Primary Luminescent Nanothermometers for Temperature Measurements Reliability Assessment

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The potential applications in disparate fields led to a rapid evolution of luminescence thermometry. In particular, luminescent thermometry based on trivalent lanthanide ions (Ln3+) has become very popular in the past decade due to the unique versatility, stability, and narrow emission band profiles covering a broad spectral range (from ultraviolet to the infrared) with relatively high emission quantum yields. Nevertheless, the reliability of Ln3+ ratiometric nanothermometry measurements is recently questioned in a few works reporting fake temperature readouts caused by experimental artifacts and even intrinsic effects. Using NaYF4:Er3+/Yb3+ @NaNdF4@PAA (PAA stands for polyacrylic acid) core–shell nanoparticles, it is shown that how the primary luminescent thermometer concept can be used to correct the thermometric parameter (the intensity ratio of the Er3+ 2H11/2 → 4I15/2 and 4S3/2 → 4I15/2 transitions) from the interference of the intruding 2H9/2 → 4I13/2 emission ensuring, thereafter, reliable temperature measurements.

1. Introduction

In the past few years, luminescence thermometry has undergone a rapid evolution instigated by the novel technological challenges at the nanoscale.[3] For example, areas like microelectronics, photonics, and nanomedicine demand accurate high spatial resolution (submicrometer) temperature measurements; a requirement that conventional thermometry cannot meet.[2,3] Luminescence thermometry exploits the temperature-dependent luminescence of a thermally imaged object, granting remote high-detection relative thermal sensitivity (>1%K-1) and spatial resolution (<10 μm) measurements in short acquisition times (<1 ms).[2–4] Among the distinct luminescent thermal nanoprobes tested, trivalent lanthanide (Ln3+) ions-based materials have become very popular due to their unique versatility, photostability, and narrow emission band profiles (<10 nm) with relatively high emission quantum yields (>50% in the visible). Moreover, the different Ln3+ ions emission covers a broad spectral range from the ultraviolet to the infrared.[1,4]

Numerous nanothermometers based on Ln3+-doped materials have been reported, among which stand out the ones based on the intensity ratio between two transitions—the ratiometric thermometers.[1,4–12] Ratiometric thermometers are held as very reliable temperature sensors, as they are not affected by local intensity fluctuations (i.e., concentration of emitting centers or excitation source fluctuations) while requiring simple instrumentation.[1,4] However, there are a few effects, including experimental artifacts (e.g., the numerical aperture of the optics used for excitation and emission detection[13]), the use of high laser power densities (P0),[14] and unverified assumptions about the thermal dependence of the optical transmittance of biological tissues,[15–17] that can induce spectral distortions on the emission of the chromophores, altering the relative intensity of the transitions and, consequently, the value of the thermometric parameter. This, ultimately, results in false temperature readouts, compromising the reliability of the thermometers. In the case of thermometers based on two thermally coupled energy levels, working outside the range of the Boltzmann equilibrium validity could also lead to erroneous temperature readouts.[5,18]

Despite the plethora of works using Ln3+-based ratiometric thermometers,[1,4–9,12,19] there has been general negligence regarding the authenticity of the temperature measurements, except some recent works.[5,11–16,18,20,21] In 2018, Labrador-Páez et al. evaluated how commonly disregarded experimental artifacts can affect the temperature measurements with Ln3+-doped infrared luminescent nanothermometers.[13] These artifacts comprise spectral distortions caused by unexpected...
modifications on the on-target laser power density due to aberrations induced by the experimental set-up numerical aperture or focus depth change, and self-absorption of the solvent (surrounding medium) or the luminescent probe itself. Self-absorption occurs due to the overlap of emission and absorption bands and was observed at the nanoscale by Rodriguez-Sevilla et al. when detecting spectral differences between the emission spectra of a single Er$^{3+}$-doped nanoparticle and an ensemble of the respective nanoparticles.\[^{28}\] Using the intensity ratio between the 2H$^{11/2}$ transitions at 769 nm ($^4G_a \rightarrow ^4H_3$) and 795 nm ($^4H_4 \rightarrow ^4H_6$) in a dispersion of SrF$_2$:Yb$^{3+}$/Tm$^{3+}$, Labrador-Páez et al. showed an apparent temperature change as a function of the acquisition depth in the dispersion volume of 28.7 K mm$^{-1}$, with a theoretically constant applied power density.\[^{14}\]

