Calibration of remote nanothermometers using nanoparticles of NaYF$_4$: Er$^{3+}$, Yb$^{3+}$, Nd$^{3+}$

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Abstract. The nanoparticles of NaYF$_4$: Er$^{3+}$, Yb$^{3+}$, Nd$^{3+}$ present fluorescent emissions by upconversion. These emissions are associated with the doping ions of Er, Yb and Nd in the NaYF$_4$ nanoparticles. The nanoparticles of NaYF$_4$ doped with Er$^{3+}$ and Yb$^{3+}$ ions produce upconversion radiation when excited by 980 nm wavelength laser. By incorporating the Nd$^{3+}$ ions, the NaYF$_4$: Er$^{3+}$, Yb$^{3+}$, Nd$^{3+}$ arrangement is formed, which produces the same excitation with an 880 nm wavelength laser, the product of a cross-transfer process between the Nd, the Yb and the Er. For applications in human tissue it is preferable to use a 880 nm wavelength laser. These nanoparticles of NaYF$_4$: Er$^{3+}$, Yb$^{3+}$, Nd$^{3+}$ have been synthesized in our laboratories with Y (79.3%), Yb (18%), Er (2%) and Nd (0.7%). In this work we have studied the fluorescence behavior of these nanoparticles, which correspond to the transitions $^2$H$_{11/2}$ $\rightarrow$ $^4$I$_{15/2}$ $\gamma$ $^4$S$_{3/2}$ $\rightarrow$ $^4$I$_{15/2}$, and that can be used in the calibration of a remote nanothermometer, because they have a sensitivity to very small changes in temperature.

1. Introduction

The nanoparticles of NaYF$_4$: Er$^{3+}$, Yb$^{3+}$, Nd$^{3+}$ show fluorescent emissions by upconversion. These emissions are associated with the doping ions of Er, Yb and Nd in the NaYF$_4$ nanoparticles. The nanoparticles of NaYF$_4$ doped with Er$^{3+}$ and Yb$^{3+}$ ions produce upconversion radiation when excited by 980 nm wavelength laser. By incorporating the Nd$^{3+}$ ions, the NaYF$_4$: Er$^{3+}$, Yb$^{3+}$, Nd$^{3+}$ arrangement is formed, which produces the same excitation with an 880 nm wavelength laser, the product of a cross-transfer process between the Nd, the Yb and the Er. For applications in human tissue it is preferable to use a 880 nm wavelength laser. These nanoparticles of NaYF$_4$: Er$^{3+}$, Yb$^{3+}$, Nd$^{3+}$ have been synthesized in our laboratories in the following proportions Y (79.3%), Yb (18%), Er (2%) and Nd (0.7%). In this work we have studied the fluorescence behavior of these nanoparticles, which correspond to the transitions $^2$H$_{11/2}$ $\rightarrow$ $^4$I$_{15/2}$ $\gamma$ $^4$S$_{3/2}$ $\rightarrow$ $^4$I$_{15/2}$, and that can be used in the calibration of a remote nanothermometer, because they have a sensitivity to very small changes in temperature.

In the last decade, the interest in the study of nanoparticles doped with lanthanides by upconversion[1][2] has grown, due to its multiple applications in the field of biomedicine[3][4]. These applications use the fact that photons in the near infrared have an effective penetration length in biological tissues and minimal background autofluorescence. So the nanoparticles doped with lanthanides are also used to measure the temperature with optical sensors. To obtain the temperature of the system, different parameters have been measured, according to
the material used, such as the absolute luminescent intensity, half-life or the relation between the emission bands[5][6][7][8].

Among the nanoparticles used for these applications, the nanocrystals doped with lanthanides stand out, due to its high photonic stability and its efficient anti-Stokes conversion from the infrared to near visible spectrum. The most studied nanocrystals are those doped with Er and Yb, that are used in luminescent thermometry, because they present sensible changes in the ratio of the emission intensities of the transitions $^2H_{11/2} \rightarrow ^4I_{15/2}$ a $^4S_{3/2} \rightarrow ^4I_{15/2}$. When changing the host or the dopants, different arrangements are proposed, according to the physiological temperature range. Among these arrangements stand out the phosphor doped with Nd[9][10], whose luminescence is greater than of other materials in the near-infrared region so they can be used as optical heaters or remote thermometers for biological systems[11][12][13].

The advances in the field of nanothermometry and optics and the constant technological development require testing new materials capable of offering the necessary characteristics for new applications. In this work, the production of NaYF$_4$ nanoparticles doped with Er, Yb and Nd is shown, forming the NaYF$_4$: Er$^{3+}$, Yb$^{3+}$, Nd$^{3+}$ array and their application as fluorescent markers and remote nanothermometers.

