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Near-infrared emitting YVO_4:Nd^{3+} nanoparticles for high sensitive fluorescence thermometry

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ABSTRACT

Nanoscale sub-degree non-contact temperature sensing is in high demand in many fields of science and technology. In this work, we report simply synthesized near-infrared emitting YVO_4:Nd^{3+} nanoparticles as ratiometric luminescence thermal sensors. For thermal sensing, the dependences of the emission bands of $^4F_{5/2} - {}^4I_{9/2}$ and $^4F_{3/2} - {}^4I_{9/2}$ transitions from 123 up to 873 K were measured and calibrated as functions of the temperature. The thermal sensitivity was obtained and compared with others Nd^{3+}-doped micro- and nanocrystals presented in the literature. Large energy gap between $^4F_{5/2}$ and $^4F_{3/2}$ levels used for nanothermometry leads to the significant enhancement of thermal sensitivity and widening of temperature sensing range compared with thermometers based on Stark sublevels intensity ratio. Effect of doping concentration on the thermal sensitivity was studied. Sub-degree thermal resolution obtained at 313 K and 673 K make YVO_4:Nd^{3+} nanoparticles perspective material for accurate temperature sensing in both biological and technical applications.

1. Introduction

Temperature is the key parameter which defines system behavior in many areas from industry to medicine. Therefore, the development of devices that allow correct and accurate determination of local temperature has been of great interest over the past few decades [1–4]. Two different measuring methods to determine the temperature are contact and non-contact. Contact thermometry has several limitations at the submicrometer scale, including stability, accuracy and the location of the sensor tip for a temperature measurement [5]. Furthermore, such factors as strong electromagnetic field, fast movements or presence of biological liquids limit using of this type of thermometers. This promotes the development of different non-contact thermometry technologies, which allows to overcome aforementioned drawbacks. However, some techniques have serious disadvantages: the main is thermal measuring only on the surface of the sample [6]. Infrared and thermoreflectance thermometers show restricted spatial resolution, whereas thermal sensing based on Raman spectroscopy can be applied only to materials showing a large Raman efficiency and thus it is restricted to a few numbers of systems [7–9].

Luminescence thermometry has emerged as one of the most promising non-contact techniques, which can be used for high temperature measurements, characterization of moving surfaces and measurements in the presence of strong electromagnetic fields [5,10]. Luminescence thermometry is based on the analysis of spectral features which depend on the temperature: intensity, spectral position, band shape, lifetime or polarization [10,11]. Luminescence intensity ratio (LIR) technique is based on LIR between thermally coupled energy levels. It has attracted much attention due to its intrinsic immunity to some external disturbances during the detection process, such as the fluorescence loss, the amount of phosphor and the fluctuations of excitation intensity [12,13]. Down- and up-converting phosphors doped with different rare earth ions, such as Nd^{3+} [14–16], Gd^{3+} [17], Dy^{3+} [18], Ho^{3+} [7], Er^{3+}, [19,20], Tm^{3+} [21,22] and Eu^{3+} [23,24] have been successfully used as LIR thermal sensors. In the case of Nd^{3+} ions, two approaches have been already proposed for monitoring temperature changes. The first method is based on the analysis of emission bands corresponding to the transitions between Stark sublevels of $^4F_{3/2}$ (R_i) and $^4I_{9/2}$ (X_j) or $^4I_{11/2}$ (Y_k) levels [25,26]. This approach has inherent limitation of quite low relative sensitivity (about 0.1% K^{-1}) and restricted thermal sensing range due to the small energy difference between the two Stark components (typically about 100 cm^{-1}). An

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alternative method relies on the $^4F_{5/2}$ – $^4I_{9/2}$ to $^4F_{3/2}$ – $^4I_{9/2}$ luminescence intensity ratio. This approach was firstly applied for thermal sensing in the biophysical temperature range by Balabhadra et al. [27]. It was found that higher energy difference between excited levels leads to a significant increase of the thermal sensitivity.

Here, we report structural and luminescence properties of YVO$_4$:Nd^{3+} nanoparticles and their possible application in nanothermometry. To the best of our knowledge, single Nd^{3+} doped phosphor was demonstrated as thermal sensor in such wide temperature range (123–873 K) for the first time. The effect of the doping concentration on thermal sensitivity was studied. The temperature uncertainty was measured using two independent approaches: from calibration curve and from temperature distribution. In order to verify possible application of YVO$_4$:Nd^{3+} nanothermometers in wide temperature range, the temperature uncertainty was obtained at 313 K and 673 K.

