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Multifunctional Tm³⁺/Yb³⁺:Na₅Y (MoO₄)₄ nanocrystals for simultaneous luminescent nanothermometry, photothermal therapy and deep bioimaging in the NIR-I window

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In this study, Tm³⁺/Yb³⁺ co-doped Na₅Y(MoO₄)₄ (NYMO) nanoparticles were successfully synthesized via the sol–gel method, and their structural, morphological, upconversion (UC) luminescence, and photothermal properties were comprehensively investigated. Upon 975 nm near-infrared (NIR) laser excitation, the NYMO nanoparticles exhibited two prominent UC emission bands at 477 nm and 796 nm, corresponding to the ¹G₄ → ³F₆ and ³H₄ → ³H₆ transitions of Tm³⁺ ions, respectively. The fluorescence intensity ratio (FIR) between these emissions enabled precise optical temperature sensing; at 298 K, the highest relative sensitivity is 2.05% K⁻¹, and at 388 K, the highest absolute sensitivity is 0.53% K⁻¹. The FIR value increased with excitation power, indicating a rise in internal temperature due to photothermal effects. This temperature increase is attributed to efficient NIR absorption and nonradiative relaxation processes, enhanced by electron–phonon interactions at elevated temperatures. Furthermore, the nanoparticles demonstrated significant NIR emission penetration into biological tissue up to a depth of 4 mm, confirming their suitability for deep-tissue imaging. Operating within the optically transparent biological window, the Tm³⁺/Yb³⁺-doped NYMO nanoparticles exhibit multifunctional capabilities, combining optical thermometry, photothermal conversion, and *in vivo* bioimaging. These results highlight NYMO nanoparticles as promising candidates for luminescent nanothermometers and photothermal agents in biomedical applications.

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1. Introduction

Currently, upconversion luminescence is recognized as a novel process in which two or more low-energy photons are sequentially absorbed, leading to the emission of a photon with higher energy.^{1,2} The trivalent rare earth (RE³⁺) ions exhibit a plethora of ladder-like 4f energy levels, creating optimal physical conditions for upconversion (UC) to transpire. The RE-doped UC materials exhibit several exceptional characteristics. These include a large anti-Stokes shift, precise emission bands, extended luminescence lifetimes and superior photostability, which make them promising materials in various applications

such as lasers, illumination, displays, anti-counterfeiting and sensors.^{3,4} Upconversion (UC) using a near-infrared (NIR) excitation source has attracted significant attention in the biomedical field due to its favorable characteristics deep penetration into biological tissues and minimal autofluorescence.^{5–7} In parallel, photothermal therapy (PTT) is a therapeutic approach that converts absorbed light energy into heat *via* photothermal therapeutic agents (PTAs), enabling efficient destruction of cancer cells or pathogens through thermal ablation.^{8,9} The RE upconversion device consists of a host matrix and selected luminescent centers of RE ions, such as Tm³⁺ and Yb³⁺, for the generation of the desired emission. Sensitizers such as Yb³⁺ or Nd³⁺ are typically used to enhance absorption and improve lasing intensity. Moreover, optimal candidates for upconversion are host materials with low phonon energy and sufficient asymmetric lattice sites to allow substitution of lanthanide ions for luminescence.^{10,11} Materials doped with RE³⁺ seem to be a promising alternative for creating optically active materials since the RE³⁺ ions have thermally linked emission levels.¹² It means that the relative ion population of these planes, as well as their emission, varies with the temperature of the active substance.^{13,14} Several optical

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parameters can be calibrated for studying the RE³⁺ emission response as a function of temperature, including the relative intensities between two thermalized emission bands, commonly known as the fluorescence intensity ratio (FIR), which is the most commonly used technique for calibrating an optical sensor.^{15,16} From a practical point of view, not all RE³⁺ ions can be used to calibrate optical responses using the FIR technique.¹⁷

