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Bright White Upconversion Luminescence in β-$NaGd_{0.794}Yb_{0.20}Ho_{0.001}Tm_{0.005}F_4$ Nanoparticles

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β-$NaGd_{0.794}Yb_{0.20}Ho_{0.001}Tm_{0.005}F_4$ nanoparticles were synthesized through a simple hydrothermal method. The nanoparticles crystallized well and exhibited nearly hexagonal morphology and ellipsoidal spheres, as characterized by X-ray powder diffraction and transmission electron microscopy. The β-$NaGd_{0.794}Yb_{0.20}Ho_{0.001}Tm_{0.005}F_4$ nanoparticles have an average size of about 23 nm. Room-temperature bright white upconversion luminescence in β-$NaGd_{0.794}Yb_{0.20}Ho_{0.001}Tm_{0.005}F_4$ nanoparticles was obtained under single-wavelength diode laser excitation of 980 nm.

Metal fluorides doped with rare-earth ions have been demonstrated many applications such as lasers, optical communications, three-dimensional display devices, and biological fluorescent labels.[1] Upconversion (UC) is a generation process that higher-energy light is converted from lower-energy radiation, usually near-infrared (NIR) or infrared (IR), in transition-metal and rare-earth (RE) ions doped into a solid-state host material.[2] White emission by frequency UC in Yb^{3+}, Ho^{3+}, and Tm^{3+} triply doped nanoparticles deserves increasing attention.[3] The realization of strong white emission requires the generation and an adequate combination of the three fundamental red, green, and blue light colors, which is a great challenge to material design including host composition and the suitable combination of sensitizers and activator ions. In 2004, Cheah et al. obtained white light in Er^{3+} and Yb^{3+} codoped porous silicon.[4] In 2005, van Veggel et al. reported that white light could be easily generated from thin film made with $La_{0.45}Yb_{0.5}Er_{0.05}F_3$, $La_{0.75}Yb_{0.2}Tm_{0.05}F_3$, and $Yb_{0.75}La_{0.2}Eu_{0.05}F_3$ nanoparticles.[5] Recently, important progress on white UC emission was obtained in glass ceramics containing YF_3 or $Pb_{1-x}Cd_xF_2$ nanoparticles.[6–9] But the combination of sensitizer and activator ions is mainly limited to Yb^{3+}, Er^{3+}, and Tm^{3+} triply doped systems. Few investigations have focused on other activator ions, such as Yb^{3+}, Ho^{3+}, Tm^{3+} and Yb^{3+}, Nd^{3+}, Tm^{3+} systems. In this letter, we report the preparation and white UC emission of β-$NaGd_{0.794}Yb_{0.20}Ho_{0.001}Tm_{0.005}F_4$ nanoparticles.

The 0.01 M $Gd_{0.794}Yb_{0.20}Ho_{0.001}Tm_{0.005}(NO_3)_3$ solution was prepared by dissolving the corresponding metal oxide in nitric acid at elevated temperature. The method of fabricating β-$NaGd_{0.794}Yb_{0.20}Ho_{0.001}Tm_{0.005}F_4$ is as follows: First, solution A was prepared by adding 5.0 mL of 12.0 M aqueous NaOH solution and 5.0 mL of 4.0 M aqueous NH_4HF_2 solution added in to the 50.0 mL of alcohol solution of oleic acid ($V_{\text{oleic acid}}$:V_{alcohol} = 2:1). Second solution B was prepared by dissolving sodium dodecyl sulfate (SDS, Aldrich) (1.25 g) in 10 mL of deionized water. Solutions A and B were mixed and stirred for 30 min and the resultant colloid solution was obtained. Subsequently 5.0 mL of 0.01 M aqueous $Gd_{0.794}Yb_{0.20}Ho_{0.001}Tm_{0.005}(NO_3)_3$ solution was added into the above colloid solutions, after stirring vigorously at 30 °C. Then the resulting colloid solution was then transferred into a 100.0-mL stainless Teflon-lined autoclave and heated at 180 °C for 24 h. The resulting suspension was cooled to room temperature right after the heating and was then stored at a constant temperature of 25 °C. After aging for 12 h, the resultant material was collected and washed several times with absolute ethanol and distilled water. The powder was obtained after centrifuging and drying in vacuum at 80 °C. Finally, the sample was immediately placed in a furnace at a heat-treatment temperature beforehand and was heated at 600 °C in a nitrogen gas stream for another 30 min.

