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Non-contact ratiometric thermometer of $NaLuF_4$: Yb^{3+}/Er^{3+} phosphors based on multi-phonon assisted excitation

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ABSTRACT

$NaLuF_4$: Yb^{3+}/Er^{3+} phosphors are synthesized via a hydrothermal method. The photoluminescence properties of the phosphors are researched at a temperature range from 296 to 461 K under 1064 nm excitation. Fluorescence intensity ratio I/I_0 shows a linear relationship with increasing the temperature from 296 to 420 K. The maximum sensitivity is obtained to be 0.0194 K^{-1} using non-contact ratiometric thermometer through multi-phonon assisted excitation.

1. Introduction

The upconversion (UC) emission materials have wide application aspects, such as optical bioimaging, communication, and optical temperature sensing [1–4]. However, the applications of the UC materials are limited greatly because of unsatisfied luminescent efficiency. Thus, how to improve the UC efficiency has been becoming an urgent task. It is fact that the UC efficiency is closely related to the phonon energy of host matrix [5,6]. In general, the lower the phonon energy of host matrix is, the higher the UC efficiency will be. Therefore, choosing suitable host matrix is considered as an efficient approach to improve the UC efficiency. It is well known that the fluoride materials are promising hosts for UC because of low phonon energy, which can effectively reduce non-radiative relaxation [7]. Hence, we choose $NaLuF_4$ which possesses lower phonon energy to be a host matrix.

For its advantages in rapid response, and high spatial and temperature resolutions [8–10], the Fluorescence intensity ratio (FIR) technique based on thermally coupled levels (TCL) which is confined in the range of 200–2000 cm^{-1} [11,12] has attracted intensive investigations. But this technique which used to determine the temperature corresponding to the variation of the FIR between two TCL can be limited by TCL and the splitting of energy levels. The sensitivity is an important property of a temperature sensing device. Therefore, it has a great significance for finding a suitable temperature measurement method to improve sensitivity.

In generally, the UC process in rare-earth single-doped materials is quite inefficient for pumping in the wavelength region of 1000–1064 nm. In order to overcome this problem, we can make use of Yb^{3+} ions which have higher absorption cross section at 980 nm to provide efficient energy transfer rate as a sensitizer [1,13]. However, under non-resonant excitation, the UC pumping mechanism of the acceptor's emitting levels is accomplished through multi-phonon assisted excitation of the sensitizer in order to compensate for energy mismatch, and successive energy transfer to the acceptor [14]. Furthermore, the phonons of crystals are associated with temperature. In a certain temperature range, the higher the temperature is, the greater the fluorescence intensity will be [14]. Based on the above, we design a temperature measurement strategy that non-contact ratiometric thermometer (NCRT) for improving the temperature sensitivity.

In this work, $NaLuF_4$: Yb^{3+}/Er^{3+} phosphors are prepared via a hydrothermal method. The photoluminescence (PL) properties of the sample excited at 1064 nm are studied as temperature increases in detail. Based on the FIR technology of thermal coupling (TC) and

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NCRT, optical temperature sensing properties of $NaLuF_4$: Yb^{3+}/Er^{3+} phosphors are also studied using 1064 nm excitation source.

2. Experimental

2.1. Sample preparation

The $NaLuF_4$: Yb^{3+}/Er^{3+} phosphors are prepared via a hydrothermal method. 12 mL methanol solution containing 15 mmol NaOH is mixed with 18 mL oleic acid under magnetic stirring to obtain a homogeneous solution. Thereafter, 0.78 mmol $Lu(NO_3)\cdot 6H_2O$, 0.2 mmol $Yb(NO_3)\cdot 6H_2O$, 0.02 mmol $Er(NO_3)\cdot 6H_2O$ are added into the solution under continuous stirring. Then, a 6 mL NH_4F solution is added into the above mixture. The mixture is transferred into a 50 mL autoclave and heated at 180 °C for 12 h. After the reaction, the resultant product is centrifuged for collection at 8000 rpm for 1 min and washes three times with ethanol, deionized water as well as cyclohexane. Finally, the phosphors are achieved after drying at 60 °C for 2 h.

2.2. Characterization

The emission spectra of the sample is recorded on a spectrometer (Jobin Yvon iHR550, HORIBA, Longjumeau, France) in the wavelength range of 500–700 nm. The crystal structure are characterized using X-ray diffraction (XRD) (Empyrean, Panalytical, Eindhoven. The Netherlands) at a scanning rate of 4° min^{-1} in the 2θ range from 10° to 60° with Cu-Ka radiation (=0.15406 nm). A Linkam THMS 600 heating stage is introduced to heat the sample and the temperature of the sample is measured by a thermocouple. For the thermometry experiments, the sample is pasted on a heating stage and heated by this heating stage. Then the temperature (T) of the sample was measured by thermocouple. The spectrum of the sample at certain temperature (T) was acquired using the iHR550 grating spectrometer.

3. Results and discussion

3.1. Structure

Fig. 1 shows XRD pattern of $NaLuF_4$: Yb^{3+}/Er^{3+} phosphors and the standard data of hexagonal phase $NaLuF_4$ (JCPDS 27–0726). From XRD pattern. It can be concluded that sample is well crystallized. No extra peaks of other phases are observed except that of NaF, indicating that the Yb^{3+} and Er^{3+} ions have been effectively built into the $NaLuF_4$ host lattice. In addition, it is noticed that the diffraction peaks shifted slightly to the low angle side, which should be attributed the substitution of smaller Lu^{3+} (83 pm) ions by larger Yb^{3+} (86 pm) and Er^{3+} (89 pm) ions [15,16].

