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Tunable Multicolour Upconversion and Paramagnetic Properties of Tm^{3+}/Er^{3+} Doped $NaYbF_4$ Micro-tubes

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ABSTRACT

In this paper, according to doping the lanthanide ions, fluorescent and magnetic $NaYbF_4$ micro-tubes with hexagonal phase were synthesized *via* hydrothermal method using oleic acid as a capping ligand and surface modifier. Some of the samples were tested by X-ray diffraction analysis, transmission electron microscopy (TEM), field-emission scanning electron microscopy (FE-SEM), energy dispersive X-ray spectroscopy and vibrating sample magnetometer (VSM). From the TEM and FE-TEM, $NaYbF_4$ micro-tubes showed high quality of hexagonal shape. In such $NaYbF_4$ system, the upconversion luminescence (UCL) colours turn from purplish blue to blue, greenish white and further to yellowish green. The upconversion luminescence mechanisms were also analyzed by spectral methods. Besides, such $NaYbF_4$ micro-tubes showed good paramagnetic characteristic at room temperature and the magnetic mass susceptibility reached to 3.43×10^{-5} emu/g per Oe and 0.51 emu/g at 15 kOe. Such excellent characteristics showed that $NaYbF_4$ is a good host material and may have good potential applications in lasers photonics and dual-modal bio-probe.

KEYWORDS

Upconversion luminescence, Rare earth-doped compounds, Tunable multicolour emissions, Paramagnetic property.

INTRODUCTION

For the excellent upconversion luminescence (UCL) properties and potential application in bio-labels, colour displays, optics and so on, rare earth-doped compounds have gotten much attention nowadays [1-5]. In recent years, upconversion luminescence of white light may be applied in 3-D solid-state display, light-emitting diodes, *etc*. Frequency upconversion has been considered as an efficient route for producing bright white light emission by selecting proper sensitizers and activator ions [6]. However, there are still some challenges to obtain white upconversion luminescence for that it needs chemically stable host and good controlled emissions of the three primary colours. There are few papers about the generation of white light emission through the frequency upconversion in fluoride glass and telluride glass host materials [7]. Recently, some papers about white light simulation showed important progress in Y_2O_3 nanocrystals and ZnO nanocrystals

[7,8]. Also, many reports [3,9-13] showed that red, green and upconversion luminescence colours were observed in $NaYbF_4$ co-doped with Er^{3+}, Tm^{3+} and Yb^{3+}. Besides, Eu^{3+}co-doped ZnO/Zn_2SiO_4:Mn^{2+}composites were synthesized *via* conventional solid state reaction route and present excellent white light property.

Although only few reports were present about white light emission in $NaLnF_4$ host with hexagonal phase, some groups [14-16] demonstrated that $NaYbF_4$ is a suitable host materials, especially when doped with Er^{3+} and Tm^{3+}. Moreover, since their good paramagnetic nature, rare earth-doped compounds have been an attractive attention for decades. For example, $NaLuF_4$:Gd^{3+}, $BaGdF_4$ and $NaErF_4$ hosts have excellent paramagnetic properties and make it ideal contrast agent for magnetic resonance imaging [17-19].

In this paper, according to a typical hydrothermal method, fluorescent/magnetic $NaYbF_4$ micro-tubes doped with Ln were synthesized. At the excitation power of 980 nm laser diode (LD), the tunable bright greenish white upconversion luminescence were achieved *via* frequency upconversion. Compared with the triply doped system such as Yb^{3+}/Er^{3+}/Tm^{3+}, the white light emission from $NaYbF_4$ host only need to readily control two doping activator ions including Er^{3+} and Tm^{3+}. Moreover, the paramagnetic property of as-prepared $NaYbF_4$ micro-tubes is demonstrated for the first time.

EXPERIMENTAL

In this paper, all of the reagents used were in analytical grade. $Ln(NO_3)_3$ (Ln = Yb^{3+}, Tm^{3+} and Er^{3+}) solutions were 0.5, 0.1 and 0.1 mol/L, respectively. These were produced by dissolving the corresponding amount of rare-earth oxide in nitric acid at high temperature and excess nitric acid was removed by evaporation.

