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NaLuF₄:Yb³⁺,Er³⁺ bifunctional microcrystals codoped with Gd³⁺ or Dy³⁺ ions: Enhanced upconversion luminescence and ferromagnetic-paramagnetic transition





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ABSTRACT

Here, NaLuF₄:Yb³⁺/Er³⁺/Gd³⁺ bifunctional microcrystals were successfully synthesized by hydrothermal method, which can emit ~652 nm red light from Er³⁺-4fⁿ electronic transition ⁴F_{9/2}-⁴I_{15/2} and ~542 nm green light from Er³⁺-4fⁿ electronic transition ⁴S_{3/2}-⁴I_{15/2}, under the excitation of 980 nm infrared light. The intensity ratio of red to green emission increases obviously with increasing the concentration of Gd³⁺ from 0 mol% to 10 mol%. Meanwhile, the red shift is also observed which is ascribed to the difference in surface property. By introducing Dy³⁺ ion into NaLuF₄:Yb³⁺/Er³⁺, the intensity of both green and red emissions changes non-monotonously due to the energy exchange between Er³⁺ and Dy³⁺, which reaches to the highest value when doping with 0.5 mol% Dy³⁺ ion. The ferromagnetic property decreases greatly. This is ascribed to the fact that the coexistence of light rare earth (Gd³⁺) and heavy rare earth (Yb³⁺/Tm³⁺) will lead to the anti-ferromagnetic coupling in the sub-lattices.

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1. Introduction

Trivalent lanthanide-doped ions have unique spectral and magnetic properties, which have a broad application prospects in many areas. Upconversion (UC) luminescence of rare earth materials provides an effective way for converting the infrared light into visible light. they are expected to be very useful in a wide range of applications, such as nano-electronics, information storage, catalysis, fluorescent probes, bio-imaging in vitro or in vivo, and biosensors [1,2].

As well known, the light-emitting properties of rare earth materials and host material are Associated with the doping concentration of rare earth ions and other factors. Recently, NaLuF4 upconversion microcrystals and nanoparticles with Yb³⁺/Er³⁺ (or Yb³⁺/Tm³⁺) have attacked more attention and become popular choices as host materials [3]. The crystal structure of NaLuF4 shows the same polymorphic forms as those of NaYF4. But, compared to

the NaYF₄ host material, NaLuF₄ matrix presents different charge environment and crystal field, and supplies emitters (e.g., Er^{3+} , Tm^{3+}) with special upconversion host phonons. In the last decade, the control synthesis of morphology, crystal phase, particle size, and core/shell structure has been developed for NaLuF₄ upconversion nanoparticles, while their upconversion luminescent characteristics are well investigated accompanied with the detailed demonstration of energy transfer mechanisms [4–16].

On the other hand, optical-magnetic bifunctional materials have recently attracted increasing attention which are constructed by combining upconversion luminescent materials with magnetic ones. E.g., Zhu et al. [17] developed Core-shell Fe₃O₄@NaLuF₄:Yb³⁺,Er³⁺/Tm³⁺ nanostructure with multifunctional properties using a step-wise synthetic method. Yan et al. reported Superparamagnetic and upconversion emitting of Fe₃O₄/ NaYF₄:Yb³⁺,Er³⁺ hetero-nanoparticles via a crosslinker anchoring strategy [18]. However, these bifunctional materials are actually the mixture of optical materials and magnetic ones which have some intrinsic problems, such as optical and magnetic phase-separation and non-uniform optical and magnetic properties.

In this work, single-phase NaLuF4:Yb^3+/Er^3+/Gd^3+ and NaLuF4:Yb^3+/Er^3+/Dy^3+ bifunctional microcrystals were

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successfully synthesized by hydrothermal method, and their optical and magnetic properties could be simultaneously tuned by changing the doping level of $Gd^{3+}/or Dy^{3+}$. The co-doping of magnetic ion $Gd^{3+}/or Dy^{3+}$ affects the magnetic property of NaLuF₄:Yb³⁺/Er³⁺ through substituting the non-magnetic ion Lu³⁺. Meanwhile, the doping of Gd^{3+} ion would change the crystal field environment of emitter Er³⁺ so that the upconversion emission of NaLuF₄:Yb³⁺/Er³⁺ changes correspondingly. Differently, Dy³⁺ ion can directly tune the upconversion luminescence of NaLuF₄:Yb³⁺/ Er³⁺ by energy exchange with Er³⁺ ions.

2. Experimental

All rare earth oxides used for the experiment are of 99.99% in purity. Rare earth chloride LnCl₃ (Ln=Lu, Yb,Er, Gd, and Dy) solution were prepared by dissolving the corresponding amount of rare earth oxides in hydrochloric acid and further tuned to the required concentration by adding distilled water. The other chemicals are analytical grade and used as starting materials without further purification.