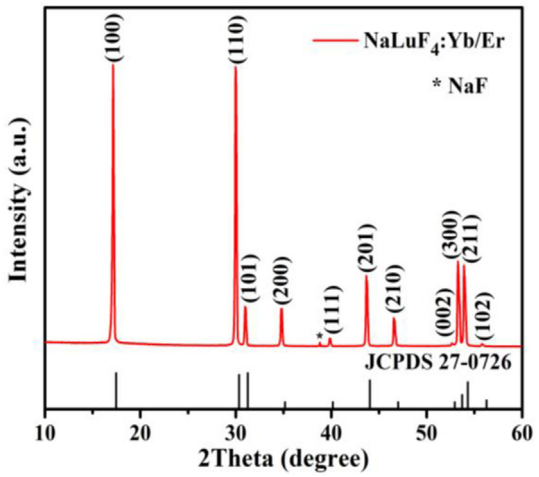

Fig. 1. X-ray diffraction of $NaLuF_4$: Yb^{3+}/Er^{3+} phosphors.

3.2. Luminescence properties

Fig. 2 (a) displays the PL spectrum of $NaLuF_4$: Yb^{3+}/Er^{3+} phosphors under excitation of different pump densities of a 1064 nm laser. The spectrums exhibit similar emissions in the wavelength range from 500 to 700 nm. The green and red emissions at 512–571 nm and 641–684 nm attribute to the $^2H_{11/2}/^4S_{3/2} \rightarrow {}^4I_{15/2}$, $_{9/2} \rightarrow {}^4I_{15/2}$ transitions of Er^{3+} ions, respectively.

In order to estimate the number of photons involved in UC process, the relationship between PL intensity and excitation power is expressed as [17,18].

$$I = P^n \quad (1)$$

where I is the PL intensity of $NaLuF_4$: Yb^{3+}/Er^{3+} phosphors, P is the excitation power, and n is the number of photons excited to the corresponding energy levels. Fig. 2 (b) shows double logarithmic plots of red and green emission intensities of $NaLuF_4$:Yb^{3+}/Er^{3+} phosphors versus a 1064 nm pump laser resource. The n of green and red emissions are found to be 2.00 and 1.90 using a 1064 nm excitation source, which implies that two photon-process is involved for 1064 nm excitation.

In order to further explain two-photons UC process under 1064 nm excitation, the energy transition mechanism of Yb^{3+}/Er^{3+} pairs is built as shown in Fig. 3. To compensate for the energy mismatch of approximately 800 cm^{-1} between the incident photon and the transition energies [14], the transition process from $^2F_{7/2}$ ground state to the $^2F_{5/2}$ excited state of Yb^{3+} ions requires the participation of two phonons. The PL of $NaLuF_4$: Yb^{3+}/Er^{3+} phosphors excited by a 1064 nm laser is mainly achieved by the $Yb^{3+} \rightarrow Er^{3+}$ energy transfer process due to the large absorption cross section of Yb^{3+} ions [1,13]. Therefore, the energy transition processes of the sample excited by a 1064 nm laser can be explained as follows: Under 1064 nm excitation, the populations in $^2F_{7/2}$ state of Yb^{3+} ions are excited to their $^2F_{5/2}$ excited state. Then, the energy transfer (ET) process $^2F_{5/2}(Yb^{3+}) + {}^4I_{15/2}(Er^{3+}) \rightarrow {}^4I_{11/}$ $_2(Er^{3+}) + {}^2F_{7/2}(Yb^{3+})$ (ET1) easily takes place, populating the $^4I_{11/2}$ excited state of the Er^{3+} ions. And then by energy transfer process $^2F_{5/2}(Yb^{3+}) + {}^4I_{15/2}(Er^{3+}) \rightarrow {}^4F_{7/2}(Er^{3+}) + {}^2F_{7/2}(Yb^{3+})$ (ET3) from the Yb^{3+} ions, the $^4F_{7/2}$ state of Er^{3+} is populated. Next, the populations in the $^4F_{7/2}$ state relax non-radiatively to the $^2H_{11/2}$ and $^4S_{3/}$ $_2$ state. Finally, the green emissions at 520 and 540 nm are produced through the $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions, respectively. For the red emission, there are two primary UC channels. Firstly, the non-radiative relaxation from $^4S_{3/2}$ to $^4F_{9/2}$ can contribute to the red emission. Secondly, part populations at $^4I_{11/2}$ state of Er^{3+} relax to the $^4I_{13/2}$ state. Then the populations of $^4I_{13/2}$ state is promoted to $^4F_{9/2}$ levels through energy transfer process $^2F_{5/2}(Yb^{3+}) + {}^4I_{15/2}(Er^{3+}) \rightarrow {}^4F_{9/2}(Er^{3+}) + {}^2F_{7/2}(Yb^{3+})$ (ET2). Therefore, green and red emissions of the sample excited at 1064 nm are two photon-process.

3.3. Optical temperature sensing

In order to investigate the optical temperature sensing behavior of the $NaLuF_4$: Yb^{3+}/Er^{3+} phosphors, the PL spectra under 1064 nm excitation in the temperature range from 296 to 461 K is recorded in Fig. 4 (a). As shown in Fig. 4 (b), I_{520}, I_{540} and I_{654} (I_{520}, I_{540} and I_{654} are the integrated intensity corresponding to the $^2H_{11/2} \rightarrow {}^4I_{15/}$