Synthesis of $NaYbF_4$ micro-tubes: The hexagonal phase prism-like $NaYbF_4$ micro-tubes were synthesized *via* modified hydrothermal method [20,21]. A typical synthesis involved 1.2 g NaOH, which was dissolved in 2 mL deionized water. Then with vigorously stirring, 8 mL ethanol and 20 mL oleic acid were added into water. After stirring for about 20 min, 1 mmol of $Ln(NO_3)_3$ were added to the solution with designed molar ratios. These mixtures were stirred for another 30 min and then, 8 mL (1.0 M) of aqueous solution of NaF was added. Finally, the result solution was transferred into a 50 mL stainless Teflon-lined autoclave and reacted for 24 h at 190 °C. The solution was cooled down to room temperature naturally after reaction completion. The as-prepared samples were washed with ethanol and deionized water several times and dried in air at 80 °C for 6 h.

Characterizations: After obtaining samples, these crystal phases were measured by X-ray diffraction (XRD) analysis, which were carried out by D/max-γA system X-ray diffractometer at 40 kv and 40 mA with CuKα radiation. And then, by JEOL-2100 high-resolution transmission electron microscope (TEM), the shape and structure were characterized by TEM and selected area electron diffraction (SAED). Also energy dispersive spectroscope (EDS) was performed with the same equipment. Furthermore, by Leo-Supra35 field emission scanning electron microscope (FE-SEM), the morphology was observed.

At last, the upconversion luminescence characteristics were tested. For instance, the upconversion luminescence spectra were recorded by spectrophotometer (R500) at the excitation of 980 nm LD and the magnetic property was obtained by Lake-shore 7410 VSM in the applied field ranging from -15 to 15 kOe. All the measures were performed at room temperature.

RESULTS AND DISCUSSION

Structural analysis: The samples of $NaYbF_4$ were characterized by XRD analysis. Fig. 1 presents the typical XRD pattern of hexagonal phase $NaYbF_4$ with Tm^{3+} doped. In the XRD and physico-chemical analysis, the results were revealed that the samples had the same phase and structure as JCPDS No.27-1427. And no other impurity phase was detected, which indicate a pure hexagonal phase of the $NaYbF_4$.

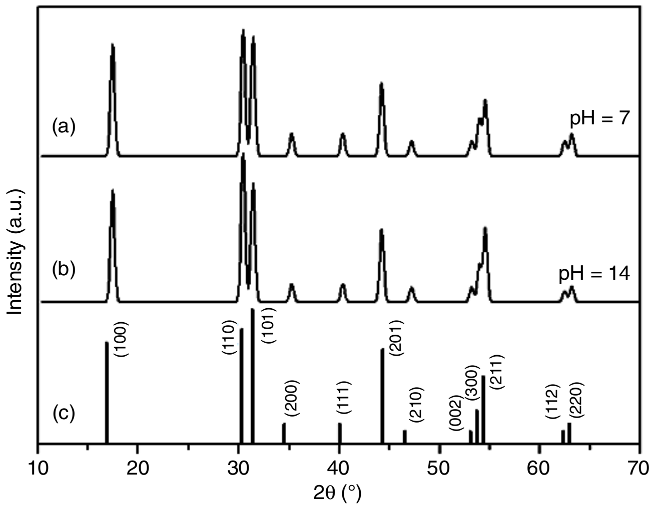

Fig. 1. Typical XRD pattern of the Tm^{3+} doped $NaYbF_4$ micro-tubes and standard hexagonal phase $NaYbF_4$ crystals

Furthermore, to obtain the microstructure of the samples, FE-SEM and TEM tests were carried out and some typical FE-SEM images were shown in Fig. 2a. As shown in Fig. 2a, the as-prepared samples present hexagonal prism tubular structures. To demonstrate inner structures, TEM characterization was performed. As shown in Fig. 2b, the diameter of the hexagonal-prism micro-tubes is around1800 nm and the length is about 7000 nm. And at the same time, the corresponding SAED was also tested. The result showed the regular diffraction spots indicating the individual micro-tubes are of single crystal nature. With the SAED result, it can show that the growth direction is along [0001] direction.

During the TEM analysis, samples were detected by the EDS and results are present in Fig. 2c. It is shown that the main materials of composition are Na, Yb and F. However, Er and Tm have not been observed due to the resolution limit. Cu and C were observed owing to TEM copper grid and covered carbon film, respectively.

