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ORIGINAL RESEARCH

Synthesis of Yb^{3+}/Er^{3+} co-dopants sodium yttrium fluoride up-conversion fluorescence materials

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ABSTRACT: Yb^{3+}/Er^{3+} co-dopants sodium yttrium fluoride micro-powders were synthesized by a combustion method and the luminescence properties investigated. The results indicated that the up-conversion material synthesized by this method has high up-conversion efficiency and the fluorescence spectrum peak was sharp. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: rare-earth; up-conversion; combustion synthesis; sodium yttrium fluoride; fluorescence materials

INTRODUCTION

Considerable attention has been devoted to the conversion of near-infrared radiation to visible light in rare earth-doped materials (1–3). Rare-earth elements have already proved to be very useful in up-conversion for applications such as colour displays, high-density optical data reading and storage (4–6), infrared laser viewers and indicators (7, 8). There have been an increasing number of investigations on rare earths in nanosized materials; among these, Yb^{3+}/Er^{3+} co-doped yttrium fluoride has been widely studied and gives high efficiency (9–12). Initial successful applications in the biological marker field in recent years and in-depth studies on the luminescence mechanism have generated interest in up-conversion fluorescence materials (13, 14).

The traditional synthesis of the fluoride salt always uses the high-temperature solid phase method, which needs rigorous synthesis conditions, complicated apparatus and long reaction times (15, 16). Recently, the co-deposition method and the hydrothermal method have been used to synthesize rare-earth-doped sodium yttrium fluoride fluorescence materials. However, the existing methods need to be improved in their up-conversion efficiency and luminescence purity.

In this study, the pre-product was prepared using a deposition method, and then doped with boron. The Yb^{3+}/Er^{3+} co-doped sodium yttrium fluoride fluorescence material was prepared by a combustion method to give a product which emitted green fluorescence with high up-conversion efficiency.

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EXPERIMENTAL

Preparation of the sample

The pre-product of rare-earth-doped sodium yttrium fluoride up-conversion fluorescence material was prepared by co-deposition. Then the rare-earth-doped sodium yttrium fluoride was treated by the combustion method. NaF (3.15 g) was ultrasonically treated until completely dissolved in 80 mL de-ionized water to make solution A. According to the assigned composition of the fluorescence material $NaY_{0.77}Yb_{0.2}Er_{0.03}F_4$, the pre-prepared 0.2 mol/L YCl_3 solution (16.0 mL), 0.2 mol/L $YbCl_3$ solution (3.4 mL) and 0.2 mol/L $ErCl_3$ solution (0.6 mL) were mixed to produce solution B, which is then rapidly injected into the NaF solution and stirred for 1 h to obtain the precipitate. The precipitate was separated by centrifugation and washed several times, then mixed with water and stirred to form a suspension. This was mixed with boric acid and urea and stirred, then was put into a crucible, which was quickly moved to the muffle furnace at a temperature of 550°C. After about 10 min, heavy smoke was produced; the crucible was removed several minutes later. Lastly, when the crucible had cooled the contents were removed and ground to form a white powder.

Characterization of the sample and assessment of fluorescence properties

The composition of the synthesized sample was analysed using an inductively coupled plasma atomic emission spectrometer (ICP-AES) and its morphology was analysed using a KYKY 2000 SEM. The up-conversion emission spectra excited by a 980 nm infrared laser were recorded with a HITACHI 850 fluorescence spectrometer. The up-conversion efficiency was obtained by calculating the fluorescence spectra integral areas, using the method proposed by Ramasamy (17).

RESULTS AND DISCUSSIONS

Investigation of composition, phase and morphology

The rare-earth components were accurately determinated with ICP-AES and the results are shown in Table 1. SEM showed that the sample comprised of 10 μm-sized particles (Fig. 1).

Fluorescence properties

The up-conversion fluorescence spectrum of the sample illuminated by the 980 nm infrared laser is shown in Fig. 2. The ratio of the green: red fluorescence peak intensity is ~12:1, which is much larger than the results obtained using other synthesis methods (18). This may be due to an improvement in the crystallinity of the sample as a result of treating the pre-product with the combustion method (19). Others (11) have prepared smaller-sized particles but the ratio of green: red fluorescence intensity is much lower. The conclusion is therefore drawn that it is not the dimensions of the material but the microstructure and crystallinity that affect the strength of the green fluorescence.

