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Improving performance of luminescent nanothermometers based on non-thermally and thermally coupled levels of lanthanides by modulating laser power†

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This work sheds light on the pump power impact on the performance of luminescent thermometers, which is often underestimated by researchers. An up-converting, inorganic nanoluminophore, $\text{YVO}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ (nanothermometer) was synthesized using the hydrothermal method and a subsequent calcination. This nanomaterial appears as a white powder composed of small nanoparticles (≈ 20 nm), exhibiting a very intense, green upconverted luminescence ($\lambda_{\text{ex}} = 975$ nm), visible to the naked eye. Its emission spectrum consists of four Er^{3+} bands (500–850 nm) and one Yb^{3+} band (>900 nm). The obtained compound exhibits temperature-dependent luminescence properties, hence it is used as an optical nanosensor of temperature. The determined band intensity ratios of the non-thermally coupled levels (non-TCLs) of $\text{Yb}^{3+}/\text{Er}^{3+}$ and thermally coupled levels (TCLs) of Er^{3+} are correlated with temperature, and they are used for ratiometric sensing of temperature. The effects of the pump (NIR laser) power on the luminescence properties of the material, including band intensity ratios, absolute and relative sensitivities and temperature resolution are analysed. It was pointed out that the applied laser power has a huge impact on the values of the aforementioned thermometric parameters, and manipulating the laser power can significantly improve the performance of optical nanothermometers.

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Introduction

The most commonly developed luminescent sensors of temperature are based on lanthanide (Ln) ions, such as Yb^{3+} , Er^{3+} , Tm^{3+} , Ho^{3+} and Nd^{3+} embedded in various matrices (e.g. Gd_2O_3 , Al_2O_3 , YF_3 , YVO_4 and NaYF_4).^{1–9} These ions exhibit unique luminescence properties, i.e. long luminescence lifetimes, narrow emission bands, multi-range emission, as well as the possibility of various energy migration processes between co-dopant ions.^{10–14}

The systems based on up-conversion (two-photon) luminescence are particularly attractive from the point of view of biological research. They enable excitation of the material in the

NIR range of the 1st (650–950 nm) or 2nd (1000–1350 nm) biological window (e.g. by Yb^{3+} excitation),¹ and detection of emissions in the 1st biological window (e.g. emission of Er^{3+} , Tm^{3+} , Ho^{3+} or Nd^{3+}).^{1–4,9,11,12,15–19} Emission and excitation in the biological window ranges result in less absorption and scattering of light by tissues such as skin and blood.^{1,15,16,18,20–22} In contrast, using conventional luminescence, where excitation often takes place in the UV or visible spectral range, a significant part of the radiation may be absorbed/scattered by the surrounding medium, diminishing excitation effectiveness of the ions embedded into the structure of such nanothermometers.^{5,20} However, for temperature nanosensors used in other applications, e.g. in catalysis and optoelectronics, alike excitation and emission can take place over the entire spectral range.^{23–25}

Optical sensors based on Ln ions usually enable temperature control based on the analysis of changes in the intensity ratios of the bands associated with their thermally and non-thermally coupled levels (TCLs and non-TCLs). In the case of two thermalized levels, where the energy of these levels does not differ too much (up to ≈ 2000 cm^{-1}), due to additional thermal energy, the photon may move from the level with lower energy to the level with higher energy. This will result in a decrease in the intensity of the lower energy band and the

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† Electronic supplementary information (ESI) available: Transmission data for the optical filter used; normalized emission spectra measured at increasing temperature; non-normalized emission spectra measured at increasing temperature; integrated luminescence intensities as a function of temperature; log–log dependence of the luminescence intensity on the laser power; and thermal cycling experiments. See DOI: 10.1039/d1nr01395e



Here we report the development of a ratiometric, optical nanothermometer, $\text{YVO}_4:\text{Yb}^{3+},\text{Er}^{3+}$ working in a broad spectral range (VIS-NIR). The nanomaterial synthesized shows green up-conversion luminescence visible to the naked eye, and good temperature response (temperature-dependent luminescence). The selected luminescence intensity ratios of the bands associated with TCLs and non-TCLs of Er^{3+} and Yb^{3+} are used as thermometric parameters. The corresponding absolute and relative sensitivities, and temperature resolutions are investigated. A very important and novel aspect of this work is the demonstration of a strong influence of the applied pump (laser) power on the values of the mentioned thermometric parameters, as well as on the thermometer performance.