The 50 K temperature rise observed by Pickel et al. (measured by the intensity ratio between the $^2H_{11/2} \rightarrow ^4I_{15/2}$ and $^4S_{3/2} \rightarrow ^4I_{15/2}$ transitions) in NaYF$_4$:Yb$^{3+}$/Er$^{3+}$ nanoparticles was considered as an artifact. This apparent self-heating takes place at high laser power density excitation ($\approx 10^{-5}$ W cm$^{-2}$) and is accredited to the increased radiative and nonradiative relaxation from higher-lying Er$^{3+}$ energy levels.\[^{14}\]

As the majority of the ratiometric methods rely on the temperature-induced variation of relative emission intensities from thermally coupled energy levels, i.e., Boltzmann statistics, it is crucial to verify the validity of a Boltzmann equilibrium.\[^{5,18}\] To reach this equilibrium, the nonradiative processes to balance the two thermally coupled states must be faster than other processes, such as optical feeding and radiative decays.\[^{50}\] Suta et al. highlighted the potential pitfalls in these Boltzmann thermometers, especially in biomedical applications that require a specific working temperature—the physiological temperature range.\[^{18}\] They used the ratio between the $^2H_{9/2} \rightarrow ^4I_{15/2}$ and $^4F_{5/2} \rightarrow ^4I_{15/2}$ transitions in LaPO$_4$:Nd$^{3+}$ nanocrystals as an illustrative example. At low-doping Nd$^{3+}$ concentrations, La$_{1-x}$Nd$_x$PO$_4$ ($x < 0.001$) nanocrystals sustain the Boltzmann equilibrium from 303 to 773 K but higher Nd$^{3+}$ concentration doping leads to a gradual breakdown of Boltzmann equilibrium at physiological temperatures (for instance, $x = 0.02$, $T_{\text{Boltzmann}} > 380$ K). Although a higher Nd$^{3+}$ content may increase the absorption efficiency, it introduces additional cross-relaxation pathways between neighboring Nd$^{3+}$ ions, competing with the nonradiative transition rates and hampering Boltzmann equilibrium.\[^{18}\] However, Geitenbeek et al. showed that cross-relaxation can provide an additional pathway for relaxation between the thermally coupled levels, thus preserving the Boltzmann behavior over a wider temperature range, as in the case of luminescence intensity ratio between the transitions from the $^5D_1$ and $^5D_0$ upper levels to the $^7F_0$ ground state at increasing doping Eu$^{3+}$ concentrations in NaYF$_4$:Eu$^{3+}$.\[^{5}\]

Thanks to Ln$^{3+}$ probes with excitation and emission within the spectral ranges known as biological windows (BWs), where absorption and scattering of radiation in biological tissues are minimized,\[^{15-17}\] their applications in thermal imaging proliferate, such as recording of in vivo thermal images\[^{24-26}\] and early tumor detection.\[^{16,27}\] However, artifacts arising from in vivo applications have been continuously disregarded by the scientific community, namely, spectral distortions induced by wavelength-dependent tissue absorption and scattering. Recent papers studied the impact of these artifacts in in vivo temperature readings\[^{15,16,20,28}\] where it was shown an error of 7 K in the absolute temperature measured by a ratiometric thermometer.\[^{15}\] Qiu et al. proposed a wavelength dual-emission ratiometric upconversion luminescence nanothermometer to circumvent the errors induced by the tissue absorption and scattering.\[^{16}\] Using a hybrid structure composed of quantum dots (PbS) and Tm$^{3+}$-doped upconversion nanoparticles (UCNPs), both with emission around 810 nm wavelength under excitation at 865 nm, the authors determined the ratio between the emissions via time-resolved decoding (PbS and Tm$^{3+}$-doped UCNP emissions have different lifetimes). They demonstrated that the ratio remained constant even for increasing depth measurements, unlike in conventional ratiometric thermometers. Similarly, Yu et al. proposed a dual-excitation decoding strategy based on near-infrared (NIR) hybrid nanocomposites with and Nd$^{3+}$-doped fluoride nanocrystals to avoid the tissue absorption effects.\[^{29}\] Even though, extra care should be taken when taking in vivo temperature reading, as optical properties of tissues could be temperature dependent, in addition to wavelength dependent.\[^{10-32}\]

