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Neodymium doped lanthanum oxysulfide as optical temperature sensors

Guicheng Jiang, Xiantao Wei, Shaoshuai Zhou, Yonghu Chen, Changkui Duan, Min Yin *

Department of Physics, University of Science and Technology of China, Hefei 230026, China

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ABSTRACT

The fluorescence intensity ratio (FIR) technique for temperature sensing has been demonstrated in La_2O_2S:Nd^{3+} phosphors. The phosphors were extensively characterized using various methods such as X-ray diffraction, photoluminescence excitation, and photoluminescence spectra. Upon ultraviolet–visible (UV–vis) or near-infrared (NIR) light excitation, two intense NIR emissions of Nd^{3+} peaking at 897 nm and 1074 nm corresponding to transitions of $^4F_{3/2} \rightarrow {}^4I_{9/2}$ and $^4F_{3/2} \rightarrow {}^4I_{11/2}$ were generated at room temperature. NIR emission of Nd^{3+} in a wide temperature range from 30 K to 600 K was investigated. Experimental results show that the temperature evaluation can be realized by monitoring the emission peak position, measuring the fluorescence intensity ratio of $^4F_{5/2}$ and $^4F_{3/2}$ or that of the two Stark components of the $^4F_{3/2}$ level in the bulk La_2O_2S:Nd^{3+}. Furthermore, the effective energy difference of the thermalized levels $^4F_{5/2}$ and $^4F_{3/2}$, and $^4F_{3/2}$ two Stark components were 987 cm^{-1} and 110 cm^{-1}, respectively. Those results imply that La_2O_2S:Nd^{3+} phosphor is a potential candidate for the optical temperature sensor.

1. Introduction

Temperature is one of the fundamental parameters whose knowledge is essential in many fields of science, engineering, and medicine. The measurement of temperature can be realized remotely by measuring the changes of luminescent properties, such as the fluorescence lifetime, absolute fluorescence intensity, the fluorescence intensity ratio (FIR), peak positions and emission bandwidths. Among them, FIR of rare earth (RE) ions as a most outstanding approach has attracted great interest in the past decades since it can improve the sensitivity and reduce the influence of measurement conditions, such as fluorescence loss, fluctuations in the excitation intensity and electromagnetic compatibility problem [1]. FIR method involves the comparison of fluorescence intensities from closely spaced energy levels which are thermally coupled. So far, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+} and Yb^{3+} trivalent rare earth ions have been found having pairs of energy levels which are separated by small energy gaps such that they may be considered to be thermally coupled and hence could be potential candidates for optical temperature sensors using the FIR technique [1–4]. One of the earliest discussions of the possible application of the FIR technique for temperature sensing was reported by Kusama et al. in 1976 [5]. Their work reported the measurement of temperature over the range from −173 to +27 °C using FIR from different energy levels of the Eu^{3+} ion in the Y_2O_2S:Eu^{3+} phosphor. Furthermore, the resolution of 10–15 °C was obtained. After that, several research groups have developed this investigation based on the FIR technique. The FIR technique for temperature monitoring using the thermally coupled $^2H_{11/2}$ and $^4S_{3/2}$ levels of Er^{3+} as the temperature sensing within 26–63 °C temperature range was reported by Vetrone et al. [6]. Rai et al. discussed the $^3P_0$ and $^3P_1 + {}^1I_6$ thermally coupled levels of Pr^{3+} for temperature sensor based on the FIR technique [7]. In the case of the Nd^{3+} ions, the emission bands corresponding to the $^4F_{5/2} \rightarrow {}^4I_{9/2}$ and $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transitions were analyzed as a function of temperature from 300 K to 700 K by Haro-Gonzalez et al [8].

Among Nd^{3+} doped matrix, lanthanide oxysulfides (Ln_2O_2S) with excellent chemical stability and thermal stability can serve as one of the most effective hosts for fluorescence applications, owing to their high absorption of light and efficient energy transfer. All these properties have lead to the proposition of Ln_2O_2S for a promising matrix for optical temperature sensor. To our knowledge, there are few works studying about Nd^{3+} ions as optical temperature sensors. Therefore, in this work, La_2O_2S:Nd^{3+} samples were studied in the temperature range from 30 K to 600 K in order to explore a new possibility of optical temperature sensor based on the FIR technique. Temperature evaluation can be realized remotely by monitoring the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ emission peak position, measuring the intensity ratio of $^4F_{5/2}$ and $^4F_{3/2}$ or that of

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* Corresponding author. Tel.: +86 551 3607412; fax: +86 551 3607417.
E-mail address: yinmin@ustc.edu.cn (M. Yin).

