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Microwave-assisted hydrothermal synthesis and temperature sensing application of Er^{3+}/Yb^{3+} doped $NaY(WO_4)_2$ microstructures

Hui Zheng [a,b], Baojiu Chen [a,*], Hongquan Yu [b,*], Jinsu Zhang [a], Jiashi Sun [a], Xiangping Li [a], Min Sun [a], Bining Tian [a], Shaobo Fu [a], Hua Zhong [a], Bin Dong [c], Ruinian Hua [c], Haiping Xia [d]

[a] Department of Physics, Dalian Maritime University, Dalian 116026, People's Republic of China
[b] College of Environmental and Chemical Engineering, Dalian Jiaotong University, Dalian 116028, People's Republic of China
[c] School of Physics and Material Engineering, College of Life Science, Dalian Nationalities University, Dalian 116600, People's Republic of China
[d] Key Laboratory of Photo-Electronic Materials, Ningbo University, Ningbo 315211, People's Republic of China

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ABSTRACT

Laurustinus shaped $NaY(WO_4)_2$ micro-particles assembled by nanosheets were synthesized via a microwave-assisted hydrothermal (MH) route. The growing mechanisms for the obtained resultants with various morphologies were proposed based on the observation of scanning electron microscopic (SEM) images. It was found that Na_3Cit added into the reaction solution greatly influenced the formation and size dimension of the nano-sheets, furthermore determined assembling of the laurustinus shaped micro-particles. The temperature sensing performance of $NaY(WO_4)_2:Er^{3+}/Yb^{3+}$ was evaluated. Thermal effect induced by the 980 nm laser irradiation in laurustinus-shaped $NaY(WO_4)_2:Er^{3+}/Yb^{3+}$ phosphor was studied. It was found that the green upconversion luminescence intensity increased in the first stage of laser irradiation, and then decreased after reaching a maximum. Based on the thermal sensing technology the laurustinus $NaY(WO_4)_2:Er^{3+}/Yb^{3+}$ microparticles were used as thermal probe to discover thermal effect of upconversion luminescence in laurustinus $NaY(WO_4)_2:Tm^{3+}/Yb^{3+}$ micro-particles.

1. Introduction

As a result of extensive study for decades, lanthanide (Ln^{3+})-doped fluorescent powders have been successfully applied in color displays, vivo bio-imaging, medical diagnosis, detection technology, and temperature sensors [1–9]. Admittedly, temperature is not only a fundamental but also significant physical parameter, especially in the area of biotechnology. For instance, a cellular event is revealed by a corresponding change in temperature. Hence, the ability to accurately detect the temperature fluctuation of a single living cell, in some occasion that of a cancer cell, could render us an insight into its physiology and pathology, thereby creating an opportunity to effective diagnosis and treatment. Traditional methods to detect temperature of intracellular temperature could not achieve proper accuracy. A recently-developed method to monitor the intracellular temperature is to use fluorescent nano- or micro-sized materials as thermal probes [10–12]. In this case, suitable biocompatible materials acting as thermal probe are urgently needed. The most important point is that the emission band shape, lifetime, intensity or peak position of these fluorescent materials should be sensitively affected by temperature. Besides, these materials should be characterized by minimal interactions with intracellular environment, certain chemical stability and appropriate size. In particular, Er^{3+}/Yb^{3+} co-doped system is regarded as an ideal choice for thermal probe technique due to the proper energy difference between $^2H_{11/2}$ and $^4S_{3/2}$ multiplets of Er^{3+} and a larger absorption cross section at near infrared (NIR) of Yb^{3+} [13,14].

With higher biocompatibility, nano- and micro-scale powders are more suitable for temperature sensing. Therefore, available host materials play another key role in this technique. Actually, owing to the low phonon energy, fluorides are the mostly investigated materials [15–19]. Some recent work still focuses on the performance of $NaYF_4$ on down and up-conversion luminescence and temperature sensing [17–19]. However, as alternative hosts, alkaline rare earth tungstates display their remarkable optical properties and excellent chemical and thermal stability, which are less extensively studied but still promising host matrixes [20–23]. $NaY(WO_4)_2$ micro- and nano-structures have been studied frequently in recent years, and it has been found that the shape control could be realized by changing reactant concentration, reaction time and temperature, type of surfactant, pH value, etc. [24,25].