The recorded XRD pattern of the obtained $\text{YVO}_4\text{:Yb}^{3+},\text{Er}^{3+}$ nanomaterial (Fig. 1a) agrees with the reference pattern from the ICDD database (International Centre for Diffraction Data, card no. 01-082-1968) of tetragonal YVO_4 , crystallizing in the $I41/amd$ space group. The significant broadening of the observed reflexes is associated with the nanocrystallinity of the obtained particles. The TEM image (Fig. 1b) shows that the obtained nanomaterial is composed of irregular agglomerated

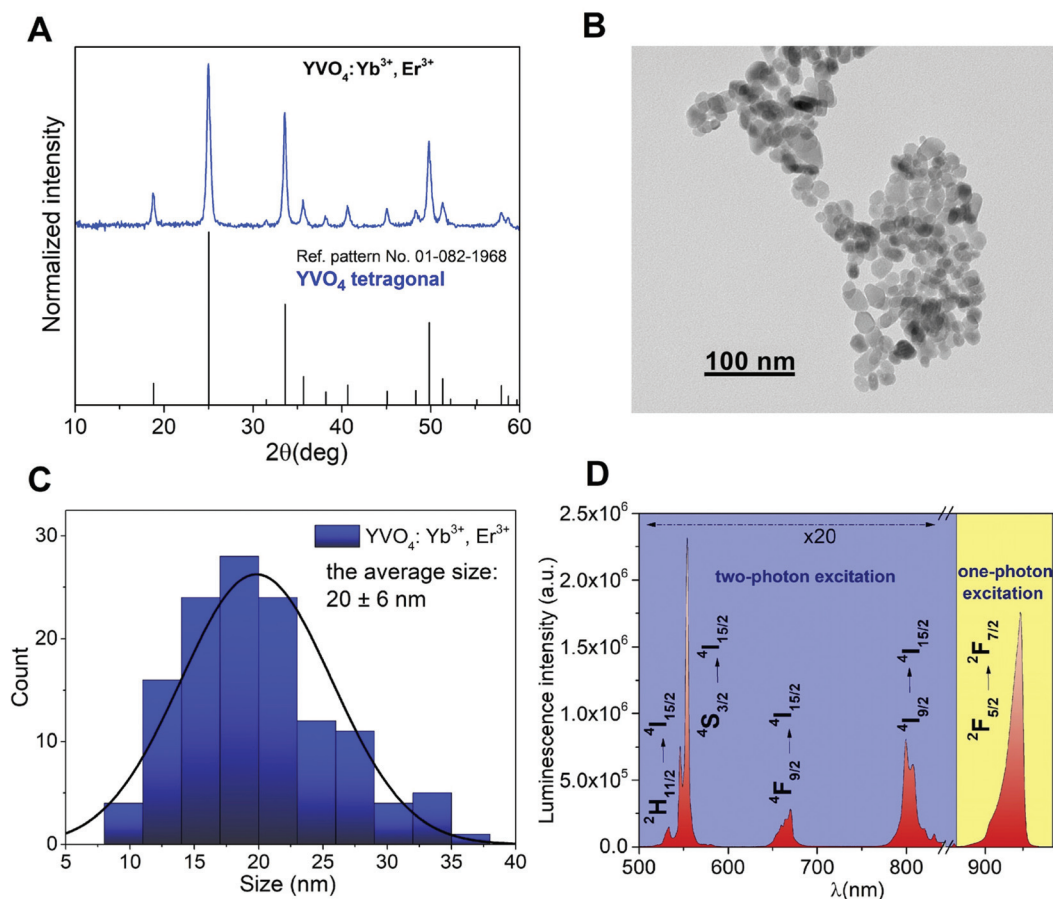


Fig. 1 (a) Powder XRD pattern of $\text{YVO}_4:\text{Yb}^{3+},\text{Er}^{3+}$; (b) TEM image of the obtained nanomaterial and (c) the corresponding size distribution histogram; and (d) emission spectrum of the obtained product recorded at $\lambda_{\text{ex}} = 975$ nm and pump power 300 mW.

nanoparticles (NPs), and their average size (long diameter) is about 20 ± 6 nm (Fig. 1c).

