Synthesis and Luminescence Properties of Er\(^{3+}\) Doped Y(OH)\(_3\), NH\(_4\)Y\(_3\)F\(_{10}\), and YF\(_3\) Nanocrystals

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Y(OH)\(_3\):Er\(^{3+}\) nanowires were synthesized by a hydrothermal method. Y(OH)\(_3\):Er\(^{3+}\) can convert into NH\(_4\)Y\(_3\)F\(_{10}\):Er\(^{3+}\) after fluorization, and NH\(_4\)Y\(_3\)F\(_{10}\):Er\(^{3+}\) can convert into YF\(_3\):Er\(^{3+}\) after being annealed. The structures of obtained Y(OH)\(_3\):Er\(^{3+}\), NH\(_4\)Y\(_3\)F\(_{10}\):Er\(^{3+}\), and YF\(_3\):Er\(^{3+}\) samples were pure hexagonal, cubic, and orthorhombic phase, respectively. Under 378-nm excitation, the three samples showed similar features. The \(^{2}H_{9/2} \rightarrow ^{4}I_{15/2}\), \(^{4}F_{3/2} \rightarrow ^{4}I_{15/2}\), and \(^{4}S_{3/2} \rightarrow ^{4}I_{15/2}\) were observed, and the most intense peak was centered at 436 nm \(^{4}F_{3/2} \rightarrow ^{4}I_{15/2}\). Under 980-nm excitation, only the upconversion emissions from NH\(_4\)Y\(_3\)F\(_{10}\):Er\(^{3+}\) and YF\(_3\):Er\(^{3+}\) were observed. These emissions come from the following transitions: \(^{2}H_{11/2} \rightarrow ^{4}I_{15/2}\), \(^{4}S_{3/2} \rightarrow ^{4}I_{15/2}\), and \(^{4}F_{9/2} \rightarrow ^{4}I_{15/2}\). The upconversion mechanism is discussed in detail.

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

1. INTRODUCTION

Recently, nanosized luminescent materials doped with rare earth (RE) ions have attracted intensive attention not only for their unique physical properties but also for their potential applications in developing novel phosphors and building miniature optoelectronic devices.\(^1\)–\(^3\) Because the reduction of particle size can result in remarkable modifications of some of their bulk properties, nanosized phosphors or optoelectronic devices usually exhibit novel capabilities, such as higher luminescence efficiency and better resolution of images in lighting and display.\(^4\),\(^5\)

Fluoride nanocrystals have attracted increasing attention, because fluorides are efficient host lattices for luminescent centers.\(^6\),\(^7\) RE ion-doped fluorides have low phonon energies and high quantum efficiencies as luminescent materials, giving them potential for widespread applications in short wavelength solid-state lasers, optical communications, display devices, and so on.\(^8\)–\(^10\) YF\(_3\) nanocrystals, a very important nano-fluoride, have been used as a host for phosphors with interesting up/down conversion luminescent properties.\(^11\)–\(^16\)

MLn\(_3\)F\(_{10}\) (M = alkaline metal, NH\(^{4+}\) and Ln = RE) is a big family of compounds including many useful materials, which has great potential as a host of the solid-state laser. Up to now, various synthesis methods have been used to prepare MLn\(_3\)F\(_{10}\). For example, NH\(_4\)Ln\(_3\)F\(_{10}\) has been synthesized by the hydrothermal method.\(^17\) Recently, NH\(_4\)Y\(_3\)F\(_{10}\) sub-microcrystals were prepared using a polyol method.\(^18\)

In this paper, Y(OH)\(_3\):Er\(^{3+}\), NH\(_4\)Y\(_3\)F\(_{10}\):Er\(^{3+}\), and YF\(_3\):Er\(^{3+}\) nanocrystals were synthesized. The structures and morphologies of products were investigated using the X-ray powder diffractometer (XRD) and transmission electron microscope (TEM). The luminescence properties were studied in detail.

2. EXPERIMENTAL DETAILS

2.1. Preparation of Y(OH)\(_3\):Er\(^{3+}\) Nanowires

NaOH and HNO\(_3\) were supplied by Beijing Chemical Reagent Company and were of analytical grade. Y\(_2\)O\(_3\) (99.99\%) and Er\(_2\)O\(_3\) (99.99\%) were supplied by Shanghai Chemical Reagent Company. All of the reagents and solvents were used as received without further purification. Ln(NO\(_3\))\(_3\) (Ln = Y and Er) stock solutions were prepared...
by dissolving the corresponding lanthanide oxides in dilute HNO$_3$.

Ln[NO$_3$]$\_2$ (total 1.5 mmol, with specifically adjusted Y$^{3+}$/Er$^{3+}$ molar ratios) was dissolved in 4 mL of deionized H$_2$O, followed by the dropwise addition of 14 mL of NaOH solution under stirring. After being stirred for 1 h, the milky colloidal solution was transferred into a 23 mL Teflon-lined autoclave and subsequently sealed and heated at 160 °C for 12 h. The resulting reaction solution along with the precipitate was cooled to room temperature naturally and then centrifuged. The precipitate was washed with deionized water several times and dried at 60 °C for 24 h in a vacuum oven to obtain Y(OH)$_3$:Er$^{3+}$ powders. It was referred to as sample A.

