



## New strategy for thermal sensitivity enhancement of Nd<sup>3+</sup>-based ratiometric luminescence thermometers



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### ABSTRACT

Accurate luminescence thermal sensing using nanophosphors that operate within biological windows is of great interest in bio- and nanomedicine. Here, we show that Nd<sup>3+</sup>-doped YVO<sub>4</sub> NPs can act as nanothermometers in the second biological window upon 808 nm excitation. Significant enhancement of thermal sensitivity and temperature resolution was achieved by optimal choice of wavelengths for ratiometric thermal calibration. It was concluded that thermal calibration should be calculated using integral intensities. The obtained temperature uncertainty together with the emission and excitation lying in the biological windows open the venue to the possible application of Nd<sup>3+</sup>-doped YVO<sub>4</sub> NPs for real time sub-tissue luminescence thermal sensing with a sub-degree resolution.

### 1. Introduction

Temperature is a fundamental thermodynamic parameter, which is the most frequently measured in science, industries, and life. According to market investigation, at present time temperature sensors occupy about 80% of market share [1,2]. However, the majority of these sensors are conventional contact thermometers, which are ineffective for precise temperature measurements at the submicron scale [3]. To overcome this intrinsic limitation, non-contact thermometry methods have been developed [4,5]. One of them is optical remote thermometry aiming at designing luminescent nanosized phosphors suitable for the local temperature sensing [6]. Accurate local temperature sensing is of great importance in a variety of technological areas such as microelectronics, microfluidics and especially in bio- and nanomedicine where temperature plays crucial role for leaving specimens [7,8].

Over the past five years, a lot of nanostructured luminescent systems such as organic dyes [9], quantum dots [10], polymeric nanoparticles [11], fluorescent proteins [12], metallic nanoparticles [13] and Ln<sup>3+</sup>-doped nanoparticles [14–17] have been proposed as noninvasive thermal sensors. Ln<sup>3+</sup>-based nanoparticles (NPs) are among the most promising candidates for luminescent thermometers due to their unique properties such as relatively long emission lifetimes and good chemical and physical stability [18–20].

Biomedical applications put more challenging requirements on the thermal sensors. The best nanothermometers should possess excitation and emission in near-infrared spectral region that covers so called biological window (BW) of tissue (650–950 nm (I-BW), 1000–1350 nm (II-BW), and 1500–1750 nm (III-BW)) due to the maximally extended penetration depth, which reflects reduced absorption and scattering cross section of light by tissue in these spectra regions [6]. Neodymium-doped NPs perfectly fit all requirements, their luminescence can be excited by radiation around 808 nm (I-BW), whereas the Nd<sup>3+</sup> ion can emit in the near-infrared region, involving Stark transitions between the <sup>4</sup>F<sub>3/2</sub> and <sup>4</sup>I<sub>J</sub> (J = 9/2, 11/2) energy levels (I-BW and II-BW, respectively) [21–23].

The aim of this work is to synthesize and study the structural and luminescence properties of aqueous colloidal solution of Nd<sup>3+</sup>-doped YVO<sub>4</sub> NPs. YVO<sub>4</sub>:Nd<sup>3+</sup> NPs were used as nanothermometers operating in the II-BW upon 808 nm excitation. Thermal sensing was based on ratiometric method using different wavelengths for calibration. To the best of our knowledge, thermal calibration was obtained from the ratio between emission intensity of the peak and valley for the first time. Such approach led to the significant enhancement of the most important in real application parameters: thermal sensitivity and temperature uncertainty. Systematic study of the effect of luminescence intensity ratio calculation technique (integral or point intensity) on the

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forementioned parameters was also carried out.

## 2. Experimental section

$\text{YVO}_4:\text{Nd}^{3+}$  nanoparticles used in this work were synthesized by modified Pechini method [24]. Previously optimal synthesis conditions of modified Pechini method were determined [25] and various oxide systems doped with  $\text{Eu}^{3+}$  and  $\text{Nd}^{3+}$  ions using this technique were prepared [26–28]. Briefly, nitrates solutions were formed by dissolving starting  $\text{Y}_2\text{O}_3$  and  $\text{Eu}_2\text{O}_3$  oxides in  $\text{HNO}_3$ . Then the citric acid solution was parallel added to this mixture to create  $[\text{Y}_{1-x}\text{Nd}_x(\text{C}_6\text{H}_8\text{O}_7)_3](\text{NO}_3)_3$  complex and to  $\text{V}_2\text{O}_5$  oxide to create  $\text{VO}(\text{C}_6\text{H}_7\text{O}_7)_2$  solution. Prepared solutions were mixed and ethylene glycol was added for polyesterification initiation. The solution was heated up to 100 °C. Then, formed polymer citrate gel was calcined at 500 °C for 1 h. Obtained powder was grinded in mortar together with potassium chloride and 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. The fine colloidal fraction of the  $\text{YVO}_4:\text{Nd}^{3+}$  powder was obtained by ultrasonic treatment and subsequent precipitation.

X-ray phase analysis was carried out with Rigaku  $\llcorner$  Miniflex II  $\gg$  diffractometer with  $\text{CuK}\alpha$ -radiation ( $\lambda = 1.5406 \text{ \AA}$ ). 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. Zeta potential was measured with Horiba SZ-100 using laser doppler electrophoresis technique. Fluorescence characterization was performed by using T64000 Raman Spectrometer. The  $\text{Nd}^{3+}$ -doped  $\text{YVO}_4$  colloidal solution was optically excited with a 808 nm single mode laser Coherent MBR-110 operating in CW mode. 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 liquid nitrogen cooled Synapse CCD detector. For thermal sensitivity and uncertainty experiments, the colloidal solution was placed on a heating stage controlled with ThorLabs TC200 with a resolution of 0.1 °C.