In this work, we show how the primary luminescent thermometer methodology\[^{13}\] can identify a spectral overlap in the region used to estimate the temperature that compromises the reliability of the temperature readout. A primary thermometer is characterized by a well-established state equation that directly relates a measurable physical quantity to the absolute temperature.\[^{1,2}\] Using an aqueous suspension of NaYF$_4$:Er$^{3+}$/Yb$^{3+}$@NaNdF$_4$@PAA nanoparticles, PAA stands for poly(acrylic acid), as a primary thermometer (at both 980 and 808 nm excitation wavelengths), it is possible to evaluate how the intruding Er$^{3+}$ $^2H_{9/2} \rightarrow ^4I_{15/2}$ transition and its overlap with the $^4S_{3/2} \rightarrow ^4I_{15/2}$ emission affects the temperature readout (measured by the intensity ratio between the $^2H_{11/2} \rightarrow ^4I_{15/2}$ and $^4S_{3/2} \rightarrow ^4I_{15/2}$ transitions) deviating the thermometric parameter from the predicted values. Supported by the primary thermometer methodology, we can determine the accurate correction of the thermometric parameter to achieve a reliable working nanothermometer. During the revision of the manuscript, we faced with a recent work by Rühl et al. that draw attention to the interference of the $^2H_{9/2} \rightarrow ^4I_{13/2}$ transition (for continuous-wave 980 laser excitation intensities above 10 W cm$^{-2}$) in the temperature determination through the intensity ratio between the $^2H_{11/2} \rightarrow ^4I_{15/2}$ and $^4S_{3/2} \rightarrow ^4I_{15/2}$ transitions in crystalline $\beta$-NaYF$_4$:Er,Yb microparticles.\[^{21}\]

2. Results and Discussion

2.1. Structural Characterization

The NaYF$_4$:Er$^{3+}$/Yb$^{3+}$@NaNdF$_4$ core–shell nanoparticles were prepared via a reported thermolysis approach with some modification.\[^{34,35}\] Transmission electron microscopy (TEM) images showed that the as-prepared NaYF$_4$:Er$^{3+}$/Yb$^{3+}$ core- and NaYF$_4$:Er$^{3+}$/Yb$^{3+}$@NaNdF$_4$ core–shell nanoparticles display spherical morphology with average sizes of 26.3 ± 2.1 and 45.9 ± 2.5 nm, respectively (Figure 1). The size difference suggests a shell thickness of about 10 nm. The shell morphology deviates from the spherical shell and is composed of epitaxially
connected nanoparticles that appear flower-like. This is because the epitaxial growth process of the NaNdF₄ shell onto the NaYF₄:Yb³⁺/Er³⁺ nanocrystal is mediated by the growth of small Nd³⁺ on the core nanocrystal surface first, which was then gradually converted into NaNdF₄ nanoparticles that further fuses into the shell.[36] The Yb³⁺ and Er³⁺ dopant concentrations in the NaYF₄:Yb³⁺/Er³⁺ core were set to be 20% and 2%, respectively, whereas the Nd³⁺ dopant concentration in the NaNdF₄ shell was 100%.

To prepare the aqueous dispersion, PAA (MW = 1800) was used to replace the pristine ligand of oleic acid (OA) on the surface of the as-prepared NaYF₄:Er³⁺/Yb³⁺@NaNdF₄ core–shell nanoparticles following a procedure previously reported by some of us.[37] Thus, the produced nanoparticles present a multiple core–shell design, where the upconverting NaYF₄:Er³⁺/Yb³⁺ core is surrounded by an inner active inorganic shell of NaNdF₄ and an outer organic shell based on PAA. These nanoparticles are dispersed in an aqueous solution at a mass concentration of 6.25 mg mL⁻¹ (4.0 × 10⁻⁹ M). This suspension is hereafter called nanofluid.

The X-ray diffraction (XRD) patterns of the parent core and core–shell nanocrystals showed a crystallographic phase of pure hexagonal structure (Figure S1, Supporting Information). The pattern of the core nanocrystals well matched the standard pattern of hexagonal NaYF₄ (JCPDS 16-0334), while that of the core–shell nanocrystals was in accordance with the standard pattern of the hexagonal NaNdF₄ (JCPDS 35-1367). The observation of the latter accordance is reasonable as the shell of NaNdF₄ takes up about 90.5% volume of the core–shell nanocrystals.