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the two Stark components of the $^4F_{3/2}$ level of Nd^{3+} ions. The temperature sensitivity is also discussed in detail. NIR emission of Nd^{3+} in a wide temperature range is demonstrated in La_2O_2S:Nd^{3+} phosphor.

2. Experimental

La_2O_2S:Nd^{3+} powder samples with different doping concentration were prepared by the high temperature solid-state reaction. Ln_2O_3 (99.99%, $Ln^{3+}=La^{3+}$, Nd^{3+}), S (powder) and Na_2CO_3 (99.99%) were mixed and ground together with a weight ratio of 100:12:30. Then the mixture was heated in a muffle furnace at 1100 °C for 2 h with a certain amount of active carbon. The products were taken out from the furnace when cooled, and washed with hot dilute HNO_3 and water for three times. After drying at 80 °C for 10 hour, the white powders of La_2O_2S:Nd^{3+} were obtained. The X-ray diffraction (XRD) patterns of the samples were recorded with an X-ray diffractometer (MAC Science Co. Ltd MXP18AHF), using nickel-filtered Cu K_α radiation. The excitation and the emission spectra were obtained with a Jobin-Yvon Fluorolog 3 system at room temperature. For low temperature-dependent measurements, the powder sample was uniaxially pressed into pellet in a steel die and mounted on a Cu sample pedestal, then loaded in a closed-cycle He cryostat. For high temperature measurements above 300 K, the sample is fixed on a copper post, whose temperature is detected by a type-K thermocouple and controlled by a temperature controller with a 100 W heat pipe. The NIR emission spectra of La_2O_2S:Nd^{3+} excited by a 532 nm green solid state Laser were obtained at various temperatures by a Zolix SBP750 monochromator equipped with an Acton ID-441-C InGaAs near infrared detector. The signal was analyzed by an EG&G 7265 DSP lock-in amplifier and stored into computer memories.

3. Results and discussion

3.1. Structural properties

The XRD patterns of La_2O_2S:0.1% Nd^{3+}, La_2O_2S:1% Nd^{3+}, La_2O_2S:10% Nd^{3+} phosphors are shown in Fig. 1. All XRD patterns are exactly matching with the hexagonal phase of oxysulfide (JCPDS Card no. 27-0263) with space group *P*3m1 [9]. Each lanthanum atom is coordinated by four oxygen atoms and three sulfur atoms in its nearest neighborhood. The diffraction peaks of La_2O_2S:Nd^{3+} phosphors shift to the high angle side with the increasing doping concentration (inset of Fig. 1), implying that the Nd^{3+} ions have been doped into the lattices of La_2O_2S. Because the radius of Nd^{3+} (1.00 Å) is slightly smaller than that of La^{3+} (1.06 Å), the lattice constants become smaller while Nd^{3+} substitutes La^{3+}.

3.2. Photoluminescence characterization

The excitation spectrum of La_2O_2S:1 mol% Nd^{3+} phosphor in the spectral region 250–850 nm is shown in Fig. 2(a). There is a broad excitation peak from 250 to 300 nm due to La_2O_2S host absorption and a lots of multiple, sharp absorption peaks at 366, 438, 480, 523, 538, 598, 649, 693, 758, 818 nm corresponding to the f–f transitions from the ground state $^4I_{9/2}$ to the excited states of $^2I_{11/2}+^2D_{5/2}+^4D_{1/2}$, $^2P_{1/2}+^2D_{5/2}$, $^4G_{11/2}+^2D_{3/2}+^2G_{9/2}$, $^4G_{9/2}$, $^4G_{7/2}+^2K_{13/2}$, $^4G_{5/2}+^2G_{7/2}$, $^2H_{11/2}$, $^4F_{9/2}$, $^4F_{7/2}+^4S_{3/2}$, and $^4F_{5/2}+^2H_{9/2}$, respectively [10–12]. Upon ultraviolet–visible (UV–vis) or near-infrared (NIR) light excitation, two intense near-infrared (NIR) emissions of Nd^{3+} peaking at 897 nm and 1074 nm assigning to transitions of $^4F_{3/2}\rightarrow{}^4I_{9/2}$ and $^4F_{3/2}\rightarrow{}^4I_{11/2}$ were generated at room temperature, as shown in Fig. 2(b). In the inset, it is noticed that the intensity of the $^4F_{3/2}\rightarrow{}^4I_{9/2}$ emission at 897 nm is the strongest when the concentration of Nd^{3+} is 1 mol%, implying that 1 mol% Nd^{3+} is the optimum doping concentration with the maximum NIR emission in La_2O_2S. Moreover, excitation and emission wavelengths of La_2O_2S:Nd^{3+} phosphor can be chosen to be in the transparent region (650–950 nm and 1000–1350 nm) of biological tissue [13], suggesting that it is a promising candidate for biological application [14].