## 3. Results and discussion

XRD pattern of  $\text{YVO}_4:\text{Nd}^{3+}$  3 at% nanopowder presented in Fig. 1a can be indexed as pure yttrium vanadate tetragonal phase without any structural impurities. All diffraction peaks match well with the standard  $\text{YVO}_4$  sample peaks (space group  $I41/amd$ , JCPDS No. 17-0341). The average size of coherent scattering region (crystallite size) was calculated using the Scherrer's approach [29]:

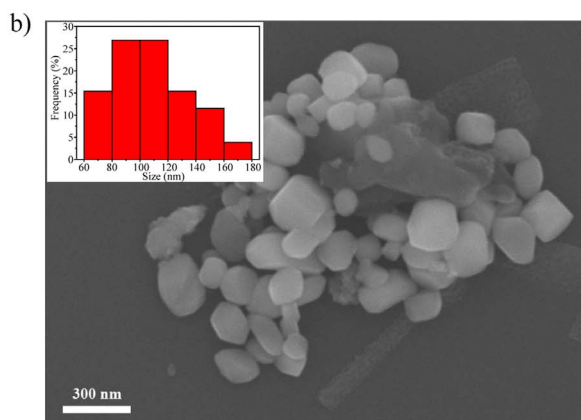
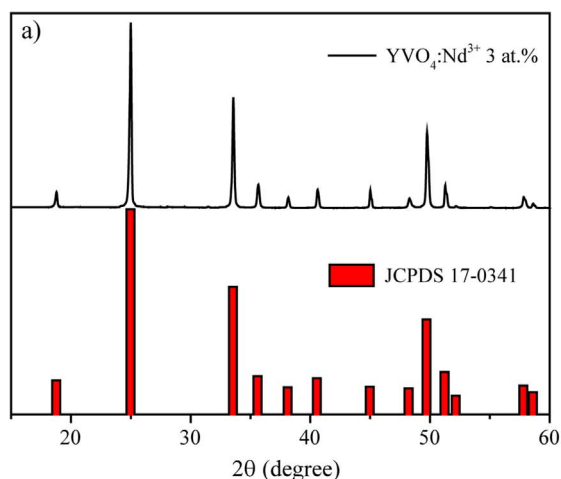


Fig. 1. (a) XRD patterns of  $\text{YVO}_4:\text{Nd}^{3+}$  3 at% nanopowder and standard card of  $\text{YVO}_4$  (JSPDS 17-0341); (b) SEM image of  $\text{YVO}_4:\text{Nd}^{3+}$  3 at% nanoparticles.

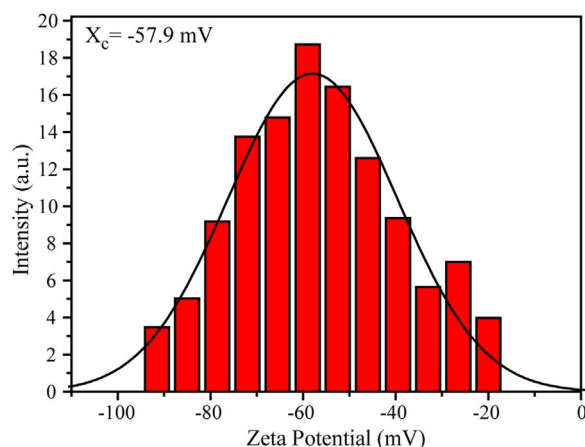


Fig. 2. Zeta-potential spectrum of  $\text{YVO}_4:\text{Nd}^{3+}$  3 at% aqueous solution.

$$D = \frac{0.9\lambda}{\cos\theta\sqrt{\beta^2 - \beta_0^2}} \quad (1)$$

where  $D$  is an average size of the ordered (crystalline) domains, which may be smaller or equal to the grain size;  $\lambda$  is the X-ray wavelength;  $\beta$  is the full width at half-maximum (FWHM) of a diffraction line located at  $\theta$  in radians;  $\theta$  is the Bragg angle;  $\beta_0$  is the scan aperture of the diffractometer. Calculated average crystallite size of  $\text{YVO}_4:\text{Nd}^{3+}$  3 at% nanoparticles was determined to be about  $(46 \pm 3) \text{ nm}$ .

Scanning electron microphotograph of the synthesized  $\text{YVO}_4:\text{Nd}^{3+}$  3 at% phosphor is presented in Fig. 1b. It is seen that sample consists of loosely agglomerated nanoparticles with average size about 100 nm. It should be noted that luminescence particles have quite broad size distribution (standard deviation 27 nm).

To establish the stability of colloidal dispersions, the Zeta potential measurement of  $\text{YVO}_4:\text{Nd}^{3+}$  3 at% colloidal solution was performed (Fig. 2). Mean value of Zeta potential was determined to be about  $-58 \text{ mV}$ , its absolute value is above 30 mV limit assumed to be required for colloidal stability in water [30]. So, we can draw the preliminary conclusion that  $\text{YVO}_4:\text{Nd}^{3+}$  3 at% colloidal solution demonstrates good stability, strictly based on Zeta potential data. Despite discussion of Zeta potential sign is out of the scope of our work, it should be noted that both negative [31] and positive [32] potential of  $\text{Nd}^{3+}$ -doped NPs was previously observed.

As it was previously demonstrated, emission of  $\text{YVO}_4:\text{Nd}^{3+}$  NPs can be effectively excited by commercial 808 nm laser diode. It was found that  $\text{Nd}^{3+}$  ions in  $\text{YVO}_4$  host have quite broad excitation bandwidths (14 nm), therefore they are practically unaffected by small changes in

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