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Simultaneous luminescence and magnetic control of $NaLuF_4$: Yb^{3+}/Er^{3+} by introducing $NaMnF_3$ and the application for detecting basic fuchsin

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ABSTRACT

In this work, we reported $NaLuF_4$:Yb^{3+}/Er^{3+} optical-magnetic bifunctional material by a facile hydrothermal method. The modulation of luminescent and magnetic properties by introducing the secondary phase $NaMnF_3$ was investigated in detail. It was found that the multi-color emissions of the proposed material can be easily controlled due to the energy level match between the Mn and the lanthanide ions. In addition, these microcrystals presented paramagnetic and ferromagnetic property, and the relative intensity showed an opposite variation to the content of $NaMnF_3$ phase. Finally, we briefly discussed the dye detection based on this bifunctional material as fluorescent probe, and the integral intensity ratio of red to green emission was found being sensitive to the concentration of the basic fuchsin (BF), and a detection limit of 0.0015 μg/ml was achieved. These findings can be helpful to understand $NaMnF_3$ induced optical-magnetic property modulation and provide some applications in the biosensing and bioimaging area.

1. Introduction

Lanthanide-doped upconversion luminescence (UCL) materials can convert near-infrared photons into visible or ultraviolet photons and possess many advantages such as high photochemical stability, large anti-Stokes shifts, long photoluminescence (PL) lifetimes, and low radiation damage [1–3], which make them wildly applied in many fields including color displays [4], solar cells [5,6], biomedical [7–9], and vivo imaging [10–12]. Among the various host materials, the fluoride crystals possess a host lattice of low phonon energy thus have attracted considerable attention. For example, Luoshan et al. reported a multi-core-shell $NaYF_4$:Yb,Er@SiO_2@Au@TiO_2 crystallites which can enhance the solar cells efficiency due to the wider solar light absorption [6]. And the precise color tuning and emission enhancement of $NaGdF_4$ codoped upconversion nanoparticle system was also investigated based on the surface plasmon resonance effect [13,14]. Ma et al. studied a novel upconversion@polydopamine core@shell nanoparticle based aptameric biosensor for biosensing and imaging of cytochrome *c* inside living cells [9]. For biomedical application, the fine-control of upconversion properties such as emission intensity ratio was quite important. Since the Yb/Er co-upconversion crystals usually emit bright green fluorescence, accompanied by darker red fluorescence, which greatly limits the application of Yb/Er co-activated upconversion crystals in tissue imaging [15,16]. Some rescent works have demonstrated that the Mn^{2+} doping not only realizes the control of crystalline phase the samples, but also improves the intensity of UCL and enhances red UCL [17–21]. And the Mn^{2+}-doped $NaYF_4$:Yb/Er upconversion nanoparticles were applied in electrogenerated chemiluminescence for the sensitive detection of bisphenol A [22]. As we know that the Mn^{2+} doped materials possessed well magnetic properties [23–25], thus the suitable Mn/Yb/Er co-doped upconversion material could be optical-magnetic bifunctional and can be promising in optical-magnetic bioimaging. In addition, the Basic fuchsin (BF) is a cationic triphenylmethane dye and is also chosen as a typical representative

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pollutant [26]. Due to its various properties such as poor biodegradation, toxicity, carcinogenicity and unsightliness, the removal of BF from wastewater systems is of great concern and should be tested and implemented promptly. Hence, it is vital and valuable to develop an effective BF detection method. However, there is still limited investigation on the control of photo-magnetic bifunctional properties and BF detection based on the Mn^{2+} doped upconversion material.

In this paper, a Yb^{3+}/Er^{3+} codoped $NaLuF_4$ optical-magnetic bifunctional material was synthesized by a facile hydrothermal method. $NaMnF_3$ was introduced into $NaLuF_4$:Yb^{3+},Er^{3+} microcrystals for simultaneously controlling their optical and magnetic properties. These upconversion microparticles were also used as an efficient fluorescent probe for detecting BF.