A facile synthesis route will greatly influence experiment results. Traditional chemical synthesis methods including vapor

* Corresponding authors at: Department of Physics, Dalian Maritime University, Dalian 116026, People's Republic of China. Fax: +86 411 84728909 (B. Chen).
E-mail addresses: chenmbj@sohu.com (B. Chen), yuhq7808@djtu.edu.cn (H. Yu).

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deposition, sol–gel process, hydrothermal and combustion methods could be advisable options for sample preparation, while a new improved approach, MH, is increasingly applied in nano- and micro-sized materials [26–28]. Compared with conventional hydrothermal (CH), MH has some obvious advantages, such as higher heating rates, reducing reaction time, better control of the reaction parameters, higher yields and improved reproducibility [28]. It is suggested that all these merits originate from the thermal effect caused by microwave, and it is well known that the microwave irradiation triggers heating by two main mechanisms, namely dipolar polarization and ionic conduction, both of which efficiently heat materials inside the reaction system. Moreover, microwave heating is environmental friendly and energy-saving. In general, MH seems to be a new alternative approach to synthesize target samples.

In this paper, laurustinus shaped $NaY(WO_4)_2$ micro-particles were successfully synthesized by a microwave hydrothermal route. It was found that the surfactant has great influence on the morphology of as-prepared samples. The morphology of the micro-particles was turned by altering the concentration of surfactant, and the growth mechanism was discussed. Temperature sensing curve of $NaY(WO_4)_2$:Er^{3+}/Yb^{3+} was calibrated and the temperature effect in $NaY(WO_4)_2$:Er^{3+}/Yb^{3+} microstructures caused by 980 nm laser irradiation was explored based on the temperature sensing of Er^{3+} ions. Meanwhile $NaY(WO_4)_2$:Er^{3+}/Yb^{3+} was used as thermal probe to examine the temperature effect of $NaY(WO_4)_2$:Tm^{3+}/Yb^{3+} microstructure induced by 980 nm laser excitation. Temperature rising phenomenon of $NaY(WO_4)_2$:Tm^{3+}/Yb^{3+} microstructure was also observed by using the thermal probe of $NaY(WO_4)_2$:Er^{3+}/Yb^{3+}.

2. Experimental section

All the rare earth oxides including Y_2O_3 (99.99%), Er_2O_3 (99.99%), Tm_2O_3 (99.99%) and Yb_2O_3 (99.99%), were purchased from Shanghai Second Chemical Reagent Factory (China). Other chemicals including sodium citrate (Na_3Cit) and $Na_2WO_4{\cdot}2H_2O$ were purchased from Tianjin Reagent Chemicals Co. Ltd. (China). All chemicals are of analytical reagent and were used without any further purification.

All the lanthanide nitrates used for preparing the samples were obtained by dissolving rare earth oxides into dilute nitric acid, and extra nitric acid was removed by evaporating the solution for several times [24]. In a typical process for the synthesis of laurustinus shaped $NaY(WO_4)_2$ microstructures, 2 mmol sodium citrate was dissolved into 5 mL distilled water, and 4 mL solution containing 2 mmol $Y(NO_3)_3$ was subsequently added into the above solution, which formed a white colloidal precipitate. After vigorously stirring for 15 min, another 5 mL solution containing 4 mmol Na_2WO_4 was added, and the pH value of the mixed solution was adjusted to 8–9 by adding NaOH (1 M). Then the mixed solution was left to 20 min additional stirring. The as-obtained mixed solution was transferred to a 30 mL silica glass vessel sealed with a special cap provided by the manufacturer, and then the vessel was put into a Microwave Synthesizer (Biotage Initiator, Sweden) and irradiated for 1 h at 180 °C. After microwave heating, the vessel was naturally cooled to room temperature. The precipitate was separated by centrifugation, washed with distilled water and anhydrous ethanol for several times, and then dried in air at 75 °C for 6 h. The final product was obtained by a calcination process at 600 °C for 1 h. The obtained samples with various doping concentrations and different reaction parameters were numbered and are listed in Table 1.