Luminescence properties

The emission spectrum was recorded in the range of 500–960 nm (Fig. 1d; $\lambda_{\text{ex}} = 975$ nm). The nanomaterial prepared shows a very intense green up-conversion (anti-Stokes) luminescence, visible to the naked eye. The emission spectrum consists of 4 narrow, sharp bands from Er^{3+} : $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ (532 nm), $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ (550 nm), $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ (664 nm) and $^4\text{I}_{9/2} \rightarrow ^4\text{I}_{15/2}$ (805 nm) associated with their $4f-4f$ radiative transitions, and one band derived from Yb^{3+} : $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ (940 nm), which is partially cut off by the filter used during the measurements (short pass 950 nm). Please note that the filter used has a negligible effect on the rate of change of the relative intensity ratios of the $\text{Yb}^{3+}/\text{Er}^{3+}$ bands as a function of temperature.²¹ The optical characteristics of the 950 nm short pass filter is included in the ESI (Fig. S1†). The Er^{3+} bands located around 664 and 805 nm, as well as the Yb^{3+} band located around 940 nm are in the 1st biological window spectral range. This is very important for the application of a luminescent nanothermometer in biological research. Fig. 2 shows

the energy level diagram for the obtained nanomaterial ($\text{YVO}_4:\text{Yb}^{3+},\text{Er}^{3+}$), taking into account the main energy transfer processes, up-conversion luminescence and thermalization of states.

In order to investigate the influence of temperature on the spectroscopic properties of the obtained nanomaterial, its emission spectra were collected as a function of increasing temperature, in the range of 293–453 K (Fig. 3; $\lambda_{\text{ex}} = 975$ nm). The measurements were carried out using different values of the laser power (100, 200 and 300 mW), in order to investigate the effect of the pump power on the thermometric properties of the material, *i.e.* performance of the luminescent thermometer. As the temperature increases, a significant decrease in the intensity of the band located around 550 nm (Er^{3+} : $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$) is observed, as a result of thermal quenching and thermalization processes. Intensity of the Er^{3+} bands located around 532, 664 and 805 nm negligibly change or slightly increase with increasing temperature. These effects can be clearly seen in the non-normalized spectra (Fig. S2†) and in the plots presenting the integrated up-conversion luminescence intensities as a function of temperature (Fig. S3†). The Er^{3+} bands located around 532 and 550 nm ($^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ and



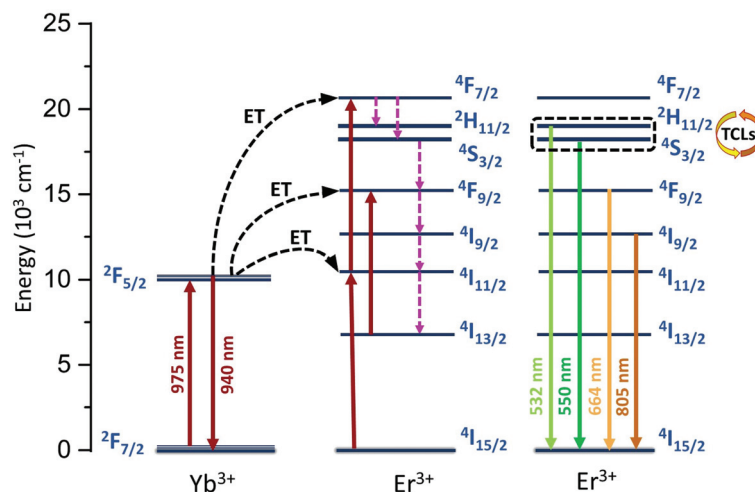


Fig. 2 Energy level diagram showing schematically the possible radiative and non-radiative processes in the $\text{YVO}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ system.