Phase identification was performed via X-ray diffractometry (XRD) (Philip Co., PW 1830), using nickel-filtered Cu Kα radiation ($\lambda = 1.5406$ Å). The size and morphology of the nanocrystals were characterized by JEM-2010 transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM). The specimen for TEM observations was placed on perforated copper grids. The UC emission spectra were recorded with a Hitachi F-4600 fluorescence spectrophotometer with a 980 nm diode laser as the excitation source.

Figure 1 shows the powder XRD patterns of the β-$NaGd_{0.794}Yb_{0.20}Ho_{0.001}Tm_{0.005}F_4$. It is evident from the intensity of the peaks in the obtained patterns that the materials in question are highly crystalline in nature. All the diffraction peaks can be readily indexed to those of the hexagonal β-$NaGdF_4$ phase with lattice constants $a = 0.6020$ nm, and $c = 0.3061$ nm, which are in good agreement with the standard values for the bulk hexagonal β-$NaGdF_4$ (JCPDS No. 27-0699). In addition, two peaks from other YbF_3 phase were observed. An average crystallite size of 23 nm of the β-$NaGd_{0.794}Yb_{0.20}Ho_{0.001}Tm_{0.005}F_4$ sample was calculated using the (110), (101),

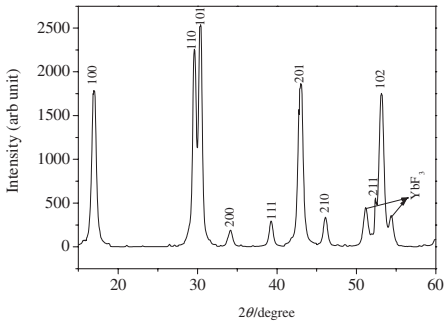

Figure 1. XRD patten of β-$NaGd_{0.794}Yb_{0.20}Ho_{0.001}Tm_{0.005}F_4$ nanoparticles.

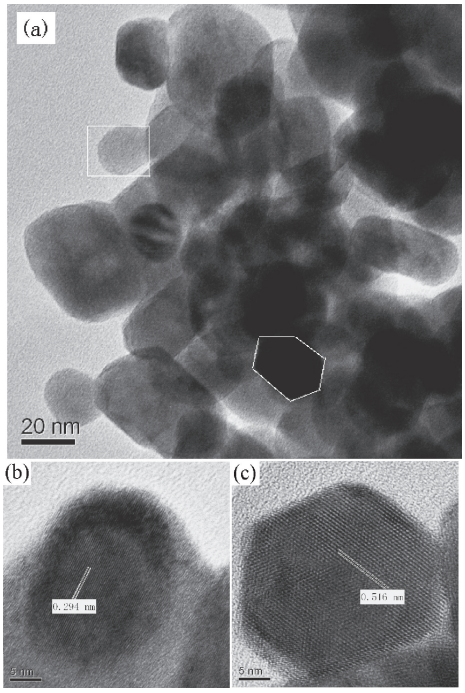

Figure 2. (a) The TEM image of the β-$NaGd_{0.794}Yb_{0.20}Ho_{0.001}Tm_{0.005}F_4$ nanoparticles, (b) and (c) HRTEM image of an individual β-$NaGd_{0.794}Yb_{0.20}Ho_{0.001}Tm_{0.005}F_4$ ellipsoidal shape and hexagonal nanoparticle.

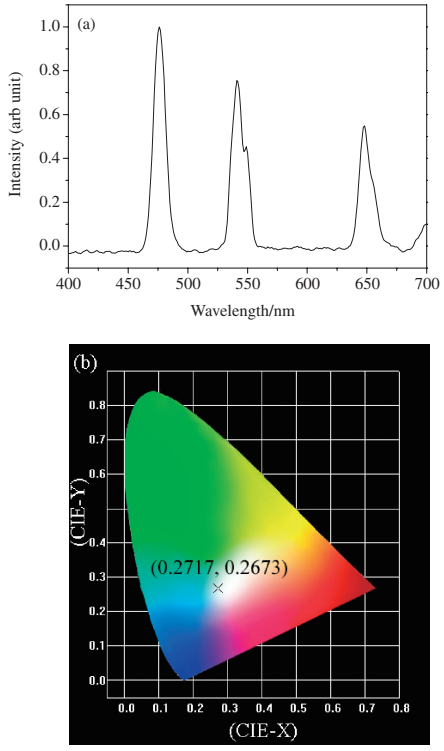

Figure 3. (a) Room-temperature UC emission spectra of the β-$NaGd_{0.794}Yb_{0.20}Ho_{0.001}Tm_{0.005}F_4$ nanoparticles under the 980-nm LD excitation with powers 350 mW, (b) (color online) CIE (X, Y) coordinate diagram showing the chromaticity points of the UC luminescence in the β-$NaGd_{0.794}Yb_{0.20}Ho_{0.001}Tm_{0.005}F_4$ nanoparticles.

and (201) diffraction peaks through the Debye–Sherrer formula. This value matches closely the particle size determined from the TEM results, which are shown in Figure 2.