Tunable multicolour emissions: To obtain the upconversion luminescence properties of the $NaYbF_4$ micro-tubes, different Ln-doped samples were tested. For comparison, three samples were tested and results were shown in Fig. 3. From

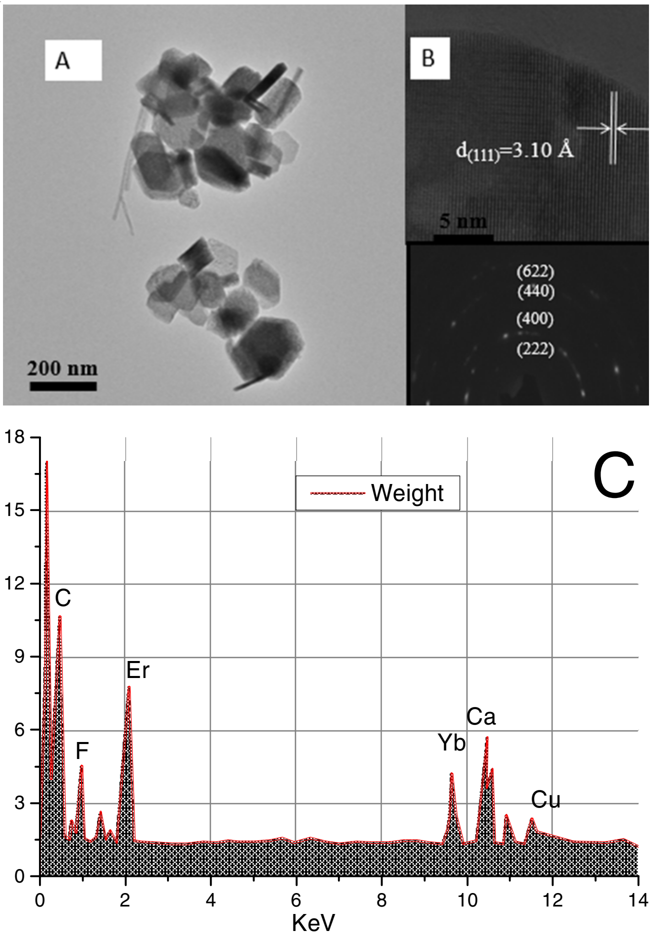

Fig. 2. (a) FE-SEM image, (b) TEM image and (c) EDS image of $NaYbF_4$

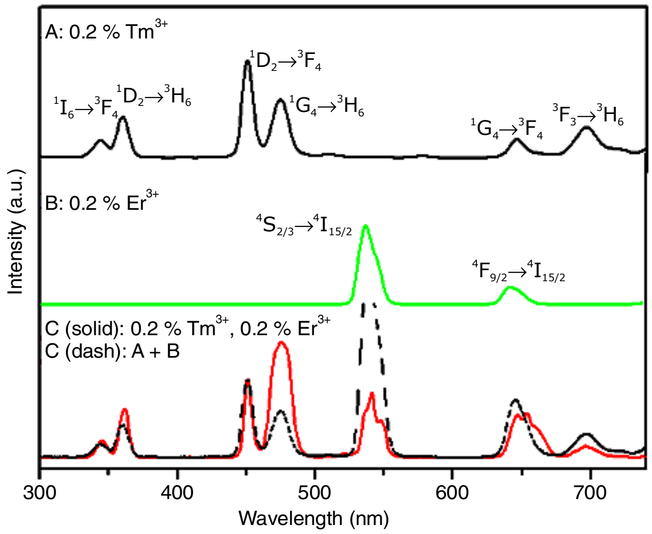

Fig. 3. Upconversion luminescence spectra (a) $NaYbF_4$:0.2 % Tm^{3+}, (b) $NaYbF_4$:0.2 % Er^{3+} and (c) $NaYbF_4$:0.2 %Tm^{3+}/0.2 % Er^{3+}