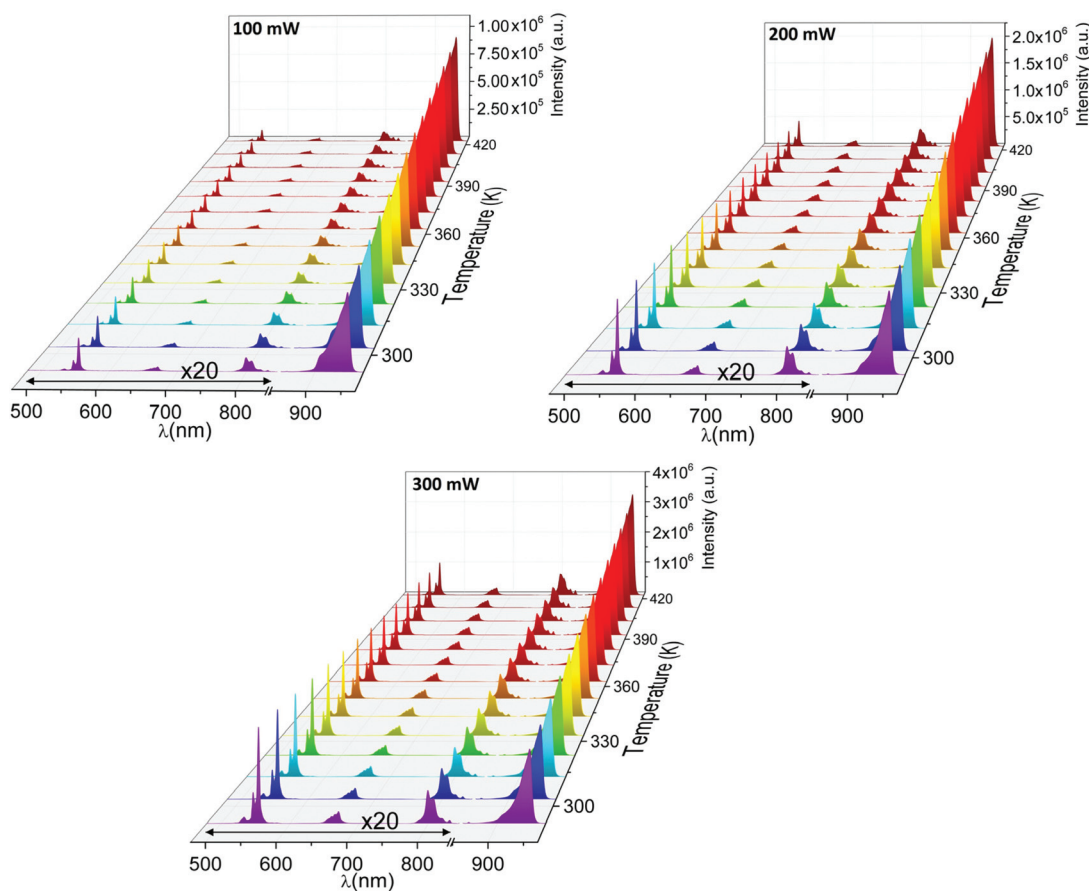


Fig. 3 Emission spectra of the synthesized $\text{YVO}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ NPs measured at increasing temperature values and with different laser power (100, 200 and 300 mW); $\lambda_{\text{ex}} = 975$ nm.

$^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$) are thermally coupled, and the energy difference between these levels is approximately 603 cm^{-1} (derived from the Boltzmann distribution). This is why, the significant, rela-

tive increase of the 532 nm band intensity, with respect to the 550 nm band, is due to the thermalization processes between the TCLs of Er^{3+} ($^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$), which can be clearly



observed in the normalized spectra (Fig. S4†). These thermalization processes conform the Boltzmann-type distribution:

$$\text{LIR} \equiv \frac{I_2}{I_1} = B \exp\left(-\frac{\Delta E}{k_B T}\right) \quad (1)$$

where LIR is the luminescence intensity ratio of the higher energy (I_2 ; 532 nm) and lower energy (I_1 ; 550 nm) bands; ΔE is the energy separation between the barycenters I_2 and I_1 ; k_B is the Boltzmann constant; T is the absolute temperature; and B is a constant, which depends on the rates of total spontaneous emission, state degeneracies, the branching ratio of the transitions with respect to the ground state, and transition angular frequencies.³⁰ At the same time, the intensity of the Yb^{3+} band around 940 nm (Yb^{3+} : $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$) increases with temperature elevation. This is because the band originates from the phonon-assisted transition of Yb^{3+} , which may be enhanced with temperature.^{8,21,24}

