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Upconversion properties and temperature sensing behaviors in visible and near-infrared region based on fluorescence intensity ratio in $LuVO_4$: Yb^{3+}/Er^{3+}

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ABSTRACT

A high temperature solid state method was used to synthesize the Yb^{3+} and Er^{3+} codoped $LuVO_4$. The efficient energy transfer (ET) processes from Yb^{3+} to Er^{3+} has been demonstrated by upconversion (UC) spectra, near-infrared (NIR) spectra and lifetime curves. The optimal doping concentration for Yb^{3+} and Er^{3+} is 20 mol % and 2 mol %, respectively. Meanwhile, the temperature sensing behaviors in visible and NIR region based on fluorescence intensity ratio (*FIR*) have been explored in detail. In visible region, the optical thermometry of $LuVO_4$: Yb^{3+}/Er^{3+} is investigated via the *FIR* of the two thermally coupled energy levels $^2H_{11/2}$ and $^4S_{3/2}$ of Er^{3+}, accompanying with a maximal absolute sensitivity S_A of 0.82% K^{-1} at 423 K. In NIR region, the *FIR*s of Peak 1 (located at 1595 nm) to Peak 3 (located at 1660 nm) and Peak 2 (located at 1637 nm) to Peak 3, which are all assigned to $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+}, can be well fitted related to the temperature, with the maximal S_A of 1.85% K^{-1} and 0.62% K^{-1} respectively. All the results suggest that $LuVO_4$: Yb^{3+}/Er^{3+} powders is a potential material for optical thermometry in both visible and NIR region based on *FIR*.

1. Introduction

Nowadays, the trivalent rare earth ions, such as Yb^{3+}/Er^{3+}, Yb^{3+}/Ho^{3+}, Yb^{3+}/Tm^{3+} etc., codoped UC luminescent materials have received widespread attention for their unique optical properties [1–3]. UC luminescence refers to the process of absorbing two or more low-energy photons and emitting one high-energy photon. Because of this, UC materials can convert the NIR light into the visible region. More importantly, UC materials have a large number of advantages over the organic dyes and quantum dots, such as narrow emission bandwidths, long luminescence lifetime, negligible autofluorescence background, high photostability and low toxicity [4–8]. The unparalleled physicochemical properties and stabilize optical properties make them more suitable to apply to photonics, 3-D displays, optical encoding, bioimaging, etc. [9–11].

Moreover, for the UC luminescence materials, the potential application in temperature sensor has also been a hot research topic in recent years. Compared with traditional contact temperature sensing materials, optical temperature sensing materials have great advantages, such as non-contact, quick response, excellent precision and high accuracy [12,13]. In especial, the optical temperature sensors which depend on the *FIR* thermometry have been regarded as the promising temperature sensing materials, resulting from the strong anti-interference capacity.

Until now, most of the optical temperature sensing investigations based on *FIR* are focus on Yb^{3+} and Er^{3+} codoped UC materials. In Yb^{3+} and Er^{3+} codoped system, Yb^{3+} ions have large absorption cross-section at 980 nm. Furthermore, the ET processes from Yb^{3+} to Er^{3+} are very efficient. Therefore, a bright green UC emission of Er^{3+} can be detected, which is attributed to $^2H_{11/2} \rightarrow {}^4I_{15/2}$ transition and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition. Fortunately, $^2H_{11/2}$ energy level and $^4S_{3/2}$ energy level are thermally coupled excited

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states, which is very well suited for the studies of optical temperature sensing based on *FIR* [14].

Nevertheless, in order to obtain excellent precision and repeatability, intense UC emission is required. As is known to all, β-$NaYF_4$ and β-$NaLuF_4$ are the two most efficient hosts for UC, resulting from their low photon energy (~360 cm^{-1}) [15–18]. However, the low chemical stability of fluoride materials, especially in high temperature range, handicaps their utilization in thermometry. Therefore, the oxides, which possess extremely chemical stability as well as low photon energy, may be the suitable candidates. [28–30] For instance, Meng et al. and Carvajal et al. have demonstrated that YVO_4: Yb^{3+}/Er^{3+} and $GdVO_4$: Yb^{3+}/Er^{3+} are wonderful UC materials for luminescence temperature sensors based on *FIR* respectively [19,20]. As another important vanadate, $LuVO_4$, with the similar structure to YVO_4 and $GdVO_4$, is also an efficient matrix for UC. More importantly, the trivalent rare earth ions doped $LuVO_4$ phosphors may show stronger UC intensity than that of YVO_4 and $GdVO_4$ phosphors, which is due to the unique electronic state at the top of the valence of lutetium. This phenomenon has been proved in several isostructural materials, such as Y_2O_3 and Lu_2O_3, β-$NaYF_4$ and β-$NaLuF_4$, YF_3 and LuF_3 [17,31–33]. However, as far as we know, the paper concerning the temperature sensing properties in $LuVO_4$: Yb^{3+}/Er^{3+} is seldom published.

In the present work, the traditional high temperature solid state method were employed to prepare the Yb^{3+} and Er^{3+} codoped $LuVO_4$ phosphors. The ET mechanisms have been studied in detail by UC and NIR spectra as well as decay curves. Meanwhile, the temperature sensing behaviors in visible and NIR region based on *FIR* have also been explored. In visible region, the optical temperature sensing was studied via the *FIR* of the two thermally coupled energy levels $^2H_{11/2}$ and $^4S_{3/2}$ of Er^{3+}. In NIR region, the *FIR*s of the splitting peaks of Er^{3+} $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition were utilized in optical thermometry, As far as we know, there is very few paper concerning this phenomenon. All the results indicates that $LuVO_4$: Yb^{3+}/Er^{3+} powders is a potential temperature sensing material in both visible and NIR region under 980 nm wavelength excitation.