The luminescent spectra of La_2O_2S:Nd^{3+} phosphors in a broad temperature range from 30 K to 600 K have been investigated, as shown in Fig. 3. The emission spectra from 800 nm to 960 nm were normalized at 897 nm for further analysis. The temperature sensing in this report could be realized in the two ways: FIR and the peak position. FIR relies on measurement of the intensity ratio between luminescence from two closely spaced energy levels, which stay in thermal equilibrium. The $^4F_{5/2}$ and $^4F_{3/2}$ energy levels in La_2O_2S:Nd^{3+} are at 12,225 cm^{-1} (818 nm) and 11,148 cm^{-1} (897 nm) with respect to the ground state of $^4I_{9/2}$ (Fig. 3). Meanwhile, the $^4F_{3/2}$ two Stark components energy levels are at 11,223 cm^{-1} (891 nm) and 11,148 cm^{-1} (897 nm), which are close to reported data of 11,189 cm^{-1} and 11,109 cm^{-1} in Ga_2O_2S:Nd^{3+} [15]. The $^4F_{5/2}$ and $^4F_{3/2}$ levels and the $^4F_{3/2}$ two Stark components

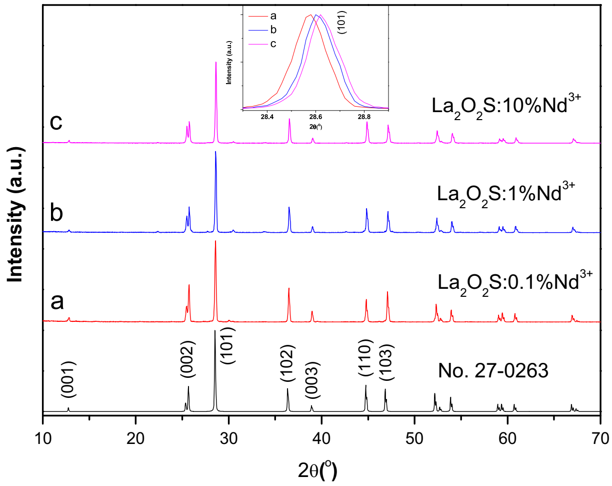

Fig. 1. Powder XRD patterns of La_2O_2S:Nd^{3+} with different Nd^{3+} concentration and the JCPDS Card no. 27-0236. The inset is the enlarged XRD pattern in (101) reflection.

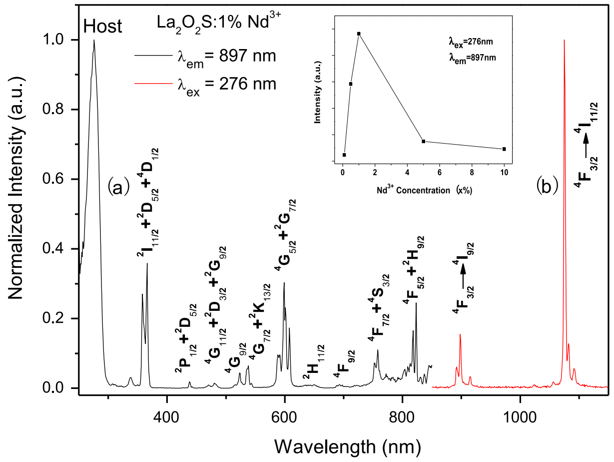

Fig. 2. Excitation and emission spectra of La_2O_2S:1 mol% Nd^{3+} phosphor. (a) Excitation spectrum monitored at 897 nm. (b) NIR emission spectrum under 276 nm excitation. The inset plots the dependence of the emission intensity at 897 nm on the doping concentration of Nd^{3+}.

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