It should be emphasized that the changes in the pump (laser) power have a significant impact on the absolute intensity of the emission bands, as well as their relative intensities (in the case of the non-TCL ones), especially for the luminescence intensity ratios of $\text{Yb}^{3+}/\text{Er}^{3+}$. The band around 940 nm corresponds to the one-photon transition $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ (see Fig. S5,† showing the determined number of photons participating in the observed transitions), *i.e.* conventional downshifting emission. So, even at a relatively low laser power (*i.e.* 100 mW), this transition is intense and clearly visible. On the other hand, in the case of the two-photon transitions coming from Er^{3+} (non-linear, up-conversion luminescence; Fig. S5†), the change of the laser power has a huge impact on the intensity of these bands. Together with decreasing laser power, the signal-to-noise ratio decreases significantly for the up-conversion emission, and the data quality deteriorates markedly. This is why, the change of the pump power influences the determined thermometric parameters associated with non-TCLs, *i.e.* LIRs of $\text{Yb}^{3+}/\text{Er}^{3+}$, but it does not affect Er^{3+} TCLs, *i.e.* LIR 532/550 nm. The LIR values for Er^{3+} TCLs, *i.e.* 532/550 nm, were correlated with temperature applying eqn (1) (Fig. 4), whereas the LIRs corresponding to the non-TCLs, *i.e.* 940/550 and 940/805 nm, were successfully correlated with temperature applying second-order polynomial fits (Fig. 5 and 6). In each case, the LIR parameter increases monotonously with increasing temperature. The use of simple polynomial fits (empirical functions) was motivated by the absence of an appropriate physical model, rationalizing the monitored changes of the LIR parameters (non-TCLs) with temperature. Details for all fits, *i.e.* values of the fitting parameters, are given in Table 1.

In order to investigate the performance of any nanothermometer, it is necessary to determine parameters such as: absolute sensitivity, relative sensitivity and temperature resolution. The absolute sensitivity (S_A) was calculated based on eqn (2). This parameter is usually expressed in K^{-1} .

$$S_A = \frac{\text{dLIR}}{\text{dT}} \quad (2)$$

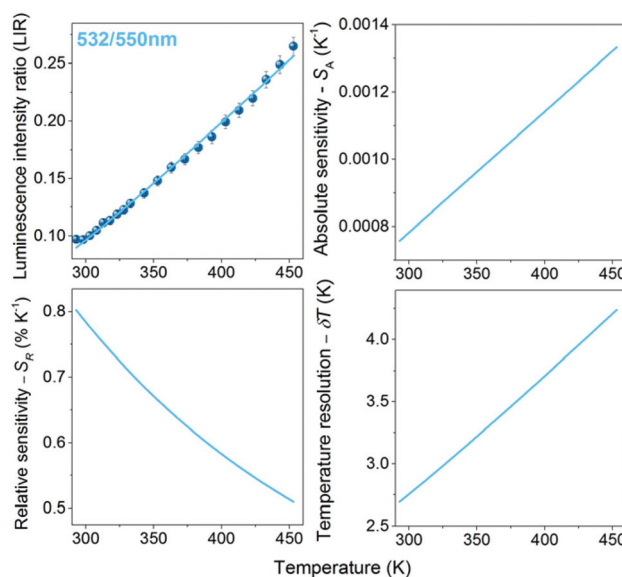


Fig. 4 Luminescence intensity ratios, the corresponding absolute sensitivity (S_A), relative sensitivity (S_R) and temperature resolution (δT) determined for Er^{3+} TCLs (532/550 nm), for the synthesized $\text{YVO}_4:\text{Yb}^{3+},\text{Er}^{3+}$ NPs, measured with laser power 300 mW; $\lambda_{\text{ex}} = 975$ nm.

