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Synthesis and Upconversion Luminescence of LaF_3 : Yb^{3+} , Er^{3+}/SiO_2 Core/Shell Microcrystals

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Abstract: LaF_3: Yb^{3+}, Er^{3+} microcrystals were synthesized by a hydrothermal method, and then, the LaF_3: Yb^{3+}, Er^{3+} microcrystals were coated with silica. Phase identification of LaF_3: Yb^{3+}, Er^{3+} and LaF_3: Yb^{3+}, Er^{3+}/SiO_2 was performed via XRD. The TEM image showed that the size of LaF_3: Yb^{3+}, Er^{3+} was 150 nm and LaF_3: Yb^{3+}, Er^{3+}/SiO_2 presented clearly a core/shell structure with 20 nm shell thickness. The upconversion spectra of LaF_3: Yb^{3+}, Er^{3+} and LaF_3: Yb^{3+}, Er^{3+}/SiO_2 in solid state and in ethanol were studied with a 980 nm diode laser as the excitation source. The upconversion spectra showed that the silica shell had little effect on the properties of fluorescence of the LaF_3: Yb^{3+}, Er^{3+} microcrystals. At the same time, the green luminescence photo of LaF_3: Yb^{3+}, Er^{3+}/SiO_2 in the PBS buffer was obtained, which indicated that the LaF_3: Yb^{3+}, Er^{3+}/SiO_2 could be used in biological applications.

Key words: upconversion luminescence; LaF_3: Yb^{3+}, Er^{3+}; SiO_2; core/shell; microcrystals; rare earths

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Recently, lanthanide-doped upconversion crystals have attracted considerable attention owing to their potential application in optics[1,2], communication[3], catalysis fields[4], and especially in biological labeling[5~7]. A new generation of highly sensitive particle-based bioassays based on the upconversion luminescence technology of rare earth doped ceramic particles (UPT) has been reported[8~14]. When compared with down-conversion fluorescent organic dyes and quantum dots, upconversion luminescence has some additional advantageous features. First, upconversion emission does not occur in nature. Unlike conventional fluorescent dyes and quantum dots, up-converting phosphors transfer low energy IR radiation to high-energy visible light by the multi-photon absorption and energy transfer process, which avoids inherent autofluorescence associated with most fluorescence-based methods. Second, up-converting phosphors generate large anti-Stokes shifts that result in well-separated emission (visible region) and excitation (Near infrared region) bands[15]. Third, the different colors of upconverting phosphor can be excited simultaneously with the same IR source (980 nm), which is necessary for multiplexing[5]. Finally, the excitation of lanthanide-doped upconversion crystals is performed using a 980 nm NIR laser, which is compact, high-

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power, and inexpensive.

It is well known that the luminescence of rare earth ions is very easily quenched by high energy vibrations originating from host materials and water molecules. Therefore, a good fluorescent host matrix with low vibrational energies is important for a high efficiency of upconversion luminescence. As a promising host matrix, LaF_3 with low phonon energy has attracted considerable attention in recent years[3,16,17]. Apart from being a good host, the upconversion phosphor can be easily bioconjugated with biomolecules to exploit their peculiar properties and unique biological applications. An alternative route is growing a silica shell around the upconversion phosphor, forming the so-called core-shell structures[18]. The silica coating can improve the photo stability and biocompatibity of the crystals and the protocol for conjugation of biomolecules to the silica surface is well established.

Therefore, in this report, LaF_3: Yb^{3+}, Er^{3+} microcrystals were synthesized by a hydrothermal process, and then the microcrystals were coated with silica. The LaF_3: Yb^{3+}, Er^{3+}/SiO_2 presents clearly a core/shell structure through TEM observation. The sample displays distinct green emission under the excitation of a 980 nm diode laser. It is worth mentioning that the LaF_3: Yb^{3+}, Er^{3+}/SiO_2 can be dispersed in ethanol and PBS buffer and can be stable for six hours without the precipitate appearing, which indicates that the LaF_3: Yb^{3+}, Er^{3+}/SiO_2 has potential applications in bioimaging and biolabeling.

1 Experimental

The LaF_3: Yb^{3+}, Er^{3+} microcrystals were synthesized by the hydrothermal method. In typical synthesis, 1.5 g cetyltrimethy lammonium bromide (CTAB) was completely dissolved in 30 ml deionized water. The 2 ml deionized water containing 0.475 mmol La $(NO_3)_3 \cdot 6H_2O$, 0.02 mmol $Yb(NO_3)_3 \cdot 6H_2O$, and 0.005 mmol $Er(NO_3)_3 \cdot 6H_2O$ was added under stirring. The 1.5 mmol KF · 12 H_2O was dissolved in 2 ml water and added to the above solution to provide F^- ions. The suspension was stirred for 30 min before being transferred into a 50 ml Teflon-lined autoclave. After the hydrothermal treatment at 120 ℃ for 12 h, the precipitate was centrifuged, washed several times with absolute ethanol and distilled water, and then dried in vacuum at room temperature. The powder was calcined at 350 ℃ for 30 min in an inert atmosphere. One half of the above power was dispersed into 15 ml ethanol under vigorous stirring. Then, 200 μl deionized water and 50 μl concentrated ammonium hydroxide (25%) were added drop wise. After the solution was stirred for 30 min, 60 μl Tetraethyl orthosilicate (TEOS) was added. The mixture was stirred for 24 h. The product was obtained after centrifuging and rinsing thoroughly with ethanol and water, and was then dried in room temperature.