X-ray powder diffraction (XRD) patterns were measured with a Rigaku D/MAX-Ultima$^+$ diffractometer in 2θ range from 15° to 70° with graphite-monochromatized Cu Kα1 radiation (λ = 0.15406 nm). The phase identifications were performed with PDF-2 database provided by the International Centre for Diffraction Data (ICDD). Morphologies were observed by a field emission scanning electron microscopy (FE-SEM, SUPRA 55 SAPPHIRE, ZEISS, Germany). Fluorescence spectra were obtained by an F-4600 spectrophotometer (Hitachi, Japan). Temperature controlling system was independently assembled, with which the prepared samples can be accurately heated to the temperature ranging from room temperature to 450 °C. A 980 nm fiber laser with maximum output power of 2 W (BTW KS3-11312-103, China) was used to excite samples for the measurements of up-conversion fluorescence spectra, its output power can be adjusted within 2 W. When the 980 nm fiber laser reaches its maximum output power, the excitation power density is about 160 W/cm^2.

3. Results and discussions

3.1. Phase identification

XRD patterns for all samples were measured in order to identify the structure and phase of the obtained samples. Fig. 1 shows the XRD patterns of all samples prepared at 180 °C for 1 h. Sharp and strong diffraction peaks referred to good crystallinity. The positions of all the diffraction peaks are in well agreements with those reported in JCPDS card (No. 48-0886). Besides, no additional diffraction peaks from other impurities can be detected, which confirmed the high phase purity of the prepared samples. It should be mentioned here that the introduction of Er^{3+}, Tm^{3+} and Yb^{3+} did not obviously affect the phase purity and the crystal structure of $NaY(WO_4)_2$ microarchitectures.

3.2. Reaction parameter effects on the morphologies

Fig. 2 shows FE-SEM images for the samples prepared under different reaction parameter conditions. In order to investigate the influence of surfactant Na_3Cit on the morphology of the resultant $NaY(WO_4)_2$, the samples were synthesized in the absence and presence of Na_3Cit, and different concentrations of Na_3Cit were also designed. Fig. 2(a) displays a typical FE-SEM image of $NaY(WO_4)_2$ prepared without Na_3Cit addition. In this case the sample exhibits irregular morphology, and some groups of gathered irregular bulk particles were formed. This fact indicates that the particles with a fixed morphology cannot be derived without addition of any surfactant. Na_3Cit is a commonly used reagent acting as surfactant in the hydrothermal reaction, which is also adopted in this study. While in the presence of 1 mmol of Na_3Cit, a mass of nano-sheets (thickness of about 20 nm) appeared with blurry edge and still aggregated to cotton-liked groups, as shown in Fig. 2(b) and (c) which is substantially different from that in Fig. 2(a), thus indicating despite addition of less amount of surfactant Na_3Cit the resultant morphology can be changed greatly. When the content of Na_3Cit increased to 2 mmol, significant morphology transformation happened. Micro-spheres were formed as shown in Fig. 2(d), whose high-magnification SEM image displays in Fig. 2(e) and (f). It is shown in Fig. 2(f) that the micro-spheres with diameter of around 1.5 μm are assembled by nano-sheets. The average thickness of the nano-sheets is around 20 nm. By further increasing the concentration of Na_3Cit to 3 mmol, laurustinus-shaped microspheres were derived, and their average size is around 2.0 μm which is larger than that as observed in Fig. 2(d). Each microsphere as shown in Fig. 2(h) of the magnification SEM image is also assembled by nano-sheets with larger thickness of 30 nm than that in Fig. 2(d). By continuously increasing the Na_3Cit content to 4 mmol in the reaction system, instead of the micro-spheres, irregular laurustinus shaped micro-particles with average diameter of