Among lanthanide elements, Yb³⁺ and Tm³⁺ are considered the most efficient sensitizers, exhibiting strong absorption cross-sections at an excitation wavelength of 975 nm, close to the near-infrared (NIR) band. The order distribution of Yb³⁺ between ²F_{7/2} and ²F_{5/2} is likewise resonant with that of other regularly employed UC lanthanides, which contain only a 4F order of the ²F_{5/2} single excited state.^{18,19} Efficient energy conversion is promoted by the f–f transitions of elemental ions (Eu³⁺, Tm³⁺ and Ho³⁺). Therefore, Tm³⁺ is a suitable sensitizer for *in vivo* experiments. It may be utilized as an excitation light source, therefore avoiding the thermal damage to biological tissues caused by the 980 nm laser. Yb³⁺ and Tm³⁺ are the most often employed ions for sensitizer conversion owing to their deep tissue penetration ability.^{20–22} The activator is responsible for releasing the light from the luminescent substance incorporated in the host matrix. The activator stimulates follow-up and then transitions to a higher energy level, hence minimizing the possibility of non-radiative energy relaxation. The energy dissipation associated with cross-relaxation may be reduced by altering the doping ratios of the various activators to regulate light emission.²³ When excited by a 975 nm laser, the UC emission of a typical activator Tm³⁺ is typically in the blue visible range, which is a relatively lower penetration depth compared to red and NIR light due to absorption and scattering by biological tissues. This implies that red and NIR emissions peak at 695 nm and 800 nm of Tm³⁺ inside the “optical window” are more suited for deep tissue imaging than those of the visible UC emissions of Er³⁺ and Ho³⁺ ions.²⁴ However, Tm³⁺ ions often display the dominating blue fluorescence that peaks at 485 nm in most host materials.^{25,26} It is required to create a technique for adjusting the upconversion emission of Tm³⁺-doped UC luminous materials to increase the red and NIR emission for possible biological applications. Generally, UC efficiency for blue emission is much lower than that of green and red. The absorption of 975 nm photons by Tm³⁺ ions is low. However, the Yb³⁺ ion is an excellent sensitizer, effectively absorbing pump light and transferring absorbed energy to coactivators.

In this work, we detail the synthesis, structural characterization, and in-depth optical evaluation of Na₅Y(MoO₄)₄ phosphors co-doped with Yb³⁺ and Tm³⁺ ions. The doping levels (0.01Tm³⁺/0.15Yb³⁺) were meticulously optimized through preliminary studies to achieve the maximum emission intensity at 975 nm near-infrared (NIR) excitation. We thoroughly examined the effects of these dopants on upconversion luminescence, temperature-dependent fluorescence properties, and photothermal conversion efficiency. Particular emphasis was placed on assessing the material's suitability for multifunctional applications, including high-sensitivity optical thermometry using fluorescence intensity ratio (FIR) techniques,

effective NIR-driven photothermal conversion, and deep-tissue *in vivo* imaging, capitalizing on its emission within the biological transparency window.

2. Experimental setup

2.1. Synthesis

The NYMO compounds co-doped with Tm³⁺/Yb³⁺ were synthesized using the Pechini sol–gel technique.²⁷ The nanoluminescent materials were prepared using several commercially available chemicals, including Y(NO₃)₃·6H₂O, (NH₄)₆Mo₇O₂₄·4H₂O, NaNO₃, NaOH, Tm(NO₃)₃·5H₂O, and Yb(NO₃)₃·5H₂O. To initiate the synthesis, all the precursors were combined in an Erlenmeyer flask and stirred with a magnetic stirrer at 70 °C. Citric acid was subsequently added, resulting in a color shift from green to blue. The mixture was continuously stirred and heated to 80 °C until it underwent hydrolysis, forming a sol and eventually transitioning into a gel. The gel was then calcined by annealing at 800 °C to generate the final product, which was then refined for analytical tests.

2.2. Characterization techniques

X-ray diffraction (XRD) patterns were obtained using a Bruker Advance diffractometer equipped with a Cu Kα₁ (λ = 1.5406 Å) radiation source. Measurements were conducted in the 2θ range of 5°–75° with a step size of 0.02°. The morphology of the synthesized samples was analyzed using a Zeiss Supra 55VP FEG-TEM and a Bruker XFlash 5030 detector. Temporal decay profiles were recorded using a 200 MHz LeCroy WS424 oscilloscope coupled with a Hamamatsu R928 photomultiplier tube (PMT). The system was driven by a 10 Hz EKSP/LA/NT342/3/UVE pulsed laser (OPO system, 10 ns pulse width). The temperature-dependent luminescence measurements were conducted by placing the as-prepared samples into a Linkam THMS600 heating stage. An Avantes high-resolution CCD detector was used to acquire the photoluminescence (PL) spectra at 975 nm excitation from a Spectra Physics 3900S tunable Ti:sapphire laser. Temperature-dependent emission measurements were taken at 5 K intervals in the range of 298–388 K. For deep-tissue penetration studies, the NYMO:0.01Tm³⁺/0.15Yb³⁺ nanophosphor was excited at 975 nm using the Ti:sapphire laser (3900S, Spectra Physics) pumped by a Millennia Prime laser (Millenia 15sJSPG). The sub-tissue penetration depths and spatial resolutions achievable with the nanoparticles were investigated using a double-beam fluorescence microscope.

3. Results and discussion

3.1. Crystal structure and morphological characterization

Fig. S1 shows the X-ray diffraction (XRD) patterns for the NYMO matrix when codoped with Tm³⁺/Yb³⁺ ions. The diffraction peaks obtained from all samples closely matched the standard positions identified for the NYMO standard chart (JCPDS #82-2368),²⁸ which confirms that doping with rare earth ions did not alter their phase structure. This indicates that the synthesized phosphors have retained a single-phase composition. The



