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Synthesis and upconversion luminescence in highly crystalline YOF:Yb^{3+}/Er^{3+} and Yb^{3+}/Tm^{3+} microboxes

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ABSTRACT

Highly crystalline YOF:Ln^{3+} (Ln = Yb, Er, Tm) microboxes were successfully synthesized for the first time by using a mixed $NaNO_3$–KNO_3 flux cooling method at a holding temperature of 600 °C for 2 h in air. The results indicated that the as-obtained products belonged to tetragonal system and exhibited microboxes morphology with side lengths of 0.5–2 μm. The upconversion luminescence properties of as-prepared YOF:Yb^{3+}/Er^{3+} and YOF:Yb^{3+}/Tm^{3+} were investigated in detail. Under 980 nm laser diode (LD) excitation, the emission intensity and the corresponding luminescence colors of YOF:Yb^{3+}/Er^{3+} and YOF:Yb^{3+}/Tm^{3+} could be precisely adjusted by changing the doping concentration of Yb^{3+} ions. Furthermore, the paper also offers a new alternative in synthesizing such materials and opens the possibility to meet the increasing commercial demand.

1. Introduction

Up-conversion (UC) nano- and micro-materials, which can convert two or more low-energy photons into one high-energy photon (anti-Stokes process), have attracted a great deal of interest over the past decade for their potential applications in the fields of the bioanalystics [1,2], solid-state lasers [3], optical telecommunication [4], displays technology [5] and solar cells [6,7]. For the doping rare-earth (RE) ions, the selection of appropriate host materials is essential for realizing favorable optical performance, such as high UC efficiency and a controllable emission profile. Generally, to achieve highly efficient radiative emission of RE, it requires the phonon energy of the host to be as low as possible, which can minimize nonradiative decay rates [8,9]. Among these UC materials, the rare earth fluoride compounds, possessing high refractive index and low phonon energy, are well known as preferable host materials for UC applications [10–12]. On the other hand, oxides have an advantage superior to fluorides in practical applications owing to their good chemical durability and excellent mechanical strength [13]. Consequently, combing the thermal stability of oxides and the low phonon energy of fluorides, rare earth oxy-fluorides (REOFs) have been considered in developing practical UC materials. In REOF crystals, YOF, is known for the low energy of its lattice phonons (<550 cm^{-1}) [14] and desirable chemical stability. Therefore, RE-doped YOF is promising candidate for UC luminescence in practical applications.

Up to now, several techniques have been employed for synthesis of REOF, such as solid state reaction [15,16], mechnochemical grinding method [17,18], sol–gel method [19], coprecipitation [20], hydrothermal method [21,22] and thermolysis method [23]. However, these processes usually suffer from the low yield, long reaction time or high environment loads. Therefore, developing an economical mass production and environmentally friendly method should be highly promising for synthesis of REOF-based optical materials.

Herein, we first reported a facile mass production method for the synthesis of uniform YOF microboxes by mixed $NaNO_3$–KNO_3 flux cooling method. In addition, the UC luminescence properties of the YOF microboxes doped with different rare earth ions (Yb^{3+}/Er^{3+}, Yb^{3+}/Tm^{3+}) with precisely tuned Yb^{3+} concentration were investigated under 980 nm LD excitation.

2. Materials and methods

All of the chemicals used in this experiment are of analytical grade reagents without further purification. $Y(NO_3)_3{\cdot}6H_2O$ (99.99%), $Yb(NO_3)_3{\cdot}6H_2O$ (99.99%), $Er(NO_3)_3{\cdot}6H_2O$ (99.9%), $Tm(NO_3)_3{\cdot}6H_2O$ (99.99%) were purchased from Beijing Founde Star Science & Technology Co., Ltd. (China). NaF (98%), $NaNO_3$ (99%), KNO_3 (99%) were provided by Sinopharm Chemical Reagent Co., Ltd. (China).

2.1. Synthesis

In a typical process for the synthesis of YOF, stoichiometric $YNO_3.6H_2O$, NaF, $NaNO_3$, KNO_3 with molar ratio of 1:4:64:32 were

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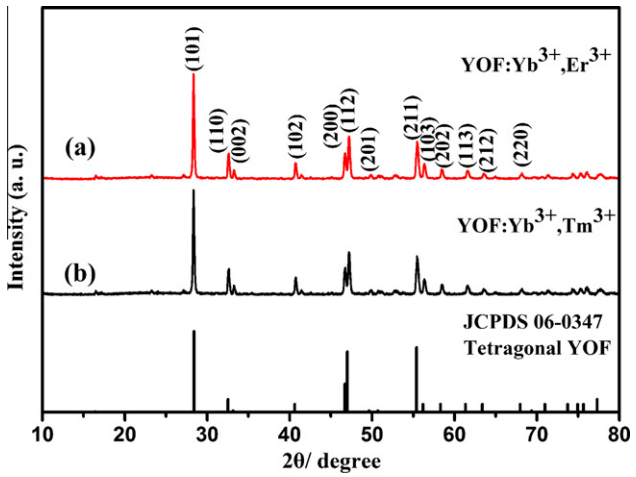

Fig. 1. XRD patterns of the as-synthesized YOF:20%Yb^{3+}, 2%Er^{3+} (a) and YOF:20%Yb^{3+}, 2%Tm^{3+} (b). The standard data for YOF (JCPDS No. 06-0347) are shown as references.

thoroughly mixed with an appropriate amount of ethanol in an agate mort and ground for 15 min. The mixture was placed into alumina crucibles with 20 cm^3 capacity, heated to 600 °C at a rate of 10 °C/min and held for 2 h in air. After cooled down to the room temperature inside in the furnace, the as-annealed samples were washed with deionized water three times and subsequently dried at 60 °C for 24 h. For UC luminescence, YOF:Yb^{3+}/Er^{3+}, YOF:Yb^{3+}/Tm^{3+} samples were prepared in a similar procedure by adding corresponding $Yb(NO_3)_3$, $Er(NO_3)_3$, $Tm(NO_3)_3$ into the precursor mixture.