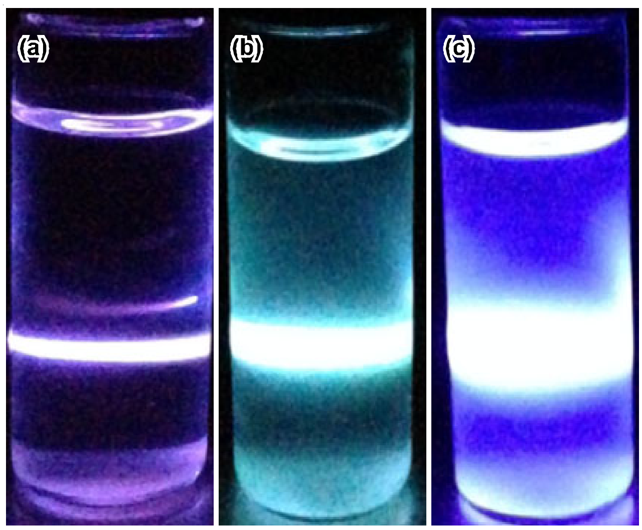

Fig. 4. Digital photographs of three samples which are excited under 980 nm LD

Fig. 3a, it shows that intense UV (345, 361 nm), blue (451, 475 nm) and weak red (649, 696 nm) emissions were observed in $NaYbF_4$:0.2 % Tm^{3+}; Fig. 3b shows that intense green (538 nm) and weak red (644 nm) emissions were observed in $NaYbF_4$:0.2 % Er^{3+}; Fig. 3c shows that blue (451, 475 nm), green (538 nm) and red (649 nm) emission were observed in $NaYbF_4$:0.2 % Tm^{3+}/0.2 % Er^{3+}, respectively.

Fig. 4 showed the digital photographs of the three samples, which are excited under 980 nm LD with a power density of 0.5 W/cm^2. Since the different doped materials, Fig. 4a demonstrates purplish blue colour, while Fig. 4b demons-trates yellowish colour. That means it may obtain white upconversion emission by precisely controlling the ratio of Tm^{3+} and Er^{3+} in Tm^{3+}/Er^{3+} co-doped system. At the same ratio of doped Tm^{3+} and Er^{3+} in $NaYbF_4$, Fig. 4c shows greenish white colour.

Fig. 5 is a schematic energy-level diagram of upconversion luminescence property. In Fig. 5a, it can be obtained that emission centers are 345, 361, 451, 475, 649 and 696 nm for $NaYbF_4$:0.2 % Tm^{3+}. It can be concluded that these emissions are due to $^1I_6\to{}^3F_4$, $^1D_2\to{}^3H_6$, $^1D_2\to{}^3F_4$, $^1G_4\to{}^3H_6$, $^1G_4\to{}^3F_4$ and $^3F_3\to{}^3H_6$ transitions of Tm^{3+}, respectively. Also, from Fig. 5b and Fig. 5, it indicated that intense emissions at 538, 644 nm are observed due to $^4S_{2/3}\to{}^4I_{15/2}$, $^4F_{9/2}\to{}^4I_{15/2}$ of Er^{3+} transitions, respectively. Com-pared with Fig. 5a and Fig. 5b, blue upconversion luminescence centered at 451 and 475 nm were generated from $^1D_2\to{}^3F_4$ and $^1G_4\to{}^3H_6$ of Tm^{3+}, respectively. Green emission centered at 538 nm was generated from $^5S_2/^5F_4\to{}^5I_8$ of Er^{3+}. Red emission band centered at 649 nm originated from the electronic transitions of $Tm^{3+}$and Er^{3+}. These results indicate that tunable purplish blue, yellowish green and greenish white upconversion luminescence can be achieved by simply doping Tm^{3+}, Er^{3+}, which is different from previous report that $NaYF_4$ and $NaGdF_4$ host require co-doping and tri-doping for multicolour tuning [12].

Magnetic property: Besides the upconversion luminescence characteristics, the $NaYbF_4$ micro-tubes have good paramagnetic property whose magnetic moment reaches 4.53 μ_B [13,22]. The magnetization of the $NaYbF_4$ micro-tubes was presented in Fig. 6, which is a function of applied field (ranging from -15 to 15 kOe) at room temperature. The typical paramagnetic behaviour of the $NaYbF_4$ micro-tubes is primarily ascribed to the one unpaired inner 4*f* electron, which is closely bound to the nucleus and effectively shielded by the outer closed shell electrons ($5s^25p^6$) from the crystal field. At 15 kOe, the magnetic mass susceptibility of $NaYbF_4$ micro-tubes reaches to 3.43×10^5 emu/g Oe and magnetization to 0.51 emu/g, which is close to the value of reported $BaGdF_5$ host [19,23,24].

