Synthesis and Luminescence Properties of YF₃:Ce³⁺/Tb³⁺ Nanocrystals

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YF₃:Ce³⁺, YF₃:Tb³⁺, and YF₃:Ce³⁺/Tb³⁺ nanocrystals were synthesized by an ethylenediaminetetraacetic acid (EDTA)-assisted hydrothermal method and characterized by X-ray diffraction and scanning electron microscope. In the excitation spectra, there is one broad excitation band at 285 nm for YF₃:Ce³⁺ and 255 nm for YF₃:Tb³⁺, which are related to the f–d excitations of the Ce³⁺ and Tb³⁺ in the host, respectively. In the emission spectra of YF₃:Ce³⁺/Tb³⁺ nanocrystals under different excitation wavelengths (285 and 255 nm), both spectra exhibit the emissions of Ce³⁺ and Tb³⁺, indicating that energy transfer could take place not only from Ce³⁺ to Tb³⁺ but also from Tb³⁺ to Ce³⁺ ions.

Keywords: Rare Earth, Nanocrystals, Luminescence, Energy Transfer.

1. INTRODUCTION

Rare earth (RE) ion-doped materials have attracted intensive attention for their potential applications in display devices, optical telecommunications, solid-state lasers, and so on.¹⁻⁶ Recently, much effort has been devoted to the synthesis of nanomaterials doped with RE ions and to the investigation of their fluorescent properties. With rapidly shrinking size, nanomaterials can exhibit novel physical and chemical properties for their extremely small size and relatively large specific surface area.⁷⁻¹¹

Among various nanomaterials, fluoride nanocrystals have been extensively studied, because fluorides have low phonon energies and optical transparency over a wide wavelength range.¹²⁻¹⁷ YF₃ nanocrystals, a very important nano-fluoride, have been used as a host for phosphors with interesting luminescence properties. Up to now, YF₃ nanocrystals with different shapes and sizes such as fibers,¹⁸ spindles,¹⁹ and truncated octahedra²⁰ have been synthesized. The luminescence properties of YF₃:Ln³⁺ (Ln³⁺ = Eu³⁺, Yb³⁺/Er³⁺, and Yb³⁺/Tm³⁺) nanocrystals have been investigated.²¹⁻²² However, Ce³⁺/Tb³⁺ co-doped YF₃ nanocrystals have never been reported.

Among RE ions, Ce³⁺ and Tb³⁺ ions are important RE ions, which have been applied in blue and green phosphors.²³, ²⁴ In the present study, YF₃:Ce³⁺/Tb³⁺ nanocrystals were synthesized by an ethylenediaminetetraacetic acid (EDTA)-assisted hydrothermal method. The luminescence properties of YF₃:Ce³⁺, YF₃:Tb³⁺, and YF₃:Ce³⁺/Tb³⁺ nanocrystals were studied in detail.

2. EXPERIMENTAL DETAILS

Y(NO₃)₃, Ce(NO₃)₃, and Tb(NO₃)₃ (purity ≥ 99.999%) were supplied by the Shanghai Chemical Reagent Company. EDTA and NaF were supplied by the Beijing Chemical Reagent Company, and were of analytical grade. Deionized water was used to prepare solutions.

In a typical synthesis, 1 mL of 0.5 M Ln(NO₃)₃ (Ln = Y, Ce, and Tb) aqueous solution and 0.5 mmol of EDTA were dispersed into 20 mL of deionized water and magnetically stirred for 1 h, forming a chelated Ln-EDTA complex. Then 4 mL of 0.5 M NaF aqueous solution was added to the solution. After vigorous stirring for 1 h, the mixture was transferred into a 50-mL Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained in an oven at 160 °C for 18 h, and then cooled slowly to room temperature. Subsequently, the suspension was centrifuged at 8,000 rpm for 10 min. The resultant product was then washed thoroughly and dried in vacuum at 80 °C.

The crystal structure was analyzed by a Rigaku RU-200b X-ray powder diffractometer (XRD) using a
nickel-filtered Cu Kα radiation (λ = 1.4518 Å). The size and morphology were investigated by scanning electron microscope (SEM, KYKY 1000B). The luminescence spectra were recorded with a Hitachi F-4500 fluorescence spectrophotometer at room temperature. For comparison of the luminescence properties of different samples, the luminescence spectra were measured with the same instrument parameters [2.5 nm for spectral resolution (FWHM) and 400 V for PMT voltage].

