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Nd^{3+}/Yb^{3+} codoped $SrWO_4$ for highly sensitive optical thermometry based on the near infrared emission

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ABSTRACT

In this paper, Nd^{3+}/Yb^{3+} codoped $SrWO_4$ phosphors for temperature sensing are investigated. Firstly, the doping ratio of Nd^{3+} and Yb^{3+} was optimized. Then, under a 980 nm excitation, the temperature response of the near infrared (NIR) upconversion emission spectra in the temperature range of 313 K–453 K was characterized. The results show that the NIR emission peaks increase notably with the increase of temperature. With the fluorescence intensity ratio (FIR) technique, thermal sensing property of the optimized phosphor was investigated. A maximum thermal sensitivity of 0.02857 K^{-1} (I_{801}/I_{869}) at 453 K was achieved, which is higher than that of the other previously reported similar materials. The minimum temperature uncertainty is about 1 K at 453 K. The results reveal that $SrWO_4$: Nd^{3+}/Yb^{3+} is a promising material for optical thermometry.

1. Introduction

Temperature dependent fluorescence of rare-earth (RE) doped materials have been widely investigated for optical thermometry [1–7]. The fluorescence intensity ratio ((FIR) method is the most commonly used method to demodulate the temperature among the methods such as analyzing the fluorescence lifetime, fluorescence intensity, spectral position and polarization etc. [2]. The FIR method measures the intensity ratio of the fluorescence emissions from two couples of thermally coupled levels (TCL) of the active RE ions to demodulate the temperature. The energy gap between the two couples of TCL is usually between 200 cm^{-1}–2000 cm^{-1}, because if it is too low the involved emission peaks will overlap with each other, whereas if it is too high the thermal coupling between them will be too weak [8]. FIR is a non-contact method. It also has the advantage of high accuracy and immunity to external environmental interferences, since it measures the intensity ratio of two emission peaks instead of measuring the intensity itself. So in this paper, FIR is used in charactering the thermal sensing property of the material.

Among various RE ions, Nd^{3+} has been one of the most effective RE ions for various fields, such as optical thermometry [9–11], biological imaging [12–14], pressure sensing [15] and luminescence [16–19]. The intensity of the NIR emissions of Nd^{3+} ion increases with temperature, which is favorable to the fluorescence intensity detection and thus is advantageous for optical thermometry with the FIR method. For example, in Ref. [9], Nd^{3+}/Yb^{3+} codoped oxyfluoride glass ceramic was found to be a good material for optical sensing with a high sensitivity, high resolution, and good accuracy. In addition, the NIR emissions of Nd^{3+} ion are in the first biological window (750–950 nm) and second biological window (1000–1450 nm). This makes it important in biological applications [13]. For example, NIR emissions (750 nm, 800 nm, 863 nm) of Nd^{3+}/Yb^{3+} codoped $NaYF_4$ have been investigated for nanothermometers and photothermal therapy [14]. The 1340 nm emission of Nd^{3+} doped SrF_2 nanoparticles has been used to produce high contrast in vivo fluorescence images [13].

In this paper, Nd^{3+}/Yb^{3+} codoped $SrWO_4$ was investigated for thermometry, for the first time to the best of our knowledge. $SrWO_4$ has excellent thermal and chemical stability. It is a good host for fluorescence materials [20–22]. Firstly, to optimize the concentration ratio of Nd/Yb, Nd^{3+}/Yb^{3+} codoped $SrWO_4$ phosphors with different Nd/Yb ratios $Sr_{0.995-x}Nd_{0.005}Yb_xWO_4$ (x = 0.01, 0.02, 0.03, 0.05, 0.07, 0.1) were synthesized with the high temperature solid-state reaction method. Then, after an XRD structure analysis, the upconversion (UC) emissions spectra of the phosphors in the range of 720–900 nm were characterized under a 980 nm excitation. The results show that there is an optimal Nd/Yb concentration ratio to get the strongest emission, i.e., $Sr_{0.945}Nd_{0.005}Yb_{0.05}WO_4$. Lastly, the optical thermometry property of Nd^{3+}/Yb^{3+} codoped $SrWO_4$ phosphors with this optimal concentration was investigated with the FIR method with the $^4F_{5/2}$ and $^4F_{3/2}$, $^4F_{7/2}$ and $^4F_{3/2}$, as well as $^4F_{7/2}$ and $^4F_{5/2}$ of Nd^{3+} as the TCL. A maximum

