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Journal of Nanoscience and Nanotechnology Vol.8, 1384-1387, 2008

Multicolor Up-Conversion Emissions of Tm³⁺/Er³⁺/Yb³⁺ Tri-Doped YF₃ Phosphors

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Tm³⁺/Er³⁺/Yb³⁺ tri-doped yttrium fluoride (YF₃) phosphors were prepared by a facile hydrothermal method. X-ray topographic analysis found that the phosphors were crystallized products. Their sizes and morphologies were characterized by scanning electron microscopy (SEM, Hitachi S-4800), which indicated that most of the YF₃ phosphors were hundreds of nanometers in size. Up-conversion (UC) spectra were recorded under 980-nm diode laser excitation at room temperature with a fluorescence spectrometer (Hitachi F-4500). Plenty of UC emissions of Tm^{3+} and Er^{3+} were observed from ultraviolet to red. For Tm^{3+} ions, a five-photon process (~291 nm and \sim 347 nm), a four-photon process (\sim 362 nm and \sim 452 nm), and a three-photon process (\sim 475 nm) were identified in the UC spectra. The UC emissions from the Er^{3+} were: ~380 nm, ~408 nm, \sim 521 nm, \sim 537 nm, and \sim 652 nm. Therefore, cyan-white light can be observed by the naked eye at 980-nm excitation, even under low excitation power density. By comparing the UC spectra of the phosphors annealed at different temperatures, we found that the intensity of the UC luminescence increased as annealing temperature increased. Furthermore, the spectral dependencies on Tm³⁺ doped concentrations were studied. The energy transfer processes and fluorescence dynamics in the tri-doped system are currently being investigated.

Keywords:

1. INTRODUCTION

Phosphors are solid inorganic crystalline materials that show luminescence under excitation.¹ Up-conversion (UC) phosphors emit higher energy photons after absorbing lower energy excitation photons.² In last few years, there has been growing interest in studying UC phosphors because they are one of the most promising materials for the production of short-wave solid-state lasers. To date, red, green, and blue laser sources pumped by infrared light have been reported.³ The UC of infrared light to visible light by rare earth (RE) ion-doped materials has been investigated extensively due to the possibility of infrared pumped visible lasers and the potential for applications in areas such as three-dimensional displays, optical data storage, optoelectronics, medical diagnostics, sensors, and undersea optical communication.4,5 In recent reports,5 a fluoride glass sample triply doped with Er^{3+} , Pr^{3+} , and

J. Nanosci. Nanotechnol. 2008, Vol. 8, No. 3

1533-4880/2008/8/1384/004

Tm³⁺ and excited by two near-infrared (NIR) lasers with distinct wavelengths produced red, green, and blue (RGB)

light, pursuing the realization of a three-dimensional solid-

state display. The generation and control of the three pri-

mary colors, RGB, through frequency UC and white light

simulation using double excitation in Er³⁺/Tm³⁺-codoped

fluoride glasses has been reported.7 In 2005, the generation

of bright white light through UC of a single NIR source

from a sol-gel derived thin film of Ln³⁺-doped LaF₃

nanoparticles was reported.8 The choice of the host mate-

rial is very important in the development of more efficient

UC optical devices based on RE-doped materials. The con-

version processes in fluoride compounds are efficient, par-

ticularly in YF₃,⁹ due to their low phonon energies. In

this article, we report on the experimental investigation of

frequency UC luminescence of Tm³⁺/Er³⁺/Yb³⁺ tri-doped

YF₃ phosphors under 980-nm continuous wave laser diode

(CW LD) excitation. The cyan-white light was observed by the naked eye under lower excitation density. The results indicate that Tm³⁺/Er³⁺/Yb³⁺ tri-doped YF₃ phosphors can

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act as suitable materials for potential three-dimensional display applications and white light sources.