2.2. Characterization

X-ray power diffraction (XRD) measurements were performed on a ARL X' TRA diffractometer at a scanning rate of 10°/min in the 2θ range from 10° to 80° with Cu Kα radiation (λ = 0.15406 nm). SEM micrographs were obtained using scanning electron microscopy (SEM, JSM-5900, JEOL Ltd., Japan). Chemical composition of the samples was obtained using an energy-dispersive spectrometer (EDS, Noran Vantage DSI, Themo Noran, Middleton, WI). The absorption spectra were measured on a spectrophotometer (Shimadzu, UV-3101PC) with a wavelength range of 300–1100 nm and a resolution of 2.0 nm. Photoluminescence emission spectra were recorded with a Jobinyvon FL3–221 fluorescence spectrophotometer at an excitation wavelength of 980 nm in the dark. All the measurements were performed at room temperature.

3. Results and discussion

3.1. Structural and morphological characterization

Fig. 1 shows the power XRD patterns of the as-prepared YOF:20%Yb^{3+}, 2%Er^{3+} (a), YOF:20%Yb^{3+}, 2%Tm^{3+} (b) as well as the standard data of pure YOF phase for comparison. All these peaks can be indexed to the tetragonal phase of YOF according to JCPDS card (No. 06-0347). The crystal structure of the tetragonal phase is determined with lattice parameters of a = 0.3918 and c = 0.5442, space group P_4/nmm [24]. As no additional peaks for other phases can be detected, we infer that Y^{3+} ions have been replaced by Yb^{3+}, Er^{3+} or Yb^{3+}, Tm^{3+} ions in any ratio with no effect on the crystallinity or phase change because of the almost same radii of Y^{3+}, Yb^{3+}, Er^{3+} or Tm^{3+} (r_Y^{3+} = 0.121 nm, r_{Yb}^{3+} = 0.118 nm, r_{Er}^{3+} = 0.120 nm, r_{Tm}^{3+} = 0.119 nm).

The as-prepared YOF:20%Yb^{3+}, 2%Er^{3+} and YOF:20%Yb^{3+}, 2%Tm^{3+} crystals with pure tetragonal phase exhibit microboxes morphology, which are displayed in Fig. 2. The SEM images in Fig. 2A and B reveal that the Yb^{3+}/Er^{3+} and Yb^{3+}/Tm^{3+} doped YOF samples are composed of relatively uniform microboxes and have smooth surfaces with side lengths of 0.5–2 μm. The EDS spectra of the obtained samples (Fig. 2C and D) indicate that fluorine, oxygen,

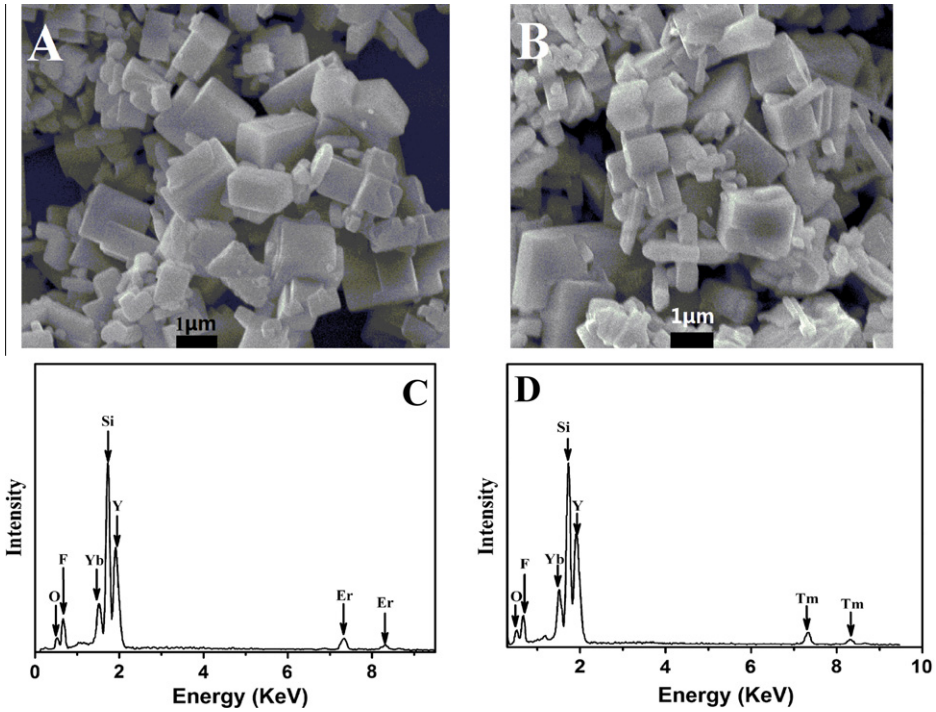

Fig. 2. (A) High magnification (×10,000) SEM images of YOF:20%Yb^{3+}, 2%Er^{3+} crystals; (B) high magnification (×10,000) SEM images of YOF:20%Yb^{3+}, 2%Tm^{3+} crystals; (C) EDS spectra of YOF:20%Yb^{3+}, 2%Er^{3+} crystals; (D) EDS spectra of YOF:20%Yb^{3+}, 2%Tm^{3+} crystals (The Si peaks arising from measurement).