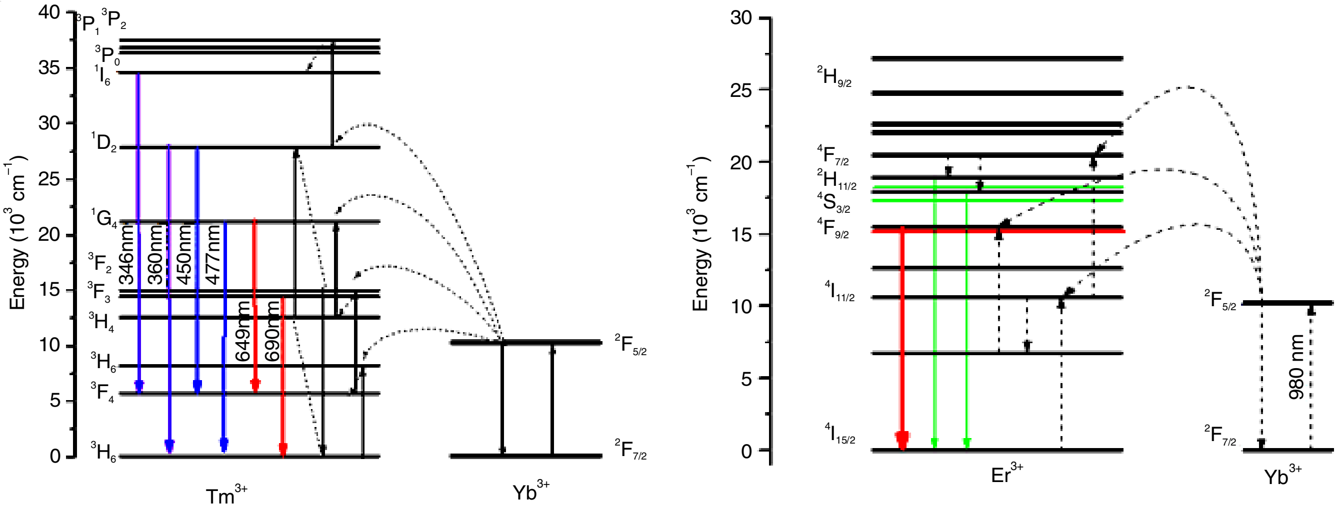

Fig. 5. (a) Schematic energy-level diagram of Er^{3+}, Yb^{3+} and Tm^{3+} and (b) proposed mechanism of upconversion luminescence

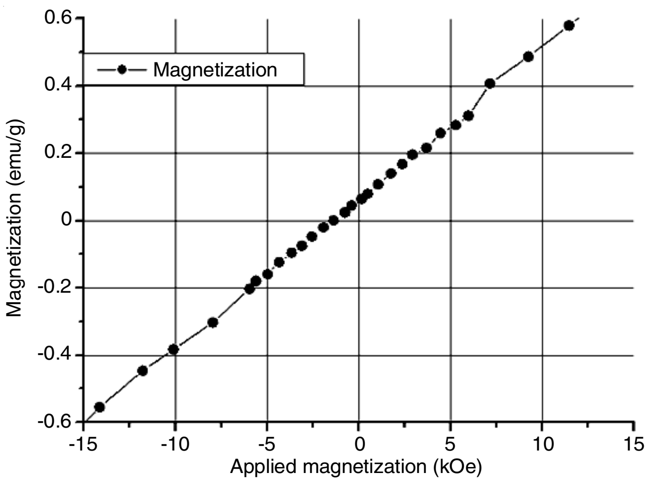

Fig. 6. Magnetization as a function of applied field for the as-synthesized $NaYF_4$ micro-tubes

Conclusion

In conclusion, *via* hydrothermal method using oleic acid as a stabilizing agent and surface modifier, the pure hexagonal prism-like $NaYbF_4$ micro-tubes were synthesized. These micro-tubes have good upconversion luminescence and paramagnetic properties. The TEM and FE-SEM results show that these micro-tubes have single crystal nature. Moreover, by tuning the content of Tm^{3+} and Er^{3+} in $NaYbF_4$ system, tunable eye-visible upconversion luminescence colours from purplish blue/blue to greenish white and further to yellowish green light can be achieved. Besides, the upconversion luminescence colour tuning from bluish green to greenish white can be induced by excitation power. More importantly, these $NaYbF_4$ micro-tubes demonstrate very good paramagnetic property. Such excellent properties mean that $NaYbF_4$ micro-tubes may have potential applications in many fields such as displays, lasers and even dual-modal bio-probes.

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