2. EXPERIMENTAL DETAILS

Tm³⁺/Er³⁺/Yb³⁺ tri-doped YF₃ phosphors were synthesized using a simple hydrothermal method. The phosphors were prepared from Y2O3 (Aldrich), Tm2O3 (Aldrich), Er₂O₃ (Aldrich), and Yb₂O₃ (Aldrich) according to the following compositions in molar fraction: $(0.79 - x) Y_2O_3 - x$ Tm_2O_3 (x = 0.001, 0.002, 0.003, 0.004, 0.005) - 0.01 $Er_2O_3 - 0.20$ Yb₂O₃. The RE oxides were dissolved in nitric acid (Aldrich 63%) to form a clear solution, and then the hydrofluoric acid (Aldrich 40%) was added dropwise. After vigorous stirring for 30 minutes, the suspension solution was transferred to a 50 mL stainless Teflon-lined autoclave and heated at 120 °C for 15 hours. After cooling to room temperature naturally, the upper clear solution was discarded, and the remainder was washed several times with deionized water. The resultant material was dried in a vacuum at 60 °C for several hours, and white powder was obtained. After annealing the powders at different temperatures (400 °C, 500 °C, and 600 °C) for 1 hour under an argon atmosphere, the phosphors were obtained.

The phase identification was performed by X-ray diffraction (XRD) (Model Rigaku RU-200b), using nickelfiltered CuK α radiation ($\lambda = 1.5406$ Å). The sizes and morphologies were characterized with a Hitachi S-4800 scanning electron microscope. Under 980-nm excitation, UC spectra were recorded with a Hitachi F-4500 fluorescence spectrometer. All measurements were performed at room temperature.

3. RESULTS AND DISCUSSION

The representative XRD patterns of $Y_{0.787}Tm_{0.003}Er_{0.01}$ Yb_{0.20}F₃ phosphors are shown in Figure 1, where (a), (b), (c), and (d) are those of the samples as-prepared and annealed at 400 °C, 500 °C, and 600 °C for 1 hour under an argon atmosphere. All diffraction peaks can be readily indexed to that of the orthorhombic phase YF₃ [space group Pnma (62)], which is in good agreement with the standard values for the bulk orthorhombic YF₃ (JCPDS 74-0911). No impurity can be identified from the XRD patterns, which shows that the phosphors are single-phased. From the patterns, one can infer that the as-prepared sample was nanometer-sized. After annealing, the samples were well-crystallized and larger in size as shown in the SEM graphs described below.

Figure 2 shows SEM images of the phosphors captured at a working voltage of 10.0 kV and 4×10^4 magnification, with samples annealed at (a) 400 °C, (b) 500 °C, (c) 600 °C, and (d) as-prepared. The inset of (d) is an image of single unit of as-prepared samples. The images show that as the annealing temperature increased the



Fig. 1. XRD patterns of the phosphors. As-prepared (a); annealed at (b) 400 $^{\circ}$ C, (c) 500 $^{\circ}$ C, and (d) 600 $^{\circ}$ C for 1 hour.

morphologies changed while the units grew rapidly and linked to each other after annealing. The as-prepared materials are bundles about 700 nm long and 200 nm thick and are composed of flakes a few nanometers thick.

In Tm³⁺/Er³⁺/Yb³⁺ tri-doped systems, different processes result in UC luminescence. Figure 3 shows the energy level diagrams of Tm³⁺, Er³⁺, and Yb³⁺. Yb³⁺ absorb photons and successively transfer energy to Tm³⁺ and Er³⁺, while the Er³⁺ also absorb the 980-nm photons. Yb³⁺ transfer energy to Tm³⁺ to populate ³H₅, ³F₂ (³F₃), and ¹G₄.¹⁰ The Tm³⁺–Tm³⁺ interaction is weak in the sample with low Tm³⁺ concentration due to the large energy mismatch (~3516 cm⁻¹) in transfer ²F_{5/2} \rightarrow ²F_{7/2} (Yb³⁺): ¹G₄ \rightarrow ¹D₂. Cross relaxation (CR) ³F₃ \rightarrow ³H₆: ³F \rightarrow ¹D₂ (Tm³⁺) may alternatively play the most important role in populating ¹D₂.¹¹ Then, state ¹I₆ can be populated by ²F_{5/2} \rightarrow ²F_{7/2} (Yb³⁺): ¹D₂ \rightarrow ¹I₆ (Tm³⁺). For Yb³⁺ and Er³⁺, green (²H_{11/2}, ⁴S_{3/2} \rightarrow ⁴I_{15/2}) and red (⁴F_{9/2} \rightarrow ⁴I_{15/2})



Fig. 2. SEM images of the phosphors. Annealed at (a) 400 $^{\circ}$ C, (b) 500 $^{\circ}$ C, (c) 600 $^{\circ}$ C for 1 hour, and (d) as-prepared. The inset of (d) is a single unit of as-prepared samples.