2. Experimental

Crystalline Nd^{3+}-doped YVO$_4$ nanoparticles were prepared using previously reported modified Pechini method with optimal synthesis conditions. [28,29] Shortly, nitrates solutions were formed by dissolving starting Y$_2$O$_3$ and Nd$_2$O$_3$ oxides in HNO$_3$. Then the citric acid solution was added parallel to this mixture to create [Y$_{1-x}$Nd$_x$(C$_6$H$_8$O$_7$)$_3$](NO$_3$)$_3$ complex and to V$_2$O$_5$ oxide to create VO(C$_6$H$_7$O$_7$)$_2$ solution. Prepared solutions were mixed and ethylene glycol was added for polyesterification initiation. Then, the solution was heated up to 100 °C, and formed polymer citrate gel was calcined at 500 °C for 1 h. The obtained powder was grinded in mortar together with potassium chloride (weight ratio 1:1), then this mixture was calcined for the second time at 950 °C for 1.5 h. To remove KCl, powder was washed three times with distilled water and finally dried. Fine colloidal fraction of the Nd^{3+}-doped YVO$_4$ powder was obtained by ultrasonic treatment and subsequent precipitation. Concentration series of Nd^{3+}-doped YVO$_4$ phosphors (C(Nd^{3+}) = 0.6, 2.4, 4.8 at%) was synthesized using the described procedure.

X-ray phase analysis was carried out with Rigaku "Miniflex II" diffractometer with CuK$_\alpha$-radiation (λ = 1.5406 Å). Scanning electron micrograph (SEM) images were made using SUPRA 40VP WDS scanning electron microscope with the accelerating voltage 2–5 kV and resolution of 4 nm. Excitation spectrum was recorded with a fluorescence spectrometer Fluorolog-3 with a Xe-arc lamp (450 W power). Fluorescence characterization was performed by using T64000 Raman Spectrometer. The Nd^{3+}-doped YVO$_4$ NPs were optically excited with a 532 nm single mode solid state laser operating in CW mode (power density 6 W/cm^2). The laser beam was focused into the sample by using a 4x long working distance microscope objective (NA 0.1). The fluorescence was collected by using the same microscope objective and was spectrally analyzed by single spectrometer and a Peltier cooled Synapse CCD detector. The thermal measurements were carried out using a heating stage Linkam THMS 600 with 0.1 °C temperature stability and 0.1 °C set point resolution.

3. Results and discussion

XRD patterns of YVO$_4$:Nd^{3+} nanoparticles (NPs) are shown in Fig. 1a. A comparison of all diffraction peaks with the reference standard of YVO$_4$ (space group *I*41/*amd*, JCPDS 17-0341) confirmed the presence of a pure tetragonal phase without any structural impurities. The cell parameters calculated with Unit Cell software have demonstrated linear relationship with the content of Nd^{3+} ions, which is consistent with Vegard's law. This result demonstrates that the neodymium ion has been efficiently and homogeneously incorporated into the host matrix due to the similar ionic radius and chemical reactivity of Nd^{3+} and Y^{3+} [30].

Scanning electron microphotograph of YVO$_4$:Nd^{3+} 2.4 at% nanophosphor is presented in Fig. 1b. As it can be seen, the powder consists of weakly agglomerated nanoparticles with average size of (70 ± 11) nm. The particle size distribution is shown in the inset of Fig. 1b.

Possible biological application requires colloidal stability in aqueous suspensions and low nanoparticles aggregation. From our previous study mean Zeta potential of YVO$_4$:Nd^{3+} aqueous colloidal solution was determined to be − 58 mV, which confirms good stability [26].

Fig. 2a (left part) shows room temperature excitation spectrum of YVO$_4$:Nd^{3+} 2.4 at% NPs measured in spectral region 400–700 nm. During scanning the excitation wavelength luminescence signal was monitored at the prominent transition $^4F_{3/2}$ – $^4I_{9/2}$ (870–925 nm) (λ_{em} = 880 nm). As can be seen, the obtained excitation spectrum consists of bands situated at 420–442, 455–490, 500–550, 550–640, and 670–700 nm, which are ascribed to the transitions from ground state $^4I_{9/2}$ to higher levels $^2D_{5/2}$, $^4G_{9/2}+{}^4G_{11/2}+{}^2K_{15/2}$, $^4G_{7/2}+{}^4G_{9/2}+{}^2K_{13/2}$, $^4G_{5/2}+{}^4G_{7/2}+{}^2H_{11/2}$, $^4F_{9/2}$, respectively [28,31].