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absolute sensitivity of 0.02857 K^{-1} and a minimum temperature uncertainty of 1.0004 K at 453 K, respectively, were achieved. These results indicate that Nd^{3+}/Yb^{3+} codoped $SrWO_4$ phosphor is a promising material for optical thermometry.

2. Materials and methods

2.1. Material preparation

A series of $Sr_{0.995\text{-}x}Nd_{0.005}Yb_xWO_4$ (x = 0.01, 0.02, 0.03, 0.05, 0.07, 0.1) phosphors were synthesized with the high temperature solid-state reaction method. The starting materials $SrCO_3$ (99.95%, Aladdin), WO_3(99.99%, Aladdin), Yb_2O_3 (99.99%, Aladdin), and Nd_2O_3 (99.99%, Aladdin) were weighed and ground thoroughly for 1 h using an agate mortar. Firstly, the mixture was put into a corundum crucible and preheated at 900 °C for 4 h and then further heated at 1300 °C for another 4 h. Finally, the temperature was gradually reduced to room temperature at a rate of ~5 °C/min. The mixture was taken out and ground into powder.

2.2. Characterization

X-Ray powder diffraction (XRD) was performed using a Bruker AXS D8 ADVANCE automatic diffractometer (Germany, Bruker) with a Cu Kα radiation source (λ = 1.5406 Å) in the 2θ range from 10° to 80° with a step of 0.1°. The UC spectra at different temperatures were obtained by a FLS920 fluorescence spectrometer (America, Edinburgh) under a 980 nm excitation. The temperature was changed from 313 to 453 K (with a step of 20 K) under the control of a TAP-02 (China, Orient KOJI Ltd) temperature controller.

3. Results and discussion

3.1. XRD analysis

Fig. 1(a) shows the XRD pattern of the $Sr_{0.995\text{-}x}Nd_{0.005}Yb_xWO_4$ (x = 0.02, 0.05, 0.07, 0.1) phosphors. The main peaks can be easily matched to the standard diffraction data for $SrWO_4$ (JCPDS Card No.08–0490). It confirms the incorporation of the dopants, i.e., Nd^{3+} and Yb^{3+} ions, into the $SrWO_4$ matrix. From Fig. 1 (b), we can see that the strongest peak detected at 2θ = 27.654° is shifted to a larger angle compared to the pure $SrWO_4$, and with the increase of Yb^{3+} concentration, the strongest peak gradually moves to a larger angle [23]. This phenomenon can be explained by the Bragg equation [24]:

$$2d \sin\theta = k\lambda \quad (1)$$

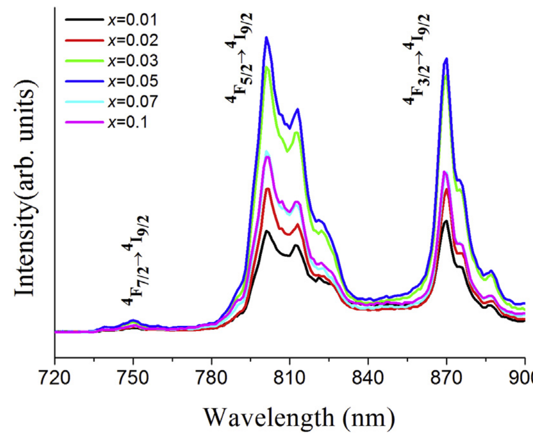

Fig. 2. UC emission spectra of $Sr_{0.995\text{-}x}Nd_{0.005}Yb_xWO_4$ (x = 0.01, 0.02, 0.03, 0.05, 0.07, 0.1) phosphors under 980 nm excitation.

d is the distance between lattice planes, θ is the diffraction angle, k is the diffraction order, and λ is the wavelength of the incident X-Ray. In the experiment, k and λ are fixed (k = 1 and λ = 1.5406 Å). When the Sr^{2+} ions (1.18 Å) are replaced by smaller Nd^{3+} (0.99 Å) and Yb^{3+} (0.86 Å) ions, d becomes smaller, and so θ increases.