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Fig. 3. (a) Level diagrams of Yb^{3+} , Tm^{3+} , and Er^{3+} and the possible ET mechanism. (b) CR schematic diagram between $Tm^{3+}-Tm^{3+}$.

upconverted emissions have been widely investigated. For the violet (408 nm) emission, there are two processes in populating the ${}^{2}H_{9/2}$ state: (1) energy transfer ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ (Yb³⁺): ${}^{4}F_{9/2} \rightarrow {}^{2}H_{9/2}$ (Er³⁺); and (2) energy transfer ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ (Yb³⁺): ${}^{4}S_{3/2} \rightarrow {}^{2}G_{7/2}$ (Er³⁺), followed by fast cascading relaxation to the ${}^{4}G_{11/2}$ and ${}^{2}H_{9}$ states. At the same time, ultraviolet 380 nm emission (${}^{4}G_{11/2} \rightarrow {}^{4}I_{15/2}$) occurred. In the Tm³⁺/Er³⁺/Yb³⁺ tri-doped systems, the interaction of the Tm³⁺ and Er³⁺ should not be ignored: ${}^{4}S_{3/2} \rightarrow {}^{4}I_{9/2}$ (Er³⁺): ${}^{3}H_{6} \rightarrow {}^{3}F_{4}$ (Tm³⁺); ${}^{4}S_{3/2} \rightarrow {}^{4}I_{11/2}$ (Er³⁺): ${}^{3}H_{6} \rightarrow {}^{3}H_{5}$ (Tm³⁺); ${}^{4}F_{9/2} \rightarrow {}^{4}I_{11/2}$ (Er³⁺): ${}^{3}H_{6} \rightarrow {}^{3}F_{4}$ (Tm³⁺); ${}^{4}F_{9/2} \rightarrow {}^{4}I_{13/2}$ (Er³⁺): ${}^{3}H_{6} \rightarrow {}^{3}H_{5}$ (Tm³⁺); ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ (Er³⁺): ${}^{3}H_{6} \rightarrow {}^{3}F_{2}$ (Tm³⁺); and ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$ (Er³⁺): ${}^{3}H_{6} \rightarrow {}^{3}F_{4}$ (Tm³⁺); etc.¹² Er³⁺ acting as sensitizers transfer energy to Tm³⁺, and the counterpart emissions become weaker. This will be studied further.

Excited state absorption (ESA) and energy transfer (ET) are efficient UC mechanisms in RE^{3+} -doped materials. In Yb^{3+} -sensitized RE^{3+} -doped materials under 980-nm laser excitation, the ET process plays an important role in the UC process because Yb^{3+} have a large absorption cross at this wave band. Figure 4 presents the UC spectrum of sample $Y_{0.787}Tm_{0.003}Er_{0.01}Yb_{0.20}F_3$ that was annealed at





Fig. 4. UC spectrum of $Y_{0.787}Tm_{0.003}Er_{0.01}Yb_{0.20}F_3$ phosphors under 980-nm, 200 mW excitation.

600 °C for 1 hour. For unsaturated UC, emission intensity I_s is proportional I^n , where I is the intensity of the excitation light and the integer n is the number of photons absorbed per up-converted photon emitted.¹³ The *n*-photon UC processes of Tm³⁺ and Er³⁺ are thoroughly discussed in our previous articles.^{14, 15} For Tm³⁺, the five-photon UC process (~291 nm emission from ${}^{1}I_{6} \rightarrow {}^{3}H_{6}$, ~347 nm from ${}^{1}I_{6} \rightarrow {}^{3}F_{4}$), four-photon UC process (~362 nm emission from ${}^{1}D_{2} \rightarrow {}^{3}H_{6}$, ~452 nm from ${}^{1}D_{2} \rightarrow {}^{3}F_{4}$) and threephoton UC process (~475 nm emission from ${}^{1}G_{4} \rightarrow {}^{3}H_{6}$) can be identified in the UC spectra, while relatively weak ~692 nm (${}^{3}F_{3} \rightarrow {}^{3}H_{6}$) emissions were also obtained in the spectra. Er³⁺ emissions are: \sim 380 nm (${}^{4}G_{11/2} \rightarrow {}^{4}I_{15/2}$), ~408 nm (${}^{2}\text{H}_{9/2} \rightarrow {}^{4}\text{I}_{15/2}$), ~521 nm (${}^{2}\text{H}_{11/2} \rightarrow {}^{4}\text{I}_{15/2}$), ~537 nm (${}^{4}\text{S}_{3/2} \rightarrow {}^{4}\text{I}_{15/2}$), ~652 nm (${}^{4}\text{F}_{9/2} \rightarrow {}^{4}\text{I}_{15/2}$). There is an approximately 580 nm emission in the UC spectrum [denoted with an asterisk (*)] for which the origins are not entirely clear. It may from the second diffraction of