The synthesized $NaYF_4$:Yb and a sample synthesized by other methods were compared for up-conversion efficiency, using the method suggested by Ramasamy (17). The results indicated that the up-conversion efficiency of the red fluorescence of the synthesized sample of rare-earth-doped sodium yttrium fluoride (wavelengths 520 nm and 539 nm) is around 25%, which was much higher than the results in the literature.

Table 1. The element constitution of Yb^{3+}/Er^{3+} co-doped sodium yttrium fluoride powders

Sample	Content (mol)	Normalized content
Yb	0.260	0.020
Er	0.046	0.035
Y	1.000	0.770

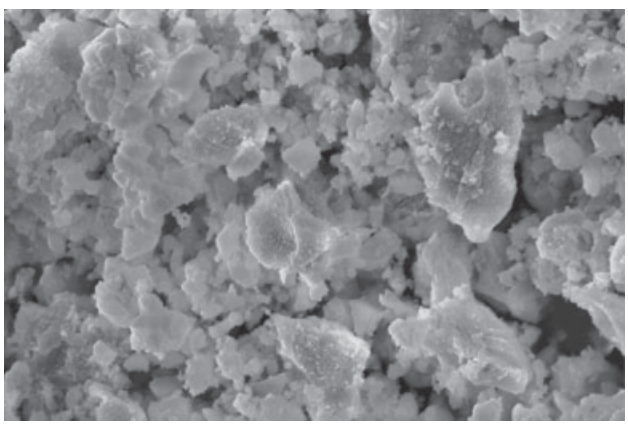

Figure 1. SEM of Yb^{3+}/Er^{3+} co-doped sodium yttrium fluoride powders.

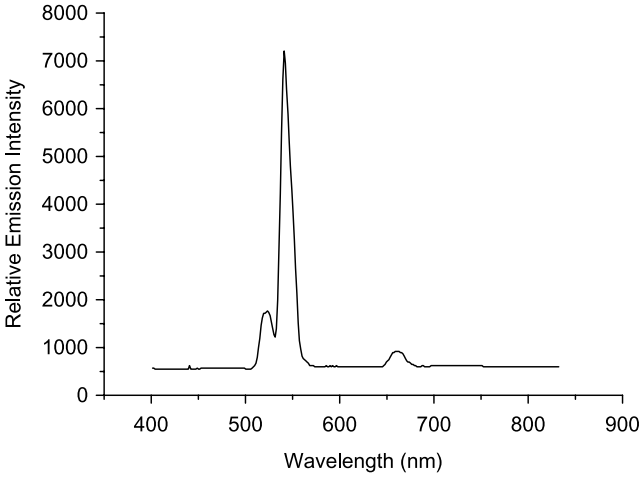

Figure 2. Infrared-to-visible up-conversion fluorescence spectrum of Yb^{3+}/Er^{3+} co-doped sodium yttrium fluoride powders.

The effect of the synthesized batch formula and conditions on the sample's results, pattern and luminescence spectrum

When synthesizing $NaYF_4$:Yb by the combustion method, boric acid was needed as a solvent. If excess boric acid was added, the product was hard and white, and the emitted fluorescence was yellow and weak. The optimal dose of boric acid selected in this experiment was 0.1–0.5 g and the urea was 16 g.

The above batch formula was adopted using temperatures of 200°C, 300°C, 400°C, 450°C, 500°C, 550°C, 600°C, 650°C, 700°C separately for the combustion synthesis method. It was found that the synthesized sample fluorescence was weak and the crystallinity poor when the temperature was below 500°C. At a temperature above 600°C, the sample was black because of decomposition of the sample. So the optimal synthesis temperature was 500–600°C. The optimal conditions for synthesizing the Yb^{3+}/Er^{3+} co-doped sodium yttrium fluoride (NaYF4:Yb,Er) up-conversion fluorescence materials by the combustion method consists of boric acid 0.1–0.5 g, urea 16 g, NaF 3.15 g, YCl_3 0.0032 mol, $YbCl_3$ 0.00068 mol, $ErCl_3$ 0.0012 mol, and temperature of about 550°C.

CONCLUSION

The Yb^{3+}/Er^{3+} co-doped sodium yttrium fluoride ($NaYF_4$:Yb,Er) synthesized by the combustion method shows good crystallinity and emitted green fluorescence

with high up-conversion efficiency. It may be applied to illumination for energy-saving or as a low background biological marker. In addition, due to its simple preparation method and good batch–batch repeatability, it is easily industrialized.

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