### 2.2. Optical Properties

Figure 2 shows the absorption spectrum of the nanofluid showing the Er³⁺ transitions between the ground (⁴I₁₅/₂) and the upper energy levels (²H₁₁/₂ + ⁴H₁₃/₂, ⁴I₀/₂, and ⁴I₁₁/₂), the Nd³⁺ ones between the ground (⁴I₀/₂) and the upper levels (²F₇/₂ + ²D₃/₂ + ⁴D₇/₂, ⁴D₇/₂, ⁴G₅/₂, ⁴G₇/₂, ²F₇/₂, ⁴F₉/₂, ²H₉/₂, and ⁴F₇/₂). The ²F₇/₂ + ²F₅/₂ Yb³⁺ transition is not discernible. As a few energy levels of Er³⁺ and Nd³⁺ intersect, all the possible transitions are shown in Figure 2.[38] The effective molar extinction coefficients (ε_{UCNP}) at 808 and 980 nm are calculated using Equation S16, Supporting Information, and the respective absorbance values are shown in Figure 2. ε_{UCNP}(808) = (1.0 ± 0.2) × 10⁶ M⁻¹ cm⁻¹ and ε_{UCNP}(808) = (2.9 ± 0.5) × 10⁶ M⁻¹ cm⁻¹. These values are within the reported molar extinction coefficients for Ln³⁺-based core–shell UCNPs (8.9 × 10⁵–1.8 × 10⁸ M⁻¹ cm⁻¹).[39,40]

The emission quantum yield (Φ) of the nanofluid upon 808 nm excitation (P₀ = 533 ± 5 W cm⁻²) is (1.4 ± 0.1) × 10⁻⁹%, for downshifting, and (1.0 ± 0.1) × 10⁻⁹%, for upconversion. Under 980 nm excitation, Φ = (3.8 ± 0.4) × 10⁻⁶, measured with a laser power density value (P₀ = 1128 ± 4 W cm⁻²) corresponding to the saturation regime. Contrary to the emission
quantum yield of downshifting transitions, which typically does not exhibit a dependence with laser power density, photon upconversion, as a nonlinear process, shows an emission quantum yield highly dependent on the excitation power density below a certain threshold value, dependent on the UCNPs.\(^\text{[41]}\) Thus, the study of the emission intensity as a function of the excitation power is important to determine the onset of the saturation regime corresponding to the maximum value of the emission quantum yield.\(^\text{[44-46]}\) Reporting the quantum yield measured on the saturation regime contributes to easier comparability of the performance of the upconverting phosphors. Several studies, however, have shown that quantum yield also depends on the measuring system, synthesis conditions, size of the host material, dopant concentration, and solvent,\(^\text{[44,45,47,48]}\) justifying, hence, the large range of reported quantum yield values for upconverting nanoparticles (0.005–10%).\(^\text{[69-72]}\)\(^\text{[46]}\) These different factors preclude a direct comparison of the emission quantum yield with other reported UCNPs.\(^\text{[55]}\)

Brightness (B), defined as the fluorescence output per fluorophore, is an important figure of merit of luminescent materials and it is determined by:\(^\text{[57]}\)

\[
B(\lambda) = \phi(\lambda) \times \varepsilon(\lambda)
\] (1)

The nanofluid showed a maximum brightness of \(38 \pm 8 \text{ M}^{-1}\text{cm}^{-1}\) at 980 nm, \(P_D = 1125 \pm 4 \text{ Wcm}^{-2}\), and \(2.9 \pm 0.6 \text{ M}^{-1}\text{cm}^{-1}\) at 808 nm, \(P_D = 533 \pm 5 \text{ Wcm}^{-2}\). Although brightness, as defined in Equation (1), is a commonly reported figure for downshifting materials,\(^\text{[58-62]}\) it is not common for upconverting materials. To enable a comparison with the literature, an alternative definition will be considered:\(^\text{[46,63]}\)

\[
B(\lambda) = \sigma_{\text{UCNP}}(\lambda) \times \phi(\lambda)
\] (2)

where \(\sigma_{\text{UCNP}}\) is the effective absorption cross-section, determined using Equation S17, Supporting Information. According to Equation (2), \(B(980) = (1.5 \pm 0.3) \times 10^{-19}\) and \(B(808) = (1.1 \pm 0.2) \times 10^{-20} \text{cm}^2\). In the same way as the quantum yield, the brightness is also affected by several experimental conditions rendering the comparison with other works difficult. Table S3, Supporting Information, however, compares the brightness of the NaYF\(_4\):Er\(^{3+}\)/Yb\(^{3+}\) @NaNdF\(_4\)@PAA nanoparticles with those of similar core–shell upconverting nanoparticles showing that despite higher absorption cross-sections, the lower quantum yields are responsible for lower brightness values.