Fig. 5. UC spectra of the phosphors $Y_{0.787}Tm_{0.003}Er_{0.01}Yb_{0.20}F_3$ annealed at (a) 400 °C, (b) 500 °C, and (c) 600 °C for 1 hour under 980-nm, 200 mW excitation.



Fig. 6. UC spectra of the phosphors $Y_{0.79-x}Tm_xEr_{0.01}Yb_{0.20}F_3$ annealed at 600 °C for 1 hour under 980-nm, 200 mW excitation, x = (a) 0.001, (b) 0.002, (c) 0.003, (d) 0.004, and (e) 0.005.

291 nm emission (${}^{1}I_{6} \rightarrow {}^{3}H_{6}$). A study of this emission will be presented in another article.

The temperature dependence of the spectroscopic properties is shown in Figure 5. [The spectra were normalized to Er^{3+} : ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ transition (652 nm).] The picture shows that the UC luminescence becomes stronger as annealing temperatures rise. At the same time, the green emissions of Er^{3+} at 537 nm (${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$) slightly decrease for Tm^{3+} and Er^{3+} interactions. In contrast, the 521 nm emissions (${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$) change irregularly, which may be related to thermal population processes and our measurement procedures. Based on the SEM and XRD of the phosphors, we ascribed the irregular change to thorough crystallization with increasing annealing temperatures. After higher annealing, the RE^{3+} were well-imbedded in the YF₃ lattice, the energy transfer processes became efficient, and Tm^{3+} and Er^{3+} interactions became stronger.

The dependence of spectra properties on the different doping concentrations of Tm^{3+} will be discussed simply. The samples $Y_{0.79-x}\text{Tm}_x\text{Er}_{0.01}\text{Yb}_{0.20}\text{F}_3$ were annealed at 600 °C for 1 hour, and excited under 200 mW. Figure 6 [normalized to Er^{3+} 537 nm emission (${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$) of each spectrum] shows the emission spectra of the samples with $x = (a) \ 0.001$, (b) 0.002, (c) 0.003, (d) 0.004, and (e) 0.005. With increasing Tm^{3+} concentration, Er^{3+} emissions at 380 nm, 408 nm, and 652 nm increases initially then decrease, but the emission at 521 nm always increases. The fluorescence mechanisms are under intensive investigation. For Tm^{3+} , all emissions become stronger with increasing Tm^{3+} concentration, possibly because Tm^{3+} competition for Yb^{3+} energy transfer becomes stronger as Tm^{3+} concentration increases. For

362 nm and 452 nm, emissions increase relatively quickly. This may be ascribed to CR: $\text{Tm}^{3+}({}^{1}\text{G}_{4}, {}^{3}\text{H}_{4}) \rightarrow ({}^{3}\text{F}_{4}, {}^{1}\text{D}_{2})$ due to high doping concentration, ¹⁶ which populates the ${}^{1}\text{D}_{2}$ state at the cost of the ${}^{1}\text{G}_{4}$ state. The process is represented schematically in Figure 3(b).

4. CONCLUSION

In conclusion, the $Tm^{3+}/Er^{3+}/Yb^{3+}$ tri-doped YF_3 phosphors were synthesized through a facile hydrothermal method. The ultraviolet, violet, blue, green, and red emissions were obtained in the UC spectra. Cyan-white light could be seen by the naked eye under 980-nm excitation because the three primary colors co-exist. The temperature dependence of the UC spectra properties indicate that Tm^{3+} emissions became stronger as annealing temperature increased. The concentration dependence of the spectra were also investigated, and Er^{3+} emissions became first stronger then weaker as Tm^{3+} concentration increased. Concentration dependence UC spectra, energy transfer processes and luminescence dynamics are being intensively studied in the tri-doped system.

Acknowledgments: This work was supported by the National Science Foundation of China (Grant No. 10474096 and 50672030).

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Received: 26 December 2006. Accepted: 28 April 2007.

J. Nanosci. Nanotechnol. 8, 1384-1387, 2008