(32), 12259–12263 (2008).
11. G. Ghosh et al., "Synthesis and characterization of PVP-encapsulated ZnS nanoparticles," *Opt. Mater.* **28**(8), 1047–1053 (2006).