Fig. 2a (right part) presents emission spectrum of YVO$_4$:Nd^{3+} 2.4 at% NPs upon 532 nm excitation. The observed spectrum consists of narrow lines attributed to the $^4F_{3/2}$ – $^4I_{9/2}$ (870–925 nm) and $^4F_{5/2}$ + $^2H_{9/2}$ – $^4I_{9/2}$ (870–925 nm) transitions. The energy levels scheme of Nd^{3+} ion in the YVO$_4$ host is presented in Fig. 2b.

Nd^{3+} based NPs provide two different methods to monitor local temperature. The first one is based on the analysis of emission bands corresponding to the transitions between Stark sublevels of $^4F_{3/2}$ (R$_i$) and $^4I_{9/2}$ (X$_j$) or $^4I_{11/2}$ (Y$_k$) levels. Due to the small energy difference between the two Stark components (typically about 100 cm^{-1}), this method cannot be used for determination of high temperatures. To overcome this limitation and to enhance thermal sensitivity, an alternative method based on the $^4F_{5/2}$ – $^4I_{9/2}$ (808 nm) to $^4F_{3/2}$ – $^4I_{9/2}$ (880 nm) luminescence intensity ratio was proposed.

Temperature dependence of luminescence spectrum of YVO$_4$:Nd^{3+} 2.4 at% NPs is shown in Fig. 3a. As one can see, intensity ratio between components $^4F_{5/2}$ – $^4I_{9/2}$ (808 nm) and $^4F_{3/2}$ – $^4I_{9/2}$ (880 nm) is quite different for different temperature. These lines are marked green and blue, respectively in Fig. 2a. Intensity ratio of marked lines should have temperature dependence in wide range due to the value of energy gap between $^4F_{5/2}$ and $^4F_{3/2}$ levels. Simple calculations and literature search lead to the conclusion that the abovementioned states are thermally coupled and it is possible to write:

$$R = \frac{I_{808}}{I_{880}} = A\cdot\exp\left(-\frac{\Delta E}{kT}\right) \tag{1}$$

where A is a temperature-independent constant, ΔE is an energy gap between $^4F_{5/2}$ and $^4F_{3/2}$ levels, k is the Boltzmann's constant, and T is the absolute temperature.

Fig. 3b–d show evolution of LIR as a function of temperature for YVO$_4$:Nd^{3+} 0.6 at%, 2.4 at%, 4.8 at% NPs, respectively. The spectral limits of the integrated emission are 795–842 nm for 808 nm line and 867–923 nm for 880 nm line. It should be noted that the temperature was varied within wide range (298–873 K) for YVO$_4$:Nd^{3+} 0.6 at% and 4.8 at% nanopowders and within range (123–873 K) for YVO$_4$:Nd^{3+} 2.4 at%. The wider temperature range was chosen for the sample with the best luminescence intensity. The control of the temperature was carried out using a microscopic attachment Linkam FTIR600. The observed experimental data is accurately fitted by the exponential Boltzmann formula. It should be noted that fitting parameter was $R^2 = 0.99$ for each sample with different doping concentration. Energy gap between $^4F_{5/2}$ and $^4F_{3/2}$ levels was determined by two independent methods. Experimental ΔE$_{spectr}$ was obtained from the measured emission spectrum as follows: ΔE$_{spectr}$ = E$_1$-E$_2$, where E$_1$ is energy of $^4F_{5/2}$–$^4I_{9/2}$ transition and E$_2$ is energy of $^4F_{3/2}$–$^4I_{9/2}$ transition. Calculated ΔE$_{calibr}$ was obtained through the thermal calibration using Eq. (1). As can be seen from Table 1, the difference between ΔE$_{spectr}$ and ΔE$_{calibr}$ is less than 10% for all studied samples. So, we can make a conclusion that thermal behavior of LIR is governed by Boltzmann's