Another very important parameter is the relative temperature sensitivity (S_R ; eqn (3)).

$$S_R = 100\% \times \frac{\text{dLIR}}{\text{dT}} \times \frac{1}{\text{LIR}} \quad (3)$$

This parameter, *i.e.* S_R , shows how the analyzed thermometric parameter (LIR) changes per 1 K (expressed in $\% \text{K}^{-1}$), and it can be used to compare the performance of different optical thermometers.

Based on eqn (4), the temperature resolutions (δT) were also determined.

$$\delta T = \frac{1}{S_R} \times \frac{\text{dLIR}}{\text{LIR}} \quad (4)$$

We have added a more detailed explanation of the temperature resolution parameter δT , and have provided derivation of the corresponding equation in the ESI† file. It is worth mentioning that δLIR is the uncertainty of the LIR parameter determination, which is calculated from eqn (5).

$$\delta \text{LIR} = \text{LIR} \times \sqrt{\left(\frac{\delta I_1}{I_1}\right)^2 + \left(\frac{\delta I_2}{I_2}\right)^2} \quad (5)$$

where $\delta I_{1,2}$ are the intensities of the noise (baseline fluctuations) and $I_{1,2}$ are the signal (band) intensities. The determined S_A , S_R and δT as function of temperature, together with the corresponding LIR values are compared in Fig. 4–6 (Er^{3+} TCL 532/550 nm – Fig. 4; $\text{Yb}^{3+}/\text{Er}^{3+}$ non-TCLs 940/550 nm and 940/805 nm – Fig. 5 and 6, respectively). Please note that the LIR, S_A and S_R parameters for the TCLs of Er^{3+} are independent (constant) of the pump power used, so Fig. 4 shows the results only for the highest applied laser power, *i.e.* 300 mW



