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Effect of Yb^{3+} concentration on upconversion luminescence and temperature sensing behavior in Yb^{3+}/Er^{3+} co-doped $YNbO_4$ nanoparticles prepared via molten salt route

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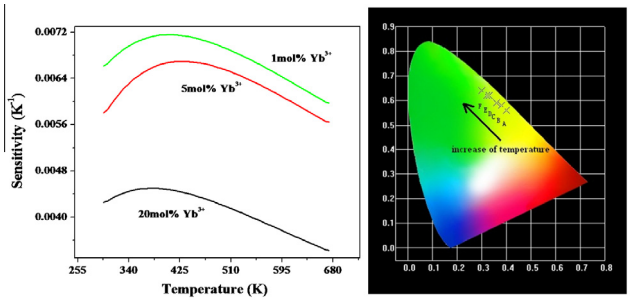
HIGHLIGHTS

- Yb^{3+}/Er^{3+} codoped $YNbO_4$ nanoparticles were prepared via modified molten salt method.
- Yb^{3+}/Er^{3+} codoped $YNbO_4$ nanoparticles exhibit high upconversion efficiency.
- The effect of Yb^{3+} concentration on sensing sensitivity is found.
- The mechanism for upconversion color change induced by temperature is supposed.

GRAPHICAL ABSTRACT



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ABSTRACT

Yb^{3+}/Er^{3+} co-doped $YNbO_4$ nanoparticles (NPs) with an average size of 35 nm were prepared via modified molten salt method for the first time. The phase purity, crystal structure, morphologies, and upconversion luminescence (UCL) properties as well as quantum yield and temperature sensing behavior of the as-prepared samples were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and upconversion luminescence (UCL) spectra, respectively. The XRD Rietveld refinements based on the XRD data were employed to reveal the phase purity and structure of the as-prepared samples. It was confirmed that the optimal doping concentration of Yb^{3+} ions in $YNbO_4$:Yb^{3+}, Er^{3+} NPs is around 10 mol%, which has a maximal quantum yield of 0.1%. The temperature sensing behavior of the as-prepared $YNbO_4$:Yb^{3+}, Er^{3+} NPs was studied based on the fluorescent intensity ratio (FIR) technique from two thermal coupled $^2H_{11/2}$ and $^4S_{3/2}$ levels. It was found that the temperature sensitivity was sensitive to the doping concentration of Yb^{3+} ions. In addition, the dependence of UCL colors on temperature was observed and the corresponding mechanism was proposed. Therefore, the as-prepared Yb^{3+}/Er^{3+} co-doped $YNbO_4$ NPs have double function of optical thermometer and safety sign for the high temperature environment.

1. Introduction

In recent years, upconversion nanoparticles (UCNPs) doped with rare-earth (RE^{3+}) ions, which can convert more than one low frequency excitation photons into a high frequency emission

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photon through multi-photon process, have triggered intensive interest because of their prominent upconversion luminescence (UCL) properties, gaining a vast application prospect in the fields of clean energy, three dimensional display, fluorescence labeling, and so on [1–5]. However, the applications of the UCNPs are being limited greatly because of unsatisfied luminescent efficiency, Therefore, how to improve the luminescent efficiency of UCNPs has been becoming an urgent task. It is a fact that the UCL efficiency is closely related to the phonon energy of host materials [6]. Usually, the lower the phonon energy of host materials is, the higher the UCL efficiency will be. Therefore, choosing suitable host materials is considered as an efficient approach to improve the UCL efficiency [7]. As is known, the fluoride crystals are promising hosts for UCL because of low phonon energy, which can reduce non-radiative loss. However, compared with fluorides, oxide matrixes should be suitable to be used in the higher temperature environments [8]. Therefore, suitable oxides with low phonon energy are more promising candidates as UCL hosts. Among various oxides matrixes, oxides containing niobium element comprise a large group of compounds, such as $ANbO_4$ (A = Gd, Y, La) compounds, which show lower phonon frequencies than other oxide compounds [9–12]. Moreover, they exhibit fergusonite structure and have wide range of interesting physical properties including high dielectric constants, photocatalytic behavior, and photoluminescence, etc. Especially, $YNbO_4$, as a well-known self-activated phosphor with a reported bandgap of 4.3 eV, shows an efficient blue luminescence upon 254-nm excitation [11]. To the best of our knowledge, however, the UCL properties of $YNbO_4$ NPs are not reported by far. On the other hand, to enhance UCL efficiency, Yb^{3+} ion is typically sensitizer in the Yb^{3+}/Er^{3+} co-doped systems because the absorption cross-section of the $^2F_{5/2}$ level of Yb^{3+} ions is much larger than that of the $^4I_{11/2}$ level of Er^{3+} in the NIR region of abound 1000 nm [6]. Moreover, large spectral overlap between Yb^{3+} emission ($^2F_{5/2} \rightarrow {}^2F_{7/2}$) and Er^{3+} absorption ($^4I_{15/2} \rightarrow {}^5I_{11/2}$) drives a very efficient energy transfer (ET) from Yb^{3+} to Er^{3+}. Therefore, strong UCL can be expected via optimizing the Yb^{3+} ions doping concentration in Yb^{3+}/Er^{3+} co-doped $YNbO_4$ NPs [13–15].