### 2.3. Primary Luminescent Thermometer Characterization

So far, only a few primary luminescent thermometers have been reported.\(^\text{[8,13,64-69]}\) Except for the semiconductor nanoparticles, that are based on the temperature-dependent emission peak position (Varshni’s Law),\(^\text{[8,64]}\) all these primary thermometers are based on the intensity ratio between two thermally coupled levels (Boltzmann statistics), such as, \(I_2/F_0\) and \(I_2/F_0\) of Eu\(^{3+}\),\(^\text{[62]}\) \(D_2\) of Tb\(^{3+}\) and the first excited triplet of ifac (tfac = 1,1,1-trifluoro-2,4-pentanedione) ligand,\(^\text{[66]}\) and \(4^3I_{11/2}\) and \(4^3S_{3/2}\) of Er\(^{3+}\).\(^\text{[31,67-69]}\) In 2017, Balabhadra et al. proposed a straightforward method to predict the temperature calibration curve of any upconverting thermometer based on two thermally coupled electronic levels independently of the medium, using Yb\(^{3+}\)/Er\(^{3+}\)-doped SrF\(_2\) nanoparticles as an illustrative example. The \(4^3I_{11/2} \rightarrow 4^1I_{15/2}\) \((I_{11})\) and \(4^3S_{3/2} \rightarrow 4^1I_{15/2}\) \((I_{15})\) emission bands intensities allowed to calculate the absolute temperature, \(T\), by:\(^\text{[33]}\)

\[
\frac{1}{T} = \frac{1}{T_0} - \frac{k_B}{\Delta E} \ln \frac{\Delta}{\Delta_0}
\] (3)

where \(k_B\) is the Boltzmann constant, \(\Delta E\) is the energy gap between the barycenters of the \(4^3I_{11/2}\) and \(4^3S_{3/2}\) levels, and \(\Delta = I_{11}/I_{15}\) is the thermometric parameter with \(\Delta_0\) being the value at the temperature \(T_0\) (see Supporting Information for the calculation of \(\Delta E\) and \(\Delta_0\)).

**Figure 3** shows the laser power density-dependent normalized emission spectra at 980 and 808 nm excitation, respectively. It is possible to identify the \(4^3I_{11/2} \rightarrow 4^1I_{15/2}\) and \(4^3S_{3/2} \rightarrow 4^1I_{15/2}\) transitions at both excitation wavelengths. However, we observe a band at 557 nm under 980 nm excitation that is absent in the emission spectra upon 808 nm irradiation. This band corresponds to the \(2H_{9/2} \rightarrow 4^1I_{13/2}\) transition of Er\(^{3+}\), which arises after the \(2H_{9/2}\) population via a three-photon absorption process. **Figure 4** shows the laser power density-dependent normalized emission spectra of NaYF\(_4\):Er\(^{3+}\)/Yb\(^{3+}\) @NaNdF\(_4\)@PAA suspension upon 980 and 808 nm laser excitations, respectively. The laser
power density set down the initial nanofluid temperature that is further incremented by a homemade Peltier system (see Experimental Section). In addition to the nanoparticle photothermal conversion (induced by the Yb\(^{3+}\) and Nd\(^{3+}\) absorptions, at 980 and 808 nm, respectively) the water absorption contributes to the initial nanofluid temperature when the nanofluid is irradiated at 980 nm (the contribution of the water absorption at 808 nm is minor, \(\approx 1.5\) K for \(P_0 = 179.5 \pm 0.5\) W cm\(^{-2}\) (Figure S5, Supporting Information). The power density values used in the emission spectra of Figure 5a,b, 71.3 \pm 0.2 W cm\(^{-2}\) (980 nm) and 179.5 \pm 0.5 W cm\(^{-2}\) (808 nm), were chosen to illustrate the initial laser-induced temperature increment for the two excitations, \(4.0 \pm 0.5\) K for 980 nm, in accordance with previous results in pure water\(^{[73]}\) and \(\approx 18\) K for 808 nm excitation. We should note that the determination of the photothermal conversion of the nanoparticles for both excitations and at distinct laser power densities are out of the scope of this work.