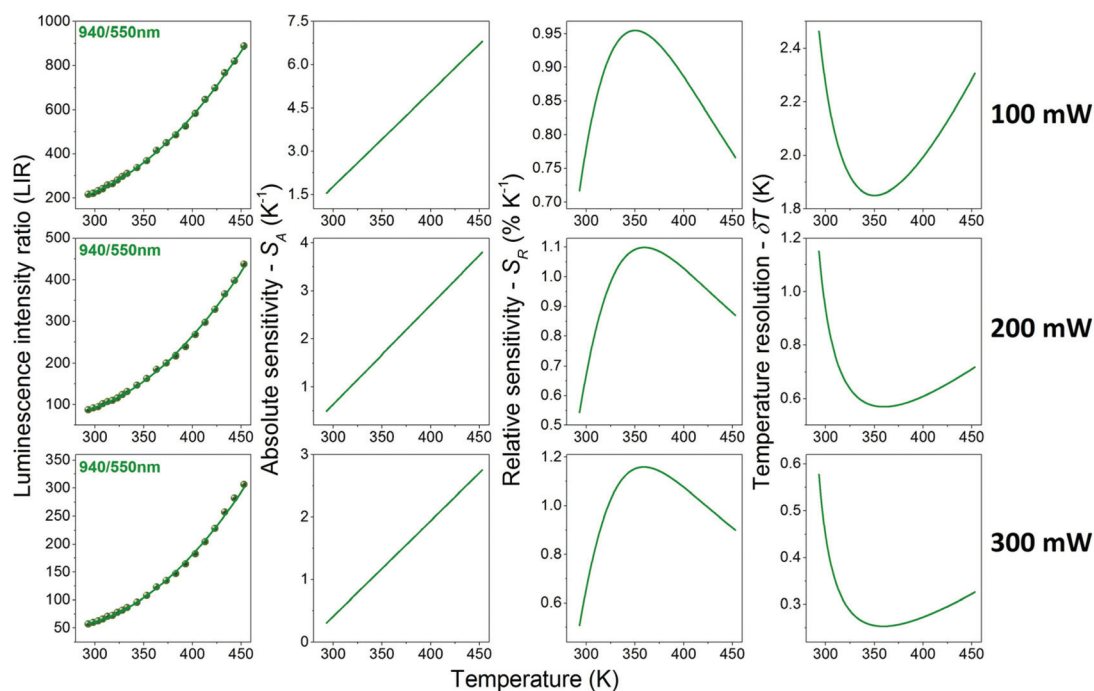


Fig. 5 Luminescence intensity ratios, the corresponding absolute sensitivities (S_A), relative sensitivities (S_R) and temperature resolutions (δT) determined for $\text{Yb}^{3+}/\text{Er}^{3+}$ (940/550 nm) non-TCLs of the synthesized $\text{YVO}_4:\text{Yb}^{3+},\text{Er}^{3+}$ NPs, measured with different laser power values (100, 200 and 300 mW); $\lambda_{\text{ex}} = 975$ nm.

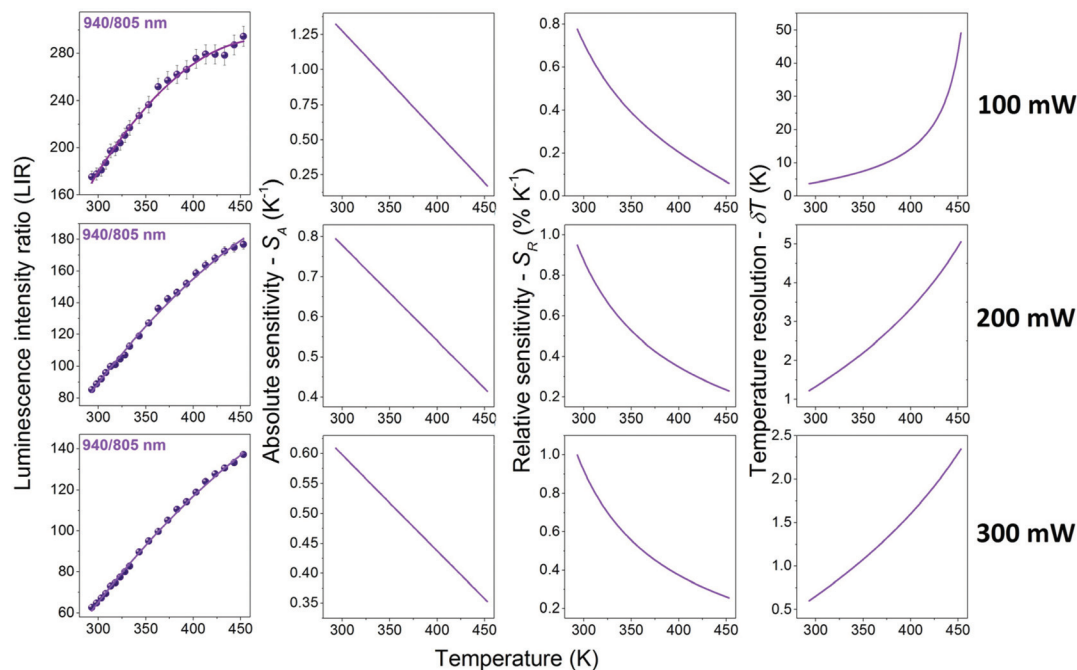


Fig. 6 Luminescence intensity ratios, the corresponding absolute sensitivity (S_A), relative sensitivities (S_R) and temperature resolution (δT) determined for $\text{Yb}^{3+}/\text{Er}^{3+}$ (940/805 nm) non-TCLs of the synthesized $\text{YVO}_4:\text{Yb}^{3+},\text{Er}^{3+}$ NPs, measured with different laser power values (100, 200 and 300 mW); $\lambda_{\text{ex}} = 975$ nm.

(the maximum power at which we did not observe laser-induced heating of the sample). On the other hand, Fig. 5 and 6 show the data for the non-TCLs of $\text{Yb}^{3+}/\text{Er}^{3+}$, for three

different values of the laser power, *i.e.* 100, 200 and 300 mW, because in this case all measured parameters depend on the pump power used.



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