2. Emission by upconversion in NaYF$_4$: Er, Yb, Nd

The nanoparticles doped with lanthanides, which are used for upconversion, are formed by a crystalline host (NaYF$_4$), a sensitizer (Yb$^{3+}$) and an emitter (Er$^{3+}$). As a crystalline host, has been used NaYF$_4$, one of the most efficient due to its low photon energy that allows to minimize the voltages in the network and the non-radiative transitions. As a sensitizer, has been used Yb$^{3+}$ ions, the most efficient because they have only one excited state, the $^2F_{5/2}$ state, which is resonant in energy with the $^4I_{11/2}$ state of the Er$^{3+}$ ions, which is used as an emitter. The state of Er$^{3+}$ has an extinction coefficient ten times smaller than that of Yb$^{3+}$, so it is excited to its $^4F_{7/2}$ state via two successive transfers of nearby Yb$^{3+}$ ion energy, which is promoted from its fundamental state $^4I_{15/2}$ to intermediate state $^4I_{11/2}$ and subsequently to the excited state $^4F_{7/2}$.

To obtain a sensitizer with excitation wavelength near 800 nm, Nd$^{3+}$ is incorporated into the first biological window of human tissue, due to its strong absorption close to this wavelength. The figure 1 shows a scheme of the extinction spectrum, taking into account the absorption and dispersion of human tissue. In this spectrum, the absorption bands that allow the definition of the two biological windows can be identified. The first biological window extends from 700 nm to 980 nm and corresponds to the spectral range defined between the visible absorption band of hemoglobin and the characteristic water absorption band. In this spectral region there is a decrease in the absorption of light, however an important optical extinction is still observed due to the residual dispersion, whose relevance decreases for longer wavelengths. The second biological window extends from 1000 nm to 1400 nm, both limits correspond to the absorption bands of water. In this spectral window the optical absorption does not completely cancel out, since the absorption coefficient of water is close to 0.5 cm$^{-1}$. However, the optical dispersion is lower compared to that of the first biological window due to the longer wavelengths.

The Nd$^{3+}$ ions are those that allow emitting in wavelengths of 980 nm. This allows the excitation of the Yb$^{3+}$ ions in order to produce upconversion between the ions of Yb$^{3+}$ and Er$^{3+}$. The figure 2 shows the scheme of the energy levels required to produce upconversion in the nanoparticles of NaYF$_4$: Er$^{3+}$, Yb$^{3+}$, Nd$^{3+}$. To produce upconversion in these nanoparticles
we have an initial pump wavelength close to 800 nm, which produces a transfer of energy close to 980 nm to Yb$^{3+}$. The emissions of the Yb$^{3+}$ ion produce a second energy transfer to the Er$^{3+}$ ion, whose emission spectrum in the visible range consists of three emissions attributed to the transitions $^2H_{11/2} \rightarrow ^4I_{15/2}$ and $^4S_{3/2} \rightarrow ^4I_{15/2}$ corresponding to wavelengths of 525 nm and 545 nm respectively, both in green, and $^4F_{9/2} \rightarrow ^4I_{15/2}$ corresponding to a wavelength of 650 nm in red.

![Figure 1](image1.png)

**Figure 1.** Extinction coefficient as a function of the wavelength in human tissue where the first and second biological windows stand out

![Figure 2](image2.png)

**Figure 2.** Diagram showing the cross-transfer process in the NaYF$_4$: Er, Yb, Nd. Two possible mechanisms A and B contributing to Er$^{3+}$ emissions are shown. The initial wavelength is 808 nm

In the transition from Yb$^{3+}$ to Er$^{3+}$, the excitation energy can be transferred to the energy level $^4I_{11/2}$ of the Er$^{3+}$, via a cross-relaxation process: $^2F_{5/2} \rightarrow ^2F_{7/2}$ (Yb$^{3+}$) $^4I_{15/2} \rightarrow ^4I_{11/2}$ (Er$^{3+}$), marked as A in the figure 2. A second cross-relaxation process from Yb$^{3+}$ to an Er$^{3+}$ ion, previously excited, gives rise to the excitation of the Er$^{3+}$ ion at higher energy levels via a new transfer process: $^2F_{5/2} \rightarrow ^2F_{7/2}$ (Yb$^{3+}$) $^4I_{11/2} \rightarrow ^4F_{7/2}$ (Er$^{3+}$) that allows green emission. Thermal processes or the presence of nearby defects produce non-radiative decays at the levels
$^{4}\text{F}_{9/2}$, $^{4}\text{S}_{3/2}$ and $^{2}\text{H}_{11/2}$ that give rise to the transitions $^{4}\text{F}_{9/2} \rightarrow ^{4}\text{I}_{15/2}$ of 650 nm, $^{4}\text{S}_{3/2} \rightarrow ^{4}\text{I}_{15/2}$ of 540 nm and $^{2}\text{H}_{11/2} \rightarrow ^{4}\text{I}_{15/2}$ of 520 nm in the Er$^{3+}$, which leads to a competition between red and green emissions. Another probable mechanism of the red emulsion is shown as B in the figure 2.