### 2.2. Preparation of NH$_4$Y$_3$F$_{10}$:Er$^{3+}$ Nanocrystals

One part of as-obtained Y(OH)$_3$:Er$^{3+}$ powders was dispersed into deionized water by ultrasonication and vigorous stirring for 2 h, and an appropriate amount of NH$_4$HF$_2$ solution was dripped into the dispersion, followed by further stirring for 2 h. The resultant milky suspensions were given another hydrothermal treatment at 150 °C for 3 h. The powders of the NH$_4$Y$_3$F$_{10}$:Er$^{3+}$ nanocrystals were finally obtained after washing with deionized water and alcohol and drying at 60 °C for 24 h in a vacuum oven. The product was referred to as sample B.

### 2.3. Preparation of YF$_3$:Er$^{3+}$ Nanocrystals

One part of the as-obtained NH$_4$Y$_3$F$_{10}$:Er$^{3+}$ nanocrystals was placed into a ceramic crucible and converted into the corresponding powder of YF$_3$:Er$^{3+}$ by annealing at 500 °C for 2 h in an inert atmosphere. The product was referred to as sample C.

### 2.4. Characterization

The crystal structure was analyzed by a Rigaku RU-200b X-ray powder diffractometer (XRD) using a nickel-filtered Cu Kα radiation ($\lambda = 1.4158$ Å). The size and morphology were investigated by transmission electron microscopy (TEM, JEM 2010 with operating voltage of 200 KV). TEM samples were prepared by ultrasonic nebulization of ethanolic dispersion on a Lacey-film copper grid. 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 and 400 V for PMT voltage).

### 3. RESULTS AND DISCUSSION

#### 3.1. Crystal Structure and Morphology

The crystal structure and the phase purity of the samples were obtained by XRD, as shown in Figure 1. The diffraction peaks in curve 1a for sample A can be indexed to pure hexagonal Y(OH)$_3$, which is in good agreement with the literature (JCPDS card No. 83-2042). The diffraction peaks in curve 1b for sample B indicate that the product is pure cubic NH$_4$Y$_3$F$_{10}$:Er$^{3+}$, which is consistent with the literature.\(^{17}\) After being annealed at 400 °C for 2 h, NH$_4$Y$_3$F$_{10}$:Er$^{3+}$ can convert into pure orthorhombic YF$_3$:Er$^{3+}$ (sample C), as is confirmed by the XRD pattern (JCPDS card No. 74-0911).

Figure 2 shows the TEM images of the samples. It is obvious that the Y(OH)$_3$:Er$^{3+}$ nanocrystals (sample A) consist of nanowires with diameter of 100 nm (Fig. 2(a)), while the NH$_4$Y$_3$F$_{10}$:Er$^{3+}$ and YF$_3$:Er$^{3+}$ nanocrystals tend to aggregate (Figs. 2(b and c)).

#### 3.2. Luminescence Properties of Y(OH)$_3$:Er$^{3+}$, NH$_4$Y$_3$F$_{10}$:Er$^{3+}$, and YF$_3$:Er$^{3+}$ Nanocrystals

Figure 3 presents the emission spectra of Y(OH)$_3$:Er$^{3+}$, NH$_4$Y$_3$F$_{10}$:Er$^{3+}$, and YF$_3$:Er$^{3+}$ nanocrystals under 378-nm excitation. The $^4S_3/2 \rightarrow ^4I_{15/2}$, $^4F_{5/2}(^4F_{7/2}) \rightarrow ^4I_{15/2}$, and $^4S_{3/2} \rightarrow ^4I_{15/2}$ were observed. In comparison with the strong emissions from $^2H_9/2, ^2F_5/2( ^2F_7/2)$, and $^4S_{3/2}$, the red emission ($^4F_{9/2} \rightarrow ^4I_{15/2}$) almost vanished. It is surprising to observe that the most intense peak is centered at 436 nm [$^4F_{5/2}(^4F_{7/2}) \rightarrow ^4I_{15/2}$].

Figure 4 presents the UC luminescence spectra (normalized to the $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition) of NH$_4$Y$_3$F$_{10}$:Er$^{3+}$ (5%) and YF$_3$:Er$^{3+}$ (5%) nanocrystals under 980-nm excitation. The spectral peaks correspond to the following transitions: $^2H_9/2 \rightarrow ^4I_{15/2}$ (∼525 nm), $^2S_{3/2} \rightarrow ^4I_{15/2}$ (∼540 nm), and $^2F_{9/2} \rightarrow ^4I_{15/2}$ (∼654 nm). The UC emission spectra (normalized to $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition)
Emission spectra of (a) Y(OH)$_3$:Er$^{3+}$ (5%), (b) NH$_4$Y$_3$F$_{10}$:Er$^{3+}$, and (c) YF$_3$:Er$^{3+}$ nanocrystals excited at 378 nm.