3.2. Upconversion emission properties

Fig. 2 displays the UC emission spectra of the $Sr_{0.995\text{-}x}Nd_{0.005}Yb_xWO_4$ (x = 0.01, 0.02, 0.03, 0.05, 0.07, 0.1) under a 980 nm excitation. The wavelength range is from 720 nm to 900 nm and the UC spectra were obtained at room temperature. Form Fig. 2 the NIR upconversion emissions from the $^4F_{7/2}\rightarrow{}^4I_{9/2}$ (750 nm), $^4F_{5/2}\rightarrow{}^4I_{9/2}$ (801 nm), and $^4F_{3/2}\rightarrow{}^4I_{9/2}$ (869 nm) transitions of Nd^{3+} ions, respectively, can be identified. It can be found that with different Yb^{3+} concentrations the peak wavelengths of these three emission bands were nearly unchanged. However, the peak intensities vary notably with the increase of Yb^{3+} concentration. From Fig. 2 we can see that the peak emission intensities firstly increase and then decrease with the increasing Yb^{3+} concentration from x = 0.01 to 0.1. The maximum is reached at x = 0.05. The phenomenon can be explained by the interaction between the neighboring Nd^{3+} and Yb^{3+} ions and concentration quenching effect of Yb^{3+} ions [25].

Fig. 3 shows the schematic energy level diagram of Nd^{3+}/Yb^{3+} codoped $SrWO_4$ phosphors. When an Yb^{3+} ion absorbs a 980 nm photon, it is excited from the ground state $^2F_{7/2}$ to $^2F_{5/2}$ [Yb^{3+}($^2F_{7/2}$)

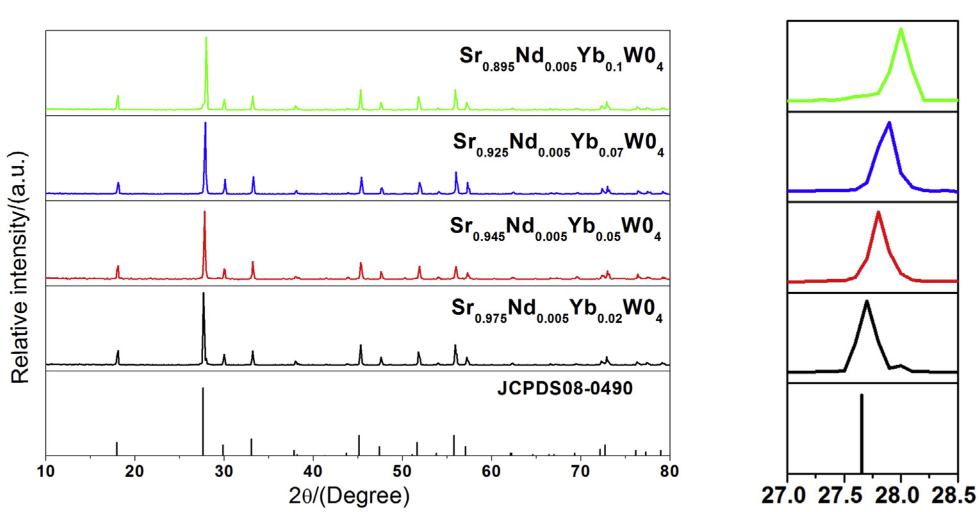

Fig. 1. XRD pattern of $Sr_{0.995\text{-}x}Nd_{0.005}Yb_xWO_4$ (x = 0.02, 0.05, 0.07, 0.1) phosphor with JCPDS File No. 08–0490.