3. Relation between temperature and probabilities of transition

The emission in the green of the Er$^{3+}$ ion, product of the energy transfer of the Yb$^{3+}$ ion, consists of two bands between 515 nm and 535 nm, centered at 525 nm and between 535 nm and 570 nm, centered at 545 nm, which come from transitions from the excited states, $^{2}\text{H}_{11/2}$ and $^{4}\text{S}_{3/2}$ respectively to the ground state. These two states are very close, separated only by hundreds of wave numbers, so they reach a thermal equilibrium governed by the Boltzmann factor:

$$\frac{I_{525}}{I_{545}} = Ae^{-\Delta E/k_BT}$$

where $A$ is a constant, $I_{525}$ and $I_{545}$ are the integrated intensities of the transitions $^{2}\text{H}_{11/2} \rightarrow ^{4}\text{I}_{15/2}$ and $^{4}\text{S}_{3/2} \rightarrow ^{4}\text{I}_{15/2}$ respectively, $\Delta E$ is the energy gap that separates the two excited states, $k_B$ is the Boltzmann constant and $T$ is the absolute temperature.

This leads to changes in the emission intensities of these bands as a function of temperature. Thus it is possible to obtain a thermometric scale that gives information on the temperature of the nanoparticles and their environment. From this equation is found a linear relationship between $\ln\left(\frac{I_{525}}{I_{545}}\right)$ and $\frac{1}{T}$, given by the equation 2 shown below:

$$\ln\left(\frac{I_{525}}{I_{545}}\right) = -\frac{\Delta E}{k_BT} + B$$

where $B$ is a constant.

Calculating the energy difference between the transitions of interest we have that $\Delta E = 1.389 \times 10^{-20}$ J, at room temperature we have that $k_BT$ is approximately $0.414 \times 10^{-20}$ J, that is, $\Delta E$ is of the order of $k_BT$. The dependence of $\ln\left(\frac{I_{525}}{I_{545}}\right)$ has been measured with temperature at temperatures close to room temperature. And with these results the value of the slope $\frac{\Delta E}{k_BT}$ is estimated in the previous equation. The calculated value is 1.006 86 K, close to the experimentally found value.

4. Experimental results

The nanoparticles of NaYF$_4$: Er$^{3+}$, Yb$^{3+}$, Nd$^{3+}$ have been synthesized by the solvothermal method [14]. The percentages used are: Y (79.3%), Yb (18%), Er (2%), Nd (0.7%). Initially, 3.6 mmol of NaCl (Sigma Aldrich), 1.427 mmol of YCl$_3 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich), 0.036 mmol of ErCl$_3 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich), 0.324 mmol of YbCl$_3 \cdot 6\text{H}_2\text{O}$ and 0.013 mmol of NdCl$_3$ (Sigma Aldrich) were dissolved, in a solution of 27 ml of ethylene glycol containing 0.45 g of branched polyethylene (Sigma Aldrich). The mixture was stirred for 60 minutes using a magnetic stirrer. Subsequently, a solution of 17 ml of ethylene glycol with 7.2 mmol of NH$_4$F (Sigma Aldrich) was added to the initial solution containing the chlorides and stirred for 30 minutes. The resulting clear solution was heated with an 85 ml teflon flask in an oven at 170 °C for 5 hours. Finally, he performed a centrifugation process at 6,000 RPM using a mixture of distilled water and ethanol for 15 minutes in order to wash them. This process was repeated several times. The resulting
product was dried for 12 hours at 80 °C. This sample was subjected to a thermal treatment for a further 5 hours at 500 °C. The final product obtained was a fine off-white powder, like the one shown in the figure 3.