2. Experimental

All rare earth oxides were of 99.99% purity. The rare earth chloride RE $(Cl)_3$ (RE = Lu, Yb and Er) solutions can be obtained by reacting the rare earth oxide with a hydrochloric acid, the concentrations of them are 0.5 mol/L, 0.5 mol/L, 0.05 mol/L respectively. All other chemicals are analytical reagent and do not require further purification. $NaLuF_4$:Yb^{3+}/Er^{3+} and $NaMnF_3$ co-existed microcrystals were prepared by a method of oleic acid-assisted hydrothermal route. A deionized water solution (3 mL) containing 3 mmol NaOH was mixed with 10 mL of ethanol and 10 mL of oleic acid under stirring. Subsequently, 0.8 mmol chloride ($LuCl_3$, $YbCl_3$, $ErCl_3$, and $MnCl_2$) and 0.15 g NH_4F were added to the above solution. In a typical procedure for the preparation of the sample with 10 mol % Mn^{2+}, 1.12 mL $LuCl_3$ solution, 290 μl $YbCl_3$ solution, 320 μl $ErCl_3$ solution, and 800 μl $MnCl_2$(0.1 mol/L) solution were added. After vigorous stirring for 30 min, the resulting solution was transferred to a 50 mL autoclave, sealed in a high temperature oven and heated at 180 °C for 10 h. Then the power was turned off and allowed to cool to room temperature. The precipitate of the sample was centrifuged and washed several times with deionized water and ethanol. Then, the obtained microparticles were dispersed in 5 mL of aqueous solution with 0.6 mL of PEG. After vigorous stirring for 1 h at 20 °C, the precipitates were separated by centrifugation, rinsed with ethanol three times to remove the excess PEG, and readily dissolved in water.

The phase identification was performed by X-ray diffraction (XRD) (D8 Advance) at a scanning rate of 7°/min in the 2θ range from 10 to 80° using Cu-Kα radiation. The collecting time for XRD data is 10 min. The morphologies of products were observed using a JEOL JSM-6700F field emission scanning electron microscopy (FESEM) operated at an acceleration voltage of 8.0 kV. Upconversion emission spectra of the samples were recorded with a Hitachi F-4500 fluorescent spectrometer. In UCL measurement, a 980 nm diode laser was used to pump the samples. The magnetization characteristics of the $NaLuF_4$ microcrystals were measured using a Lake-shore 7410 vibrating sample magnetometer.

3. Results and discussion

3.1. Crystal structures and the phase

The crystal structures and the phase purity of the products were determined by XRD and presented in Fig. 1. It is clear that the sample with 0%Mn^{2+} has the crystal hexagonal phase $NaLuF_4$, while the samples with 10–50%Mn^{2+} are composed of two crystal phases, i.e. the hexagonal $NaLuF_4$ (JCPDS 27-0726) and the orthorhombic $NaMnF_3$ (JCPDS 18-1224) and the sample with 80%Mn^{2+} is also composed of two crystal phases, i.e. the hexagonal $NaYbF_4$ (JCPDS 27-0726) and the orthorhombic $NaMnF_3$. The relative concentration of the hexagonal phase $NaLuF_4$ to the orthorhombic phase $NaMnF_3$ can not be precisely addressed according to the XRD spectra, but can be theoretically estimated to be 7:1, 6:2 and 3:5 for the samples with 10%, 20% and 50%Mn^{2+}, respectively.

The size and morphology were investigated by SEM, which is

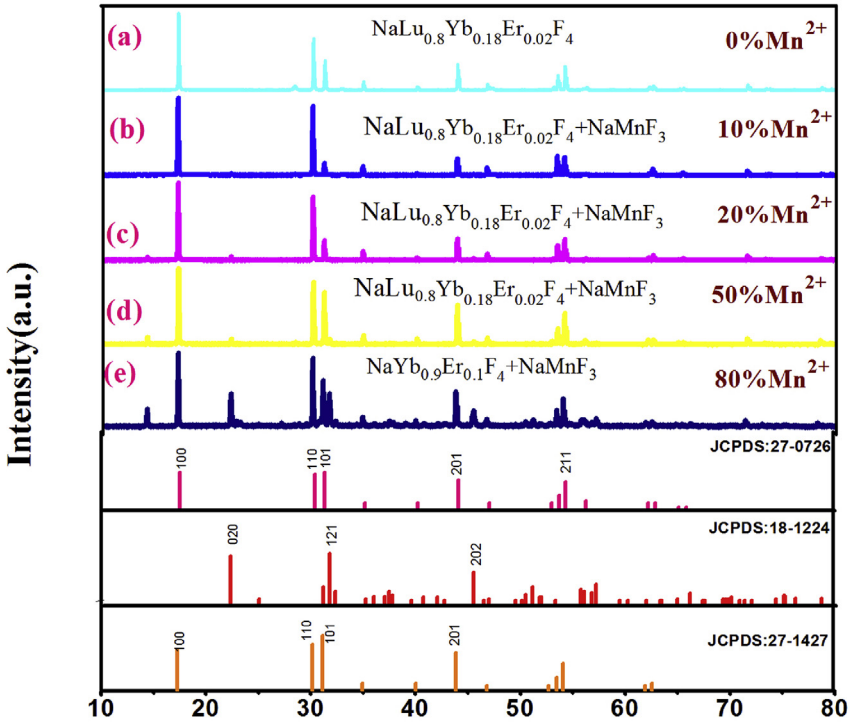

Fig. 1. XRD patterns of microcrystals with different initial Mn^{2+} contents: (a) 0%, (b) 10%, (c) 20%, (d) 50%, and (e) 80%.