In what follows, we will demonstrate that the NaYF\(_4\):Er\(^{3+}\)/Yb\(^{3+}\)@NaNdF\(_4@PAA\) nanofluid behaves as a primary luminescent thermometer for both 980 and 808 nm excitations. The \(\Delta\) parameter is calculated by the usual way considering the ratio between the integrated areas of the \(I_H (511–533\) nm) and \(I_S (533–570\) nm), as shown in Figure 5c. Substituting the corresponding determined parameters for each excitation (\(\Delta_0, T_0, \Delta E\), see Supporting Information) in Equation (3), we can calculate the absolute temperature value and compare it with the measured one (using the thermocouple immersed in the suspension). While at 808 nm excitation, the calculated and measured temperatures are in very good agreement (Figure 5c, red circles), at 980 nm there is an evident and expected divergence (Figure 5c, black squares) as the \(\Delta\) calculation overlooking the presence of the overlapped \(^2\!H_{9/2} \rightarrow ^4\!I_{13/2}\) band, leading to a temperature miscalculation. However, and as shown in Figure 5c (blue squares), correcting \(I_S\) from the interference of the \(^2\!H_{9/2} \rightarrow ^4\!I_{13/2}\) transition, to account for only the emissions of the two thermally coupled levels (\(^2\!H_{11/2}\) and \(^2\!S_{3/2}\)) the calculated temperature matches the measured one demonstrating that the NaYF\(_4\):Er\(^{3+}\)/Yb\(^{3+}\)@NaNdF\(_4@PAA\) nanofluid works as a primary thermometer under both 980 and 808 nm excitations (Figure 5d).

The most common figures of merit used to compare the performance of luminescent thermometers are the relative thermal sensitivity, \(S_r\), and the temperature uncertainty \(\delta T\) determined by\(^{[3,4,74]}\)

\[
S_r = \frac{1}{\Delta} \frac{\partial \Delta}{\partial T} = \frac{\Delta E}{k_B T^2}
\]

and
\[
\delta T = \frac{1}{S_t} \frac{\delta \Delta}{\Delta}
\]  

(5)

where \(\delta \Delta\) is the uncertainty in the determination of \(\Delta\) (Equation S20 and S21, Supporting Information).

**Figure 6** shows the primary thermometer performance in the 304 – 321 K (980 nm) and 318 – 327 K (808 nm) ranges. For 980 nm excitation, the thermometer exhibits a maximum \(S_t\) value of 1.1 ± 0.1% K\(^{-1}\) (304.1 K) and a \(\delta T\) of 0.08 – 0.09 K (304 – 321 K), while for 808 nm excitation the maximum \(S_t\) is 1.0 ± 0.1% K\(^{-1}\) (318.0 K) and \(\delta T\) is 0.28 – 0.30 K (318 – 327 K). As expected, \(S_t\) follows the same tendency for both excitations, as it is only dependent on \(\Delta\), which is independent of the excitation. Moreover, it shows a very similar \(S_t\) compared with other \(\text{Er}^{3+}/\text{Yb}^{3+}\)-based thermometers [1.0 – 1.3% K\(^{-1}\)].\(^{33,67,69}\) As it is dependent on \(S_t\) and \(\delta \Delta/\Delta\), \(\delta T\) was estimated for each excitation and temperature, it is higher at 808 nm, due to the contribution of \(\delta \Delta/\Delta\). The values are within the typical range reported for other \(\text{Er}^{3+}/\text{Yb}^{3+}\)-based thermometers [0.15 – 0.45 K].\(^{33,67,69}\)

### 3. Conclusion

In this work, we proved that the \(\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}@\text{NaNdF}_4@\text{PAA}\) nanofluid works as primary thermometers upon 980 and 808 nm excitations with relative thermal sensitivities and temperature uncertainty around 1.0% K\(^{-1}\) and 0.1 – 0.3 K, respectively, which is within the typical values reported for ratio-metric luminescent thermometers. To the best of our knowledge, this is the first example reporting a primary thermometer operating under two distinct wavelength excitations. Primary thermometers benefit from the intrinsic advantages of the methodology,\(^{11}\) particularly, the avoidance of repeating and time-consuming calibrations whenever the working medium is changed and has also potential applications in media where the calibration is impossible, such as intracellular temperature measurements. Moreover, we demonstrate how this concept is useful to detect spectral interferences on the \(\text{Er}^{3+}\) \(^{2}H_{11/2} \rightarrow ^{4}I_{15/2}\) and \(^{4}S_{3/2} \rightarrow ^{4}I_{15/2}\) transitions used for the temperature readout, as, for instance, is the case of the interference of the intruding \(^{2}H_{9/2} \rightarrow ^{4}I_{11/2}\) emission, and how its correction will subsequently improve the reliability of the temperature readout.
4. Experimental Section

