Bright-green Upconversion Emission of Hexagonal LaF$_3$: Yb$^{3+}$, Er$^{3+}$ Nanocrystals

Gejihu De, Weiping Qin,* Jisen Zhang, Dan Zhao, and Jishuang Zhang

Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Science, Changchun 130033, P. R. China

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LaF$_3$: Yb$^{3+}$, Er$^{3+}$ nanoparticles were synthesized through a simple hydrothermal method. The nanoparticles were well-crystallized and exhibited hexagonal structure with fine morphology, as indicated by powder X-ray diffraction, electron diffraction, and transmission electron microscopy. The nanocrystals present a bright-green upconversion luminescence under the 978-nm excitation of a laser diode, which provides a promising upconversion phosphor for optoelectronic or biological applications.

Fluorides doped with rare earth (RE) ions have been used in a wide range of applications such as lasers, optical communications, and display devices. The tendency towards nanoscale science attracted the interest in nano-sized optical functional materials. For fluorides, various nanostructures, such as nanotubes and nanowires, have been fabricated by hydrothermal method. With the rapid shrinking in size in optical devices, nanometer-scale fluorides may play an essential role for their applications in high-density optical data storage, underwater communication, color displays, and infrared nanosensors in the near future. Recently, BaF$_2$: Nd nanoparticles (NPs) have been synthesized by a reverse microemulsion technique. Er$^{3+}$, Nd$^{3+}$, and Ho$^{3+}$-doped LaF$_3$ NPs have also been prepared using capping agents, by which the obtained NPs are dispersible in organic solvents. Furthermore, Heer et al. have reported the highly efficient multicolor upconversion (UC) emission in transparent colloids of lanthanide-doped NaYF$_4$ nanocrystals (NCs). Meanwhile, RE-doped fluoride NCs have also been demonstrated to be a kind of promising UC fluorescence labels in biological detections.

The UC fluoride phosphors have been used to enhance the near-infrared response of silicon solar cell. Nevertheless, in practical applications, some problems still arise from either the synthesis procedure or materials quality. The crystal structure and crystallization of the host turn out to affect the optical properties of luminescent centers. Thus, it is highly desirable to develop a method for fabricating monodisperse and well-crystallized fluoride NCs. In this letter, we report the preparation of Yb$^{3+}$-Er$^{3+}$ codoped LaF$_3$ NCs and its green UC properties.

The LaF$_3$: Yb$^{3+}$, Er$^{3+}$ NCs were synthesized by a simple hydrothermal method. In typical synthesis, cetyltrimethylammonium chloride (CTAC, Aldrich) was selected as template. The rare earth solution were prepared by dissolving 0.95 mmol of La(NO$_3$)$_3$·6H$_2$O (Aldrich), 0.04 mmol of Yb(NO$_3$)$_3$·6H$_2$O (Aldrich) and 0.01 mmol of Er(NO$_3$)$_3$·6H$_2$O (Aldrich) into 12 mL of deionized water. Then 0.60 g of CTAC was completely dissolved into the rare earth solution to form clear mixture. The KF solution was obtained by dissolving 3 mmol of KF·2H$_2$O (Aldrich) into 4 mL of deionized water to provide F$^-$ ions. The KF solutions were added into the mixture under vigorous stirring to obtain the fluoride precursor. The suspension was stirred for additional 30 min before being transferred into a 25 mL Teflon-lined autoclave. After the hydrothermal treatment at 120 °C (in air) for 12 h, the precipitate was then centrifuged, washed with absolute ethanol and distilled water several times, and then dried in a vacuum at room temperature. Finally, the powder was calcined at 400 °C for 30 min in an inert atmosphere.

The phase purity of the as-prepared products was evident with X-ray diffractometry (XRD) (model Rigaku RU-200b), using nickel-filtered Cu Kα radiation (λ = 1.5406 Å). The size and morphology were characterized by TEM (JEM, 2000EX 200 kV). The UC luminescence spectra were measured with a Hitachi F-4500 fluorescence spectrophotometer under the excitation by 978-nm light from a laser diode (LD, 2W).

Figure 1 presented the XRD pattern of the as-prepared sample. All the diffraction peaks can be readily indexed to the hexagonal LaF$_3$ phase (space group $P6_3\overline{2}21$ (182)) with lattice constants $a = 0.716$, $c = 0.733$ nm, in good agreement with the standard values for the bulk hexagonal LaF$_3$ (JCPDS No. 72-1435). No impurity can be identified from the XRD pattern, suggesting that our synthesis was a promising method to prepare pure and single phased lanthanide fluorides.

The morphology of the final product was characterized by the TEM observation. As can be seen in the typical TEM images (Figure 2a), most of the particles dispersed on the copper grids show hexagonal morphology. The average edge length of the hexagon is about 15 nm. Figure 2b gives a magnified image of single LaF$_3$: Yb$^{3+}$, Er$^{3+}$ NCs. Each nanocrystal exhibits good shape with hexagonal edges. The electron diffraction patterns of the NCs are shown in Figure 3.
Figure 3. (a) Room-temperature UC emission spectra of hexagonal NCs LaF₃ : Yb⁺⁺, Er⁺⁺. (b) UC spectra of the LaF₃ : Yb⁺⁺, Er⁺⁺ NCs under the 978-nm excitation with different powers (40–140 mW). (c) The dependence of the UC luminescence intensity on the excitation power for the green emissions.

Figure 4. Schematic diagram of Yb⁺⁺-sensitized Er⁺⁺ upconversion in LaF₃ : Yb⁺⁺, Er⁺⁺ hexagonal NCs under 978-nm excitation.

(Arrows indicate the transitions from the initial levels to the final ones.)

References