Temperature-sensitive fluorescent materials are increasingly receiving attention, because it can provide a non-contact temperature measurement via probing the dependence of fluorescence intensities on temperature, where the calibration is made by analyzing the changes on the relative emission intensities of the thermalized levels with the increase of temperature of the samples [16]. Compared with conventional temperature monitoring devices, the advantages of this method, known as the fluorescence intensity ratio (FIR) technique, are that it can reduces the influence of different factors of measuring conditions, resolution, and time exposure [17–19]. In this technique, two thermally coupled levels of RE^{3+} ions are essential. There is growing interest in the use of RE^{3+}-doped materials as optical temperature sensors. Especially, Er^{3+} ion is primarily due to their high electrical passiveness, negligible electromagnetic interference, wide dynamic range and multiplexing capabilities [14,20,21]. What is more, Er^{3+} ion has two thermally coupled energy levels, $^2H_{11/2}$ and $^4S_{3/2}$, with a small energy gap of around 770 cm^{-1}, the same order of magnitude as the thermal energy K_BT (~210 cm^{-1}) at room temperature, and relatively high radiative emitting efficiencies to the ground states [16,22–24]. Therefore, it is expected that the high sensing sensitivity can be achieved in Er^{3+} doped materials for the practical applications. To realize the goal, some parameters including Er^{3+} concentration, particle size and phonon energy of host were studied previously [16,25–27]. However, the effect of Yb^{3+} ions concentration on sensing sensitivity always has been ignored.

Based on the above points, in this paper, we employed a modified molten salt method to prepare Yb^{3+}/Er^{3+}-codoped $YNbO_4$ NPs for the first time. The effects of Yb^{3+} ions concentration on UCL and optical temperature sensing properties were studied. The optimal doping concentration of Yb^{3+} ions in $YNbO_4$ NPs was confirmed to be around 10 mol%. The dependence of sensitivity on Yb^{3+} ions concentration was found. The lower the Yb^{3+} ions concentration is, the higher sensitivity of $YNbO_4:Yb^{3+}$, Er^{3+} NPs is. Finally, we also observed a temperature-dependent change in the color perception of the emission arising from the change of the ratio of red and green emissions. Therefore, this work will provide an efficient approach to prepare niobates NPs, having a great application potential for optical temperature sensor as well as safety sign for the high temperature environment.

2. Experimental section

2.1. Materials

All the raw materials used in this work were purchased from Aladdin (Shanghai, China), which include $Ln(NO_3)_3{\cdot}6H_2O$ (99.99%, Ln = Y, Yb, Er), MNO_3 (AR, 99%, M = K, Na), $NbCl_5$ (99.9%) and ammonia (AR, 25–28%). They were used directly as received without any further purification.

2.2. Synthesis of $YNbO_4:Yb^{3+}$, Er^{3+} NPs

$YNbO_4:Yb^{3+}$, Er^{3+} NPs were prepared via modified molten salt process for the first time. In a typical procedure for the synthesis of $YNbO_4:Yb^{3+}$, Er^{3+} NPs, a precursor was prepared via co-precipitation method first. Firstly, 2.79 mmol of $Y(NO_3)_3{\cdot}6H_2O$, 3 mmol of $NbCl_5$, 0.15 mmol of $Yb(NO_3)_3{\cdot}6H_2O$, and 0.06 mmol of $Er(NO_3)_3{\cdot}6H_2O$ were dissolved in 200 mL of deionized water to form an aqueous solution in a beaker. Then, 50 mL of dilute ammonia aqueous solution [concentrated $NH_4OH:H_2O$ = 1:4 (v/v)] was added dropwise to the above aqueous solution under vigorously magnetic stirring. Keeping the agitation for 30 min, the white precipitate was collected by centrifugation and washed with deionized water several times. The precursor was obtained after being dried at 80 °C for 24 h. In order to prepare the final $YNbO_4:Yb^{3+}$, Er^{3+} NPs, 0.35 g of the as-prepared precursor was mixed with 60 mmol of nitrates mixture [$NaNO_3:KNO_3$ = 1:1 (molar ratio)] by hand-grinding with an agate mortar and pestle for 30 min. Then, the mixture was transferred into a covered ceramic crucible and calcined in muffle furnace at 650 °C in air for 6 h, where the heating rate is 10 °C/min. After being cooled to room temperature naturally, the product was washed with deionized water and collected by centrifugation. Finally, $YNbO_4:Yb^{3+}$, Er^{3+} NPs were obtained after the white precipitate was dried at 100 °C in an oven for 8 h.

2.3. Characterization

The X-ray diffraction (XRD) patterns of the samples were obtained on a Shimadzu XRD-6000 diffractometer with CuKα radiation (λ = 0.15406 nm) for phase identification and structural refinements. The data were collected in the range of 10–100° with the step of 0.02° and speed of 1°/min. The size, shape and structure of the samples were characterized by emission scanning electron microscopy (FE-SEM, Hitachi S-4800). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were recorded on a JEOL JEM-2100 at an accelerating voltage of 200 kV. The upconversion (UC) emission spectra were recorded on a fluorescence spectrophotometer (Hitachi F-4600) equipped with a power-tunable 980 nm optical fiber laser (4 W, BWTKS3-11312, BWT Beijing Ltd., China) as the excitation source. All the UC spectra of the obtained samples were measured under the same condition. For the temperature-dependent UC emission spectra measurements, a self-made