UC luminescence spectra (normalized to $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition) of (a) NH$_4$Y$_3$F$_{10}$:Er$^{3+}$ (5%) and (b) YF$_3$:Er$^{3+}$ (5%) nanocrystals under 980-nm excitation.

Dependence of the UC emission spectra (normalized to $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition) of YF$_3$:Er$^{3+}$ nanocrystals with different Er$^{3+}$ concentration: (a) 0.1%, (b) 0.5%, (c) 2%, (d) 5%, and (e) 10%.

To get a closer insight into the possible mechanism of UC luminescence, we investigated the variation of its intensity with excitation power. For an unsaturated UC process, the emission intensity is proportional to the $n$-th power of the excitation intensity, and the integer $n$ is the number of the laser photons absorbed per upconverted photon emitted. $^{19}$ Figure 6 shows the double logarithmic plots of the emission intensity as a function of excitation power for the $^4S_{3/2} \rightarrow ^4I_{15/2}$, $^4F_{9/2} \rightarrow ^4I_{15/2}$, and $^4F_{9/2} \rightarrow ^4I_{15/2}$ emissions. For YF$_3$:Er$^{3+}$ (1%) nanocrystals, the slopes of the linear fittings are 1.89 for $^4F_{9/2} \rightarrow ^4I_{15/2}$, 1.82 for $^4S_{3/2} \rightarrow ^4I_{15/2}$, and 2.02 for $^2H_{11/2} \rightarrow ^4I_{15/2}$. The values of $n$ are characteristics...
for UC luminescence occurring through the two-photon mechanisms. For YF$_3$:Er$^{3+}$ (5%) nanocrystals, the corresponding slopes of the linear fittings decrease to 1.65, 1.61, and 1.79 respectively. Pollnau et al. attributed this phenomenon to the "saturation" process due to the competition between linear decay and UC processes for the depletion of the intermediate excited states. According to their report, the value of $n$ for a two-photon process is $\sim$2 when the linear decay of the intermediate state is dominant, while $n$ is $\sim$1 when the UC is the dominant mechanism in the Er$^{3+}$ codoped system. This implies that the YF$_3$:Er$^{3+}$ nanocrystals belong to materials with efficient UC when the Er$^{3+}$ content reaches 10%. Figure 7 shows the possible UC emission mechanisms in YF$_3$:Er$^{3+}$ nanocrystals. Two 980-nm infrared photons may elevate an electron from the ground level up to the $^4$F$_{7/2}$ state. This may occur through excited-state absorption or energy transfer. When the Er$^{3+}$ concentration is high enough, the cross-relaxation $^4$F$_{7/2} \rightarrow ^4$F$_{9/2} \rightarrow ^4$I$^1_{11/2} \rightarrow ^4$I$^1_{9/2}$ can occur, resulting in the enhanced red emission.

4. CONCLUSION

In summary, Y(OH)$_3$:Er$^{3+}$ nanowires were synthesized by a hydrothermal method. Y(OH)$_3$:Er$^{3+}$ can convert into NH$_4$Y$_3$F$_10$:Er$^{3+}$ after fluorization and NH$_4$Y$_3$F$_10$:Er$^{3+}$ can convert into YF$_3$:Er$^{3+}$ after being annealed. The structures of obtained Y(OH)$_3$:Er$^{3+}$, NH$_4$Y$_3$F$_10$:Er$^{3+}$, and YF$_3$:Er$^{3+}$ nanocrystals are pure hexagonal, cubic, and orthorhombic phase, respectively. Under 378-nm excitation, the three samples show similar features. The $^4$H$_{9/2} \rightarrow ^4$I$^1_{15/2}$, $^4$F$_{5/2}(^4$F$_{7/2}) \rightarrow ^4$I$^1_{15/2}$, and $^4$S$_{3/2} \rightarrow ^4$I$^1_{15/2}$ were observed, and the most intense peak was centered at 436 nm ($^4$F$_{5/2}(^4$F$_{7/2}) \rightarrow ^4$I$^1_{15/2}$). Under 980-nm excitation, only the upconversion emissions of NH$_4$Y$_3$F$_10$:Er$^{3+}$ and YF$_3$:Er$^{3+}$ were observed. The $^4$G$_{11/2} \rightarrow ^4$I$^1_{15/2}$, $^4$I$^1_{9/2} \rightarrow ^4$I$^1_{15/2}$, $^4$H$_{11/2} \rightarrow ^4$I$^1_{15/2}$, $^4$S$_{3/2} \rightarrow ^4$I$^1_{15/2}$, and $^4$F$_{9/2} \rightarrow ^4$I$^1_{15/2}$ were observed. The upconversion mechanism was discussed in detail.

Acknowledgments: This research was supported by Natural Science Foundation of China (Grant Nos. 50672030, and 10874058).

References and Notes


Received: 9 November 2008. Accepted: 7 April 2009.