![Figure 3. NaYF$_4$: Er, Yb, Nd nanoparticle fabricated at the laboratory](image3.png)

These nanoparticles convert 808 nm radiation into shorter wavelength radiation such as green and red. The green emissions correspond to the $^2H_{11/2} \rightarrow ^4I_{15/2}$ and $^2S_{3/2} \rightarrow ^4I_{15/2}$ transitions. In order to observe this emission under a biological tissue, an experimental arrangement was mounted, schematized in the figure 4. For this experiment a laser diode of 2 W of power was used, a Nikon camera model D3300 with an IR filter, to register the observed images, eliminating the source of excitation and attenuating the emission in red. The nanoparticles were placed inside the chicken tissue. The figures 5 and 6 show the emission of the nanoparticles when passing through a chicken tissue of approximately 2 mm and 4 mm respectively. They show that the efficiency of the emissions is much greater when the particles are covered by a 2 mm thick chicken tissue.

![Figure 4. Disposition of the equipment to record the images obtained by the emission of the nanoparticles inside the chicken skin](image4.png)

![Figure 5. Emission of the nanoparticles inside 2 mm thick of chicken tissue](image5.png)

![Figure 6. Emission of the nanoparticles inside 4 mm thick of chicken tissue](image6.png)

To observe the changes in the intensities of the emission bands $^2H_{11/2} \rightarrow ^4I_{15/2}$ and $^2S_{3/2} \rightarrow ^4I_{15/2}$ from Er$^{3+}$ in nanoparticles of NaYF$_4$: Er$^{3+}$, Yb$^{3+}$, Nd$^{3+}$ when the temperature changed, the emission spectra of these nanoparticles were analyzed for different temperatures close to physiological temperatures. The assembly of this experiment is shown in the figure 7 of the
experiment setup to obtain the emission spectra. For this, a laser diode of 808 nm and up to 2 W of output power was used, a B&W Tek Model BTC-110S spectrometer connected to an optical fiber and controlled by a PC where the data obtained is also stored, a filter IR to eliminate the excitation source of the nanoparticles. The observed emissions correspond to a tablet of NaYF$_4$: Er$^{3+}$, Yb$^{3+}$, Nd$^{3+}$, and are shown in the figure 8. This tablet of 0.02 g of mass was obtained after compressing the powder sample to form a tablet of 0.2 mm in thickness and 6 mm in radius. This tablet was placed on a copper rod 22 mm in diameter and 23 mm in height. The copper bar, wrapped by coated nichrome wire, was connected to a variable voltage source between 0 V and 5 V, in order to vary the temperature of the nanoparticles tablet. To record the temperature and to be able to calibrate the emission spectra, a type J thermocouple was used, which made contact with the tablet. Likewise, converging lenses were used to focus both the incident radiation and the one emitted by the nanoparticles.

![Experiment setup to obtain the emission spectra](image)

Figure 7. Experiment setup to obtain the emission spectra

![Emission spectra of NaYF4: Er$^{3+}$, Yb$^{3+}$, Nd$^{3+}$ with excitation wavelength of 808 nm obtained at 41.8 °C, 49.0 °C, 55.0 °C, 62.1 °C and 71.0 °C temperatures](image)

Figure 8. Emission spectra of NaYF4: Er$^{3+}$, Yb$^{3+}$, Nd$^{3+}$ with excitation wavelength of 808 nm obtained at 41.8 °C, 49.0 °C, 55.0 °C, 62.1 °C and 71.0 °C temperatures

The emission spectra obtained consist of two bands between 510 nm and 565 nm. When the temperature of the nanoparticles varies, it is observed that the relative intensity between
these bands changes, registering a relative growth of the band between 510 nm and 535 nm, corresponding to the transition $^2S_{3/2} \rightarrow {}^4I_{15/2}$, maintaining the same band shapes. The result obtained shows the hypersensitivity of the relation between the intensities of these bands with temperature. This ratio can be used as a parameter to measure the temperatures of the nanoparticles. In order to study the dependence of this ratio of intensities, the integrated intensities of the emission spectra obtained were analyzed. For this the area covered by the first band ($I_{525}$) was integrated, as well as the area covered by the second band ($I_{545}$). The figure 9 shows the graph of $\ln \left( \frac{I_{525}}{I_{545}} \right)$ as a function of $\frac{1}{T}$. A linear dependence is observed where the slope corresponds to $\frac{\Delta E}{k_B}$.

![Figure 9. Nanothermometer calibration curve for a NaYF$_4$: Er$^{3+}$, Yb$^{3+}$, Nd$^{3+}$ tablet when excited with a laser of 808 nm and 2 W power. The points correspond to the experimental data and the line represents the best fit.](image)

By adjusting the experimental data to the expression of $\ln \left( \frac{I_{525}}{I_{545}} \right)$ it was found that the slope of the line is $-1, 1 \times 10^{-20}$, which is in accordance with the result of $-1, 0 \times 10^{-20}$ that was previously calculated. The difference can be attributed to the fact that the bands are not really centered at 525 nm and 545 nm. The adjustment of the curve has a $R^2$ of 0.99478, which shows how precise the fit is. This line allows calibrating the nanometer. The linear behavior observed in the figure reveals that a precise determination of the relationship between the luminescent intensities of these hypersensitive lines allows to determine the temperature of the nanoparticles of NaYF$_4$: Er$^{3+}$, Yb$^{3+}$, Nd$^{3+}$ for temperatures close to room temperature.