Yttrium chloride hexahydrate (YCl₃·6H₂O, 99.99%), ytterbium chloride hexahydrate (YbCl₃·6H₂O, 99.99%), erbiunm chloride hexahydrate (ErCl₃·6H₂O, 99.99%), and neodymium oxide (Nd₂O₃, 99.99%) were purchased from Aladdin. All other chemicals were purchased from Sigma-Aldrich and used as received.

**Synthesis of Core Nanoparticles of NaYF₄:Er³⁺/Yb³⁺:** About 0.78 mmol YCl₃·6H₂O, 0.2 mmol YbCl₃·6H₂O, and 0.02 mmol ErCl₃·6H₂O were added to a 250 mL flask containing 6 mL of OA and 15 mL of 1-octadecene (ODE) and heated to 150°C under argon protection for 60 min. After the mixture solution cools down to room temperature, 10 mL methanol solution containing 4 mmol NH₄F and 2.5 mmol NaOH was slowly added and stirred for 30 min. The solution was heated to 100°C for 30 min to degas methanol and water. Then, the reaction solution was heated to 300°C for 20 min and maintained at this temperature for 60 min. The resulting solution was cooled down and centrifuged with excess addition of ethanol. The final products are collected in 10 mL hexane.

**Synthesis of Core–Shell Nanoparticles of NaYF₄:Er³⁺/Yb³⁺@NaNdF₄:** About 0.5 mmol Nd₂O₃ was dissolved in 10 mL of 50% trifluoroacetic acid with refluxing at 90°C until the mixture becomes a transparent solution. Then the solution was evaporated under flowing argon at 70°C to prepare the Nd³⁺ trifluoroacetate precursor, Nd(CF₃COO)₃. The core nanoparticles of NaYF₄:Er³⁺/Yb³⁺ (0.5 mmol), 2 mmol sodium trifluoroacetate, 10 mL OA, and 10 mL ODE were all loaded into a 250 mL flask. The reaction vessel was then heated to 120°C to remove hexane and water and subsequently heated to 320°C under argon for 45 min. The resultant core–shell nanoparticles were collected by centrifugation, washed with ethanol, and dispersed in 10 mL hexane for further use.

**Preparation of PAA-Coated NaYF₄:Er³⁺/Yb³⁺@NaNdF₄ Core–Shell Nanoparticles:** The OA ligand of the as-prepared core–shell nanoparticles (2 mL) was mixed with N-hydroxysulfo succinimide sodium salt (NOBSf) (0.01 m) in dimethylformamide (DMF). The mixture solution was shaken for 10 min and collected via centrifugation. The precipitated nanoparticles were redispersed in DMF (5 mL) and washed with toluene (5 mL) and hexane (5 mL). The core–shell nanoparticles with the ionic BF₄⁻ ligand were mixed with 0.2 g PAA in 5 mL DMF. The mixture solution was heated at 80°C for 30 min and cooled down to room temperature. After centrifuging with acetone, the aqueous solution of PAA-coated core–shell nanoparticles (the nanofluid) was obtained.

**Transmission Electron Microscopy:** The obtained core–shell nanoparticles of NaYF₄:Er³⁺/Yb³⁺@NaNdF₄ was diluted 10 times with hexane and then 10 μL nanoparticles were dropped on the carbon support films. The TEM images were recorded on a JEOL JEM-2010 microscope at an acceleration voltage of 200 kV.

**X-Ray Diffraction:** Powder XRD experiments were conducted on a Rigaku D/Max 2550 diffractometer with Cu Kα radiation (λ = 1.5418 Å) from 10° to 80° at a scanning rate of 4° min⁻¹.

**UV/Visible–NIR Absorption Spectroscopy:** Visible and NIR absorption spectra were recorded at room temperature, using a dual-beam spectrometer (Lambda 950, Perkin-Elmer) with a 150 mm diameter Spectralon integrating sphere over the range 250–1250 nm with a resolution of 1.0 nm. The baseline was recorded with two 10 nm path–length quartz cuvettes (two polished windows) containing the reference fluid, H₂O. The molar extinction coefficient was estimated from the Beer–Lambert law.