Phase identification was performed via X-ray diffractometry (XRD) (model Rigaku RU-200b), using nickel-filtered Cu Kα radiation (λ =0.15406 nm). The size and morphology of LaF_3: Yb^{3+}, Er^{3+} and LaF_3: Yb^{3+}, Er^{3+}/SiO_2 were characterized by TEM (JEM, 2000EX 200 kV). The upconversion emission spectra of powder and suspension (in ethanol) were performed with a Hitachi F-4500 fluorescence spectrometer. An adjustable laser diode (980 nm, 2 W) was used as the excitation source. The luminescence photo of suspension was obtained with a 980 nm diode laser continuously scanning the sample during 8-second exposure time of the digital camera after the LaF_3: Yb^{3+}, Er^{3+}/SiO_2 were dispersed into PBS (pH =7.4) for 2 h.

2 Results and Discussion

2.1 XRD analysis

Fig. 1 shows the XRD pattern of LaF_3: Yb^{3+}, Er^{3+} microcrystals and LaF_3: Yb^{3+}, Er^{3+}/SiO_2. The position and intensity of all diffraction peaks of the two samples are in good agreement with the standard values for bulk hexagonal LaF_3(JCPDS No. 72-1435). No impurity can be identified from the XRD pattern, which suggests that our synthesis is a promising method to prepare pure hexagonal phase LaF_3.

2.2 TEM observations

The morphology of LaF_3: Yb^{3+}, Er^{3+}/SiO_2 was characterized by the TEM image (Fig. 2). As seen in

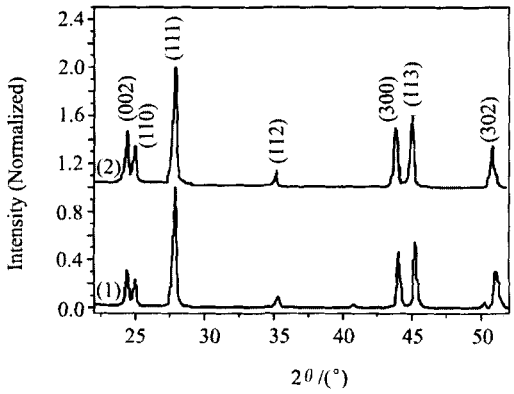

Fig. 1 XRD pattern of hexagonal LaF_3: Yb^{3+}, Er^{3+} microcrystals (1) and LaF_3: Yb^{3+}, Er^{3+}/SiO_2(2)

the typical TEM image, the size of the LaF_3: Yb^{3+}, Er^{3+} crystals is about 150 nm. It is also observed that the particle has a core-shell structure. The silica shell thickness is about 20 nm and can vary with the dosage of tetraethyl orthosilicate (TEOS) and the reaction time. At the same time, the silica shell has little effect on the properties of fluorescence of LaF_3: Yb^{3+}, Er^{3+}, as seen later. The electron diffraction pattern taken from individual LaF_3: Yb^{3+}, Er^{3+}/SiO_2 core/shell is also shown in Fig. 2 (insert in Fig. 2). The electron diffraction pattern further clearly indicates the crystalline nature of LaF_3: Yb^{3+}, Er^{3+}/SiO_2.

2.3 Upconversion emission spectra

For the LaF_3: Yb^{3+}, Er^{3+}/SiO_2 core/shell materials, bright-green luminescence could be clearly observed with naked eyes when the sample was excited by a 980 nm diode laser. This suggests that the microcrystals are promising upconversion phosphors. Fig. 3(a) presents the room-temperature upconversion emission spectra of the LaF_3: Yb^{3+}, Er^{3+} and LaF_3: Yb^{3+}, Er^{3+}/SiO_2 microcrystals in solid state. Under 980 nm NIR excitation, three emission peaks in the visible range are assigned to $^2H_{11/2}\rightarrow{}^4I_{15/2}$(520 nm), $^4S_{3/2}\rightarrow{}^4I_{15/2}$ (541 nm) and $^4F_{9/2}\rightarrow{}^4I_{15/2}$(651 nm) transitions of Er^{3+} ions, respectively. However, when LaF_3: Yb^{3+}, Er^{3+} and LaF_3: Yb^{3+}, Er^{3+}/SiO_2 were dispersed in ethanol, the emission peak corresponding to the $^2H_{9/2}\rightarrow{}^4H_{15/2}$ transition of Er^{3+} at 408 nm is present in the emission spectra (Fig. 3(b)). An explanation to account for the enhancement of $^2H_{9/2}\rightarrow{}^4H_{15/2}$ transition of Er^{3+} in the ethanol is the heat effect. As already known, the 980 nm diode laser generates considerable heat, which increases the temperature of the solid sample rapidly. However, the heat is quickly diffused in the ethanol owing to the flow of the liquid. Fig. 4(a) shows the dispersity of the LaF_3: Yb^{3+}, Er^{3+}/SiO_2 in the PBS buffer. Fig. 4(b) shows the luminescence photo of the sample with a 980 nm diode laser continuously scanning the sample during the 8 s exposure time of the