5. Conclusions
(i) The 525 nm and 545 nm emissions of NaYF$_4$: Er$^{3+}$, Yb$^{3+}$, Nd$^{3+}$ nanoparticles within chicken meat have been used to obtain the temperature of the nanoparticles and that of their environment.

(ii) The same luminescent emissions have been observed when placing the nanoparticles of NaYF$_4$: Er$^{3+}$, Yb$^{3+}$, Nd$^{3+}$, between two pieces of chicken 2 mm and 4 mm thick.
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References
[1] Tian L. Xu Z. Zhao S. Cui Y. Liang Z. Zhang J. and Xu X. The upconversion luminiscence of \( \text{Er}^{3+}/\text{Yb}^{3+}/\text{Nd}^{3+} \) triply-doped \( \beta\)-\( \text{NaYF}_4 \) nanocrystals under 808-nm excitation. Materials, 7:7289–7303, 2014.
[2] Jaque D. Martínez Maestro L. Del Rosal B. Haro-Gonzalez P. Benayas A. Plaza J. L. Martín Rodríguez E. and García Solé J. Nanoparticles for photothermal therapies. Nanoscale, 2014.
[3] Peng H. Stich M. Yu J. Sun L. Fischer L. and Wolfeis O. Luminescent europium (iii) nanoparticles for sensing and imaging of temperature in the physiological range. Adv. Mater., 2010.
[4] Zhou J. Liu Q. Feng W. Sun Y. and Li F. Upconversion luminescent materials: Advances and applications. Chem. Rev., 2015.
[5] Ye F. Wu C. Jin Y. Chan Y. Zhang X. and Chiu D. Ratiometric temperature sensing with semiconducting polymer dots. J. Am. Chem. Soc., 2011.
[6] Kim M. and Yoda M. Infrared quantum dots for liquid-phase thermometry in silicon. Meas. Sci. Technol., 2011.
[7] Zhou J. Xu S. Zhang J. and Qui J. Upconversion luminescence behavior of single nanoparticles. Nanoscale, 2015.
[8] Debasu M. Ananias D. Pastoriza-Santos I. Liz-Marzán L. Rocha J. and Carlos L. All-in-one optical heater-thermometer nanoprotfolio operative from 300 to 2000 k based on \( \text{Er}^{3+} \) emission and blackbody radiation. Adv. Mater., 2013.
[9] Xue F. and Wang H. The stable and water-soluble neodymium-doped lanthanide fluoride nanoparticles for near infrared probing of copper ion. Talanta, 2012.
[10] Bednarkiewicz A. Wawrzynczyk D. Nyk M. and Strek W. Optically stimulated heating using \( \text{Nd}^{3+} \) doped \( \beta\)-\( \text{NaYF}_4 \) colloidal near infrared nanophosphors. Appl. Phys. B, 2011.
[11] M. Rocha U. Kumar K. Jacinto C. Navarro E. Martín Rodríguez E. Pedroni M. Speghini A. Hirata G. Martín I. Del Rosal B. Pérez-Delgado A. Misiak M. Bednarkiewicz A. Vanetsev A. Orlovskii Y. Jovanović D. Dramičanin and Jaque D. Neodymium-doped nanoparticles for infrared fluorescence bioimaging: The role of the host. Appl. Phys., 2015.
[12] L. Bednarkiewicz A. Stefanski M. Tomala R. Hreniak D. Marciniak and Strek W. Near infrared absorbing near infrared emitting highly-sensitive luminescent nanothermometer based on \( \text{Nd}^{3+} \) to \( \text{Yb}^{3+} \) energy transfer. Phys. Chem. Chem. Phys., 2015.
[13] Wawrzynczyk D. Bednarkiewicz A. Nyk M. Strek W. and Samoc M. Neodymium (iii) doped fluoride nanoparticles as non-contact optical temperature sensors. Nanoscale, 2012.
[14] Puga R. Palacios E. Velasco M. Hernández J. and Loro H. Synthesis de partículas \( \alpha\)-\( \text{NaYF}_4 \): Er, yb por el método solvotermal para florescencia por upconversion. REVCIUNI, 2014.