2.1. Sample preparation

Here, NaLuF₄: 18%Yb³⁺/2%Er³⁺/x%Gd³⁺ (x = 0, 10, 20, 30, 40, and 50), and NaLuF₄:18%Yb³⁺/2%Er³⁺/x%Dy³⁺ (x = 0.2, 0.5, and 1.0) microcrystals were synthesized by the hydrothermal method using trisodium citrate as stabilizing surfactant. Typically, 0.294 g of trisodium citrate and 10 mL of distilled water were firstly mixed together under agitation to form a homogeneous solution. Secondly, 1 mmol LnCl₃ (Ln=Lu, Yb, Er, Gd or Dy) aqueous solution with designed molar ratios and 16 mL of 8 mmol NaF solutions were added under constant vigorous stirring for 10-15 min. The solution was transferred to a 50 mL stainless steel autoclave and heated at 190 °C for 10 h. Thirdly, the autoclave was cooled down to room temperature naturally. The samples were washed three times by the mixture of ethanol and distilled water, accompanied with centrifugal separation in order to remove oleic acid and other residual solvents. Finally, these samples were dried at 60 °C for 24 h in a loft drier.

2.2. Characterization

X-ray power diffraction (XRD) patterns were performed using a Bruker/AXS D8-ADVANCE X-ray diffractometer equipped with a copper target ($\lambda = 1.5406$ nm) for 2θ range from 10° to 70° by a step of 0.02°. Scanning electron microscope (SEM) images were recorded on a JSM- 6380LV scanning electron microscope. Upconversion emission spectra of these samples were recorded with a Hitachi F-4700 fluorescence spectrophotometer, while the pump excitation source for characterization was an external 980 nm semiconductor laser. The magnetization of these NaLuF₄ microcrystals was recorded using a Lake-shore 7410 vibrating sample magnetometer.

3. Results and discussion

3.1. Crystal structure

XRD patterns of NaLuF₄:Yb³⁺, Er³⁺ with different Gd³⁺ concentration are shown in Fig. 1. All diffraction peaks of the NaLuF₄ samples match very well with the standard diffraction peaks of hexagonal phase structure NaLuF₄ (Joint Committee for Powder Diffraction Studies (JCPDS) card 27-0726). It can be seen from Fig. 1 that no other impurity diffraction peaks are observed, which demonstrating all the Gd³⁺ ions are successfully incorporated into the host matrix and formed a solid solution hexagonal structure. In



Fig. 1. XRD patterns of the NaLuF₄:Yb³⁺, Er³⁺ with x%Gd³⁺: (a) x = 0%, (b) x = 10%, (c) x = 20%, (d) x = 30%, (e) x = 40%, (f) x = 50%.

addition, the unit-cell volume increases with increased Gd^{3+} concentration due to the substitution of Lu^{3+} by the larger Gd^{3+} ions, which causes that the diffraction peaks shifting to lower angles. As can be seen from Fig. 1, there are two characteristic peaks located at ~30° in the diffraction peaks of NaLuF₄ samples, which correspond to (110) and (101) crystal planes. With the increase of the concentration of Gd^{3+} in NaLuF₄ samples, it is clear that the diffraction peak of (110) crystal face increased gradually relative to that of (101) crystal face, which suggests that the preferable orientation of crystal growth is gradually changed to along the (110) axis.

To further reveal the phase and size control, these prepared microcrystals were measured by a JSM- 6380LV SEM. It is clear in Fig. 2 that these NaLuF₄ microcrystals with different Gd^{3+} concentration have the shape of regular hexagonal microplates or irregular hexagonal rods. With the increasing of Gd³⁺ concentration from 30 mol% to 50 mol%, the particle size is gradually reduced, which is equal to 2.8 μ m, 2.3 μ m, and 1.2 μ m in diameter for 30, 40, and 50 mol% Gd³⁺ doping, respectively. Furthermore, it is observed from Fig. 2 that the morphology of NaLuF₄ doped with 10 mol% and 20 mol% Gd³⁺ ion are different from the other four samples. Usually, the difference in morphology may leads to the differential surface properties [19]. In other hand, the upconversion emission is highly depended on the surface properties. Then, it can inferred that the upconversion emissions of the samples doped with 10 mol % and 20 mol% Gd³⁺ ions are different from the other four samples. This suggestion is confirmed by the following fluorescent spectra.

3.2. UC luminescence properties

The upconversion fluorescence spectra of these samples were recorded with a Hitachi F-7000 spectrophotometer, which are shown in Fig. 3. It can be seen that β -NaLuF₄:8%Yb³⁺,2%Er³⁺

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