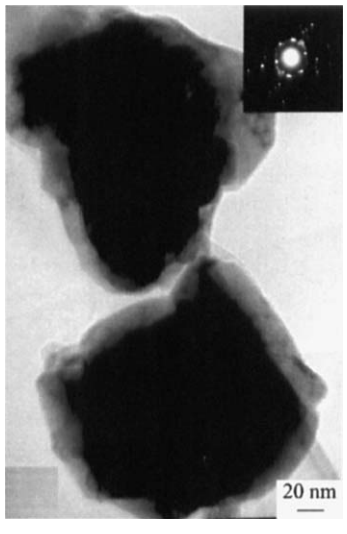

Fig. 2 TEM image of LaF_3: Yb^{3+}, Er^{3+}/SiO_2 (Inset are the electron diffraction pattern of LaF_3: Yb^{3+}, Er^{3+}/SiO_2)

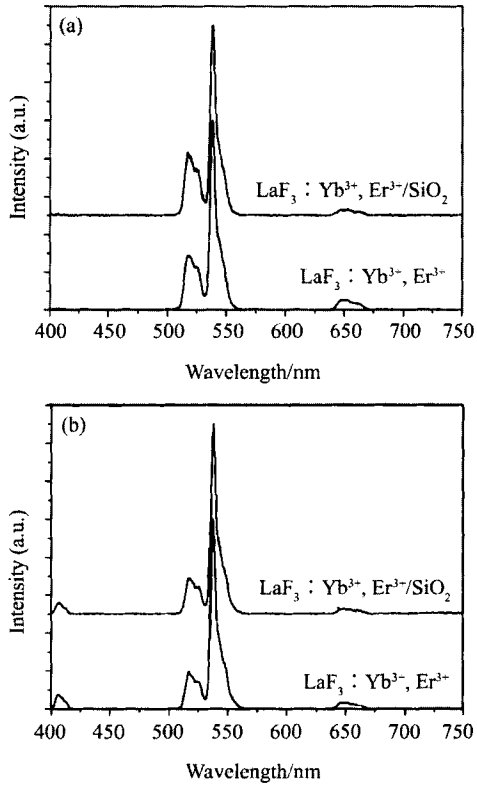

Fig. 3 Room-temperature upconversion emission spectra of the LaF_3: Yb^{3+}, Er^{3+} and LaF_3: Yb^{3+}, Er^{3+}/SiO_2 in solid state (a); Room-temperature upconversion emission spectra of the LaF_3: Yb^{3+}, Er^{3+} and LaF_3: Yb^{3+}, Er^{3+}/SiO_2 in ethanol (b)

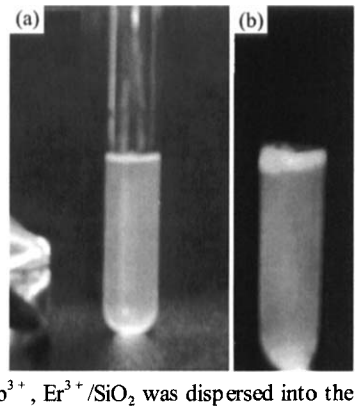

Fig. 4 LaF_3: Yb^{3+}, Er^{3+}/SiO_2 was dispersed into the PBS buffer (a); Luminescence photo of the sample with a 980 nm diode laser continuously scanning the sample during the 8 s exposure time of the digital camera after the sample was dispersed into the PBS buffer for 2 h (b)

the digital camera after the sample was dispersed into PBS for 2 h. The suspension was stable for 6 h without precipitate appearing, which indicates that LaF_3: Yb^{3+}, Er^{3+}/SiO_2 microcrystals have potential applications in biological fields.

3 Conclusion

In summary, Yb^{3+}-Er^{3+} codoped LaF_3 microcrystals were synthesized by the hydrothermal method, and then, LaF_3: Yb^{3+}, Er^{3+} microcrystals were coated with silica. XRD analysis showed that the produces were in hexagonal phase. The TEM image shows that the LaF_3: Yb^{3+}, Er^{3+} microcrystals' size was about 150 nm, and LaF_3: Yb^{3+}, Er^{3+}/SiO_2 showed clearly the core/shell structure with a 20 nm silica shell. The upconversion spectra of LaF_3: Yb^{3+}, Er^{3+} and LaF_3: Yb^{3+}, Er^{3+}/SiO_2 in solid state and in ethanol showed that the silica shell had little effect on the properties of fluorescence of LaF_3: Yb^{3+}, Er^{3+} microcrystals. The LaF_3: Yb^{3+}, Er^{3+}/SiO_2 microcrystals displayed distinct green emission under the excitation of a 980 nm diode laser and could be dispersed in the PBS buffer and be stable for 6 h without precipitate appearing, which indicated that the microcrystals could be used in bioimaging and biolabeling based on the upconversion luminescence.

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