3. RESULTS AND DISCUSSION

3.1. Crystal Structure and Morphology

The SEM images and XRD pattern of the product are shown in Figure 1. An abundance of almost uniform and regular nanospindles with an average length of about 300 nm and a mean width of 200 nm can be seen in Figures 1(a–c). Each nanospindle consists of many nanoparticles with a mean size of 20 nm. The XRD pattern of the sample is presented in Figure 1(d). All of the diffraction peaks can be readily indexed to those of orthorhombic YF₃ (JCPDS 74-0911). No other impurity peaks are detected.

3.2. Luminescence Properties of YF₃:Ce³⁺/Tb³⁺ Nanocrystals

Ce³⁺-doped ionic crystals have attracted increasing attention for their applications in scintillators and tunable lasers in the ultraviolet and visible ranges. The luminescence of Ce³⁺ ion is induced by the transitions from 5d to 4f states. The 5d states strongly couple to the host material because it is out of 5s and 5p shells, resulting in a brodening of the 5d state.²⁵,²⁶ Figure 2 shows the room-temperature excitation (monitored at 395 nm) and emission (excited at 285 nm) spectra of the YF₃:Ce³⁺ nanocrystals. The excitation band is centered at 285 nm, and the emission band is centered at 395 nm. They are related to the f–d excitation of the Ce³⁺.

Figure 3(a) shows the excitation spectrum (monitored at 540 nm) of YF₃:Tb³⁺ nanocrystals. It can be seen that the excitation spectrum consists of three components, having peaks at 215, 239, and 255 nm. The most intense excitation peak is centered at 255 nm, which is related to the f–d excitation of the Tb³⁺. Figure 3(b) shows the emission spectrum of YF₃:Tb³⁺ nanocrystals under 255-nm excitation. The emission peaks are found at 489, 540, 585, and 618 nm, which are assigned to the 5D₄ → 7F₆, 5D₄ → 7F₅, 5D₄ → 7F₄, and 5D₄ → 7F₃ transitions, respectively.

Figure 4 shows the excitation spectrum (monitored at 540 nm) of YF₃:Ce³⁺/Tb³⁺ nanocrystals. As the emission of 5D₄ → 7F₅ for Tb³⁺ (at 540 nm) was monitored, a broad band was observed, which could be deconvolved into four individual Lorentz type peaks. Among them, peaks 1–3 originated from the allowed f–d transitions of Tb³⁺ (Fig. 3(a)), and peak 4 originated from the allowed...
that energy transfer could take place not only from Ce\(^{3+}\) to Tb\(^{3+}\) but also from Tb\(^{3+}\) to Ce\(^{3+}\) ions. The emissions from Ce\(^{3+}\) are dominant under 280-nm excitation, while the emission from Tb\(^{3+}\) is dominant under 255-nm excitation. The schematics of the energy transfer and luminescent processes in YF\(_3\):Ce\(^{3+}\)/Tb\(^{3+}\) nanocrystals are shown in Figure 6.

4. CONCLUSION

In summary, YF\(_3\):Ce\(^{3+}\), YF\(_3\):Tb\(^{3+}\), and YF\(_3\):Ce\(^{3+}\)/Tb\(^{3+}\) nanocrystals were synthesized by a hydrothermal method. EDTA was chosen to reduce particle sizes in the synthesis of the product. The structure and morphology of the product were investigated using XRD and SEM. The excitation and emission spectra of the YF\(_3\):Ce\(^{3+}\), YF\(_3\):Tb\(^{3+}\), and YF\(_3\):Ce\(^{3+}\)/Tb\(^{3+}\) nanocrystals were measured by fluorescence spectrophotometer. In the excitation spectrum of YF\(_3\):Ce\(^{3+}\), there is one broad excitation band located at 285 nm arising from 5\(d\)–4\(f\) transition of Ce\(^{3+}\) in the host. In the excitation spectrum of YF\(_3\):Tb\(^{3+}\), there is one broad excitation band located at 255 nm arising from 5\(d\)–4\(f\) transitions of Tb\(^{3+}\) in the host. To study the energy transfer between Ce\(^{3+}\) and Tb\(^{3+}\) ions, the emission spectra of YF\(_3\):Ce\(^{3+}\)/Tb\(^{3+}\) nanocrystals under different excitation wavelengths were measured. The emissions of Ce\(^{3+}\) and Tb\(^{3+}\) were observed, indicating that energy transfer could take place not only from Ce\(^{3+}\) to Tb\(^{3+}\) but also from Tb\(^{3+}\) to Ce\(^{3+}\) ions.

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References and Notes

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