2. Experimental

2.1. Chemicals

Rare earth oxides of SpecPure grade (Lu_2O_3, Yb_2O_3, Er_2O_3, 99.99%) were purchased from Beijing Founde Star Science & Technology Co, Ltd. Analytical grade NH_4VO_3 was obtained from Chongqing Chuandong Chemical (Group) Co, Ltd. All of the chemical reagents were employed as starting materials without further purification.

2.2. Synthesis of $LuVO_4$: x mol%Yb^{3+}/y mol%Er^{3+} (x = 0, 1, 5, 10, 20, 30; y = 0, 0.1, 0.5, 1, 2, 3)

$LuVO_4$: *x* mol% Yb^{3+}/*y* mol% Er^{3+} powders were synthesized by traditional high temperature solid state method. Specifically as follows, 2 mmol Re_2O_3 (Lu_2O_3, Yb_2O_3 and Er_2O_3 in proportion) powders and 4 mmol NH_4VO_3 were weighed and mixed in an agate mortar. Next, the mixture were pulverized for 40 min. Then, place the powders to an alumina crucible which has a lid. The powders were firstly pre-sintered at 600 °C for 6 h followed by an intermediate grinding for 15 min to improve sample homogeneity and then sintering at 1200 °C for 6 h. Finally, the samples were obtained after being naturally cooled down to room temperature and pulverized into fine powders for measurements. All the reaction were in a box-type furnace with air atmosphere under the heating rate of 2 °C/min. The reaction equation can be expressed as following: $Lu_2O_3 + 2NH_4VO_3 \rightarrow 2LuVO_4 + 2NH_3\uparrow + H_2O\uparrow$.

2.3. Characterization

Powder X-ray diffraction (XRD) data were obtained by Cu Kα radiation (λ = 1.540 56 Å) on a Bruker D8 advance diffractometer over the angular range $10° \leq 2\theta \leq 80°$. The UC and NIR emission spectra were identified by an FLS920 spectrometer purchased from Edinburgh Instruments. The fluorescence lifetimes were measured by a Tektronix digital oscilloscope (TDS 3052) equipped with an optical parametric oscillator (OPO) as the excitation source. The lifetimes were calculated by integrating the area under the corresponding lifetime curves with the normalized initial intensity.

3. Results and discussion

3.1. Structure

Fig. 1 (a) and (b) show the XRD patterns of $LuVO_4$: x mol% Yb^{3+}/1 mol% Er^{3+} and $LuVO_4$: 20 mol% Yb^{3+}/y mol% Er^{3+} as well as the standard XRD data of $LuVO_4$ (JCPDS 17-0880). All the XRD diffraction peaks of the samples match well with the pure tetragonal phase $LuVO_4$. Moreover, no other phase is detected with the increasing Yb^{3+} or Er^{3+} concentration in the XRD patterns,

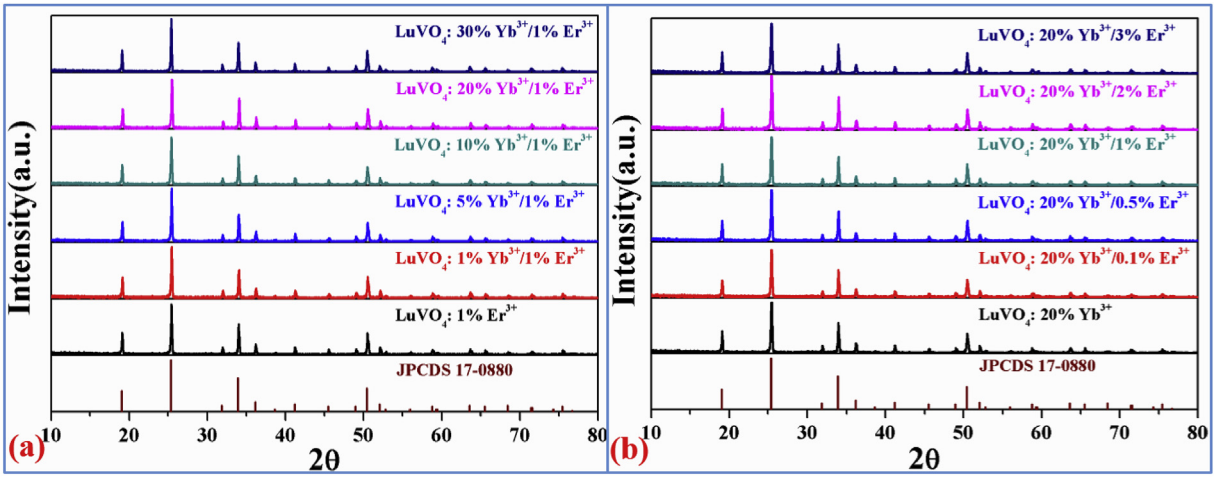

Fig. 1. The XRD patterns of $LuVO_4$: *x* mol%Yb^{3+}/*y* mol%Er^{3+} (*x* = 0, 1, 5, 10, 20, 30; y = 0, 0.1, 0.5, 1, 2, 3) with the standard XRD data of $LuVO_4$ (JCPDS 17-0880).