**Quantum Yield Measurements:** The absolute emission quantum yields were measured using a Quantaurus-QY Plus UV/NIR absolute photoluminescent quantum yield spectrometer (C13534-31, Hamamatsu), an integrating sphere as sample chamber, and two detectors (BT-CCD, 300–950 nm, and InGaAs, 900–1650 nm). External laser diodes (FC–980–SW and FC–808–5W, CNI Lasers) were used for 980 and 808 nm excitation, respectively. Three measurements were made for each sample so that the average value is reported. The method is accurate within 10%, according to the manufacturer.

**Photoluminescence and Temperature-Dependent Measurements:** The nanofluid was placed in a quartz cuvette (104F, 0.1 K accuracy). To avoid direct exposure to the laser, the thermocouple was placed near the laser spot away from its limits. For 980 nm excitation, a pulsed laser (BrixX 980–1000 HD, Omicron Lase) at a frequency of 1.5 MHz, was focused through an optical lens (7.5 cm focal distance) to enhance P₀ from 29.4 ± 0.1 to 112.3 ± 0.3 W cm⁻² (Figure S8 and S9, Supporting Information). For 808 nm excitation, a continuous wave laser (LC Model No. DL808–3W–T, CrystaLaser) was focused through the same optical lens with P₀ ranging from 73.8 ± 0.2 to 267.1 ± 0.7 W cm⁻² (Figure S8 and S9, Supporting Information). To enable the power variation on the 808 nm laser neutral density filters (NE02B–B, NE05B–B, and NET0B–B, Thorlabs) were placed between the laser beam and the sample (Supporting Information for further details).

For temperature-dependent measurements, a homemade Peltier (0.1 K sensitivity) was placed in thermal contact with the cuvette. First, we turned...
on the excitation laser (980 or 808 nm) at a fixed $P_D$ inducing a temperature increment in the nanofluid. Then, we set the Peltier for a fixed temperature higher than the increment induced by the laser excitation. The emission spectra and thermocouple reading are recorded after the nanofluid reached the set-point temperature ($t > 800 \text{s}$).

**Transition Areas Calculation:** The areas corresponding to the $^4I_{11/2} \rightarrow ^4I_{15/2}$ ($I_S$) and $^4S_{3/2} \rightarrow ^4I_{15/2}$ ($I_H$) transitions were estimated using two different approaches, according to the excitation wavelength. Upon 980 nm excitation, the $^4H_{9/2} \rightarrow ^4I_{11/2}$ transition overlaps with $^4S_{3/2} \rightarrow ^4I_{15/2}$ and, thus, a spectral deconvolution procedure is mandatory to calculate the integrated area of the latter transition and the corresponding thermometric parameter. On the contrary, there is no sign of the $^4H_{9/2} \rightarrow ^4I_{13/2}$ transition upon 808 nm excitation, the integration of $I_H$ and $I_S$ was carried out over the wavelength ranges 511–533 nm ($I_H$) and 533–570 nm ($I_S$). Taking the average spectra of the total measurements made for each temperature (or $P_D$) a baseline subtraction was applied to remove the spectrometer electric noise. To perform the deconvolution, the signal of each average spectrum was first converted from wavelength to energy units applying the Jacobian transformation\(^\text{[75]}\) (details in Supporting Information). Then, the [17 500, 19 500] cm$^{-1}$ spectral region was fitted using the multiple peak fit routine of the OriginLab software. Good fits to the experimental data ($R^2 > 0.99$) were obtained with a minimum number of Gaussian functions equal to seven (two, three, and two functions for the $^4H_{9/2} \rightarrow ^4I_{13/2}$, $^4S_{3/2} \rightarrow ^4I_{15/2}$, and $^4H_{11/2} \rightarrow ^4I_{13/2}$ transitions, respectively). $I_H$ and $I_S$ are estimated by the sum of the fitted areas of the corresponding Gaussians of the $^4S_{3/2} \rightarrow ^4I_{15/2}$ and $^4H_{11/2} \rightarrow ^4I_{13/2}$ transitions, respectively (Figure S6, Supporting Information). The multiparametric Gaussian fits were carried out considering error weighting in the $I(E)$ values and $\partial I/E$ was estimated in each average spectrum using the SNR values on the readout fluctuations of the baseline (details in Supporting Information).

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

Research data are not shared.

**Keywords**

lanthanide-based upconversion nanoparticles, luminescent nanothermometry, nanothermometry reliability, primary thermometers

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