The morphology of the final product was characterized by the TEM observation. As shown in a typical TEM image Figure 2a, most of the particles dispersed on the copper grids show hexagonal and ellipsoidal sphere morphology. The average edge length of the hexagon is about 23 nm. Figures 2b and 2c present typical HRTEM images of an ellipsoidal shape nanoparticle and a hexagonal nanoparticle indicated in Figure 2a, respectively. This image revealed that the crystals are structurally nonuniform with a clearly resolved interplanar spacing of about 0.294 and 0.516 nm which corresponds to (101) and (100) planes, respectively.

The room-temperature UC emission spectrum of the β-$NaGd_{0.794}Yb_{0.20}Ho_{0.001}Tm_{0.005}F_4$ nanoparticles with the pump power is presented in Figure 3a. The excitation wavelength is 980 nm, which agrees well with the Yb^{3+} ions $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition. This fluorescence corresponds to the following Tm^{3+} transitions: $^1G_4 \rightarrow {}^3F_4$ (ca. 450 nm), $^1G_4 \rightarrow {}^3H_6$ (ca. 476 nm) and Ho^{3+} transitions: $^5F_5 \rightarrow {}^5I_8$ (ca. 480 nm), $^5S_2$, $^5F_4 \rightarrow {}^5I_8$ (ca. 542 nm), $^5F_5 \rightarrow {}^5I_8$ (ca. 650 nm), respectively.

Figure 3b shows that the calculated color coordinates are 0.2717, 0.2673. They fall within the white region of the 1931 CIE diagram. This white light is bright and can been seen by naked eye even at a laser pump power of only 350 mW.

In conclusion, the β-$NaGd_{0.794}Yb_{0.20}Ho_{0.001}Tm_{0.005}F_4$ nanoparticles were synthesized through a simple hydrothermal method. The nanoparticles crystallized well and exhibited nearly hexagonal and ellipsoidal sphere morphology, as characterized by powder XRD, TEM, and HRTEM. TEM showed that the β-$NaGd_{0.794}Yb_{0.20}Ho_{0.001}Tm_{0.005}F_4$ nanoparticles have an average size of about 23 nm. Room-temperature bright white UC luminescence in β-$NaGd_{0.794}Yb_{0.20}Ho_{0.001}Tm_{0.005}F_4$ nanoparticles was obtained under single-wavelength diode laser excitation of 980 nm. The white light consists of the blue, green, and red UC radiations which correspond to the transitions $^1G_4 \rightarrow {}^3H_6$ of Tm^{3+}, $^5F_4 \rightarrow {}^5I_8$, and $^5F_5 \rightarrow {}^5I_8$ of Ho^{3+} ions, respectively. The spectral positions of the three colors produced CIE-X = 0.2717 and CIE-Y = 0.2673 coordinates.

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References

1 F. Auzel, *Chem. Rev.* **2004**, *104*, 139.
2 R. Serna, J. M. Ballesteros, M. J. de Castro, J. Solis, C. N. Afonso, *J. Appl. Phys.* **1998**, *84*, 2352.
3 L. W. Yang, H. L. Han, Y. Y. Zhang, J. X. Zhong, *J. Phys. Chem. C* **2009**, *113*, 18995.
4 L. Luo, X. X. Zhang, K. F. Li, K. W. Cheah, J. X. Shi, W. K. Wong, M. L. Gong, *Adv. Mater.* **2004**, *16*, 1664.
5 S. Sivakumar, F. C. J. M. van Veggel, M. Raudsepp, *J. Am. Chem. Soc.* **2005**, *127*, 12464.
6 F. Lahoz, I. R. Martin, J. M. Calvilla-Quintero, *Appl. Phys. Lett.* **2005**, *86*, 051106.
7 A. S. Gouveia-Neto, L. A. Bueno, R. F. do Nascimento, E. A. de Silva, E. B. da Costa, V. B. do Nascimento, *Appl. Phys. Lett.* **2007**, *91*, 091114.
8 N. K. Giri, D. K. Rai, S. B. Rai, *J. Appl. Phys.* **2008**, *104*, 113107.
9 D. Chen, Y. Wang, K. Zheng, T. Guo, Y. Yu, P. Huang, *Appl. Phys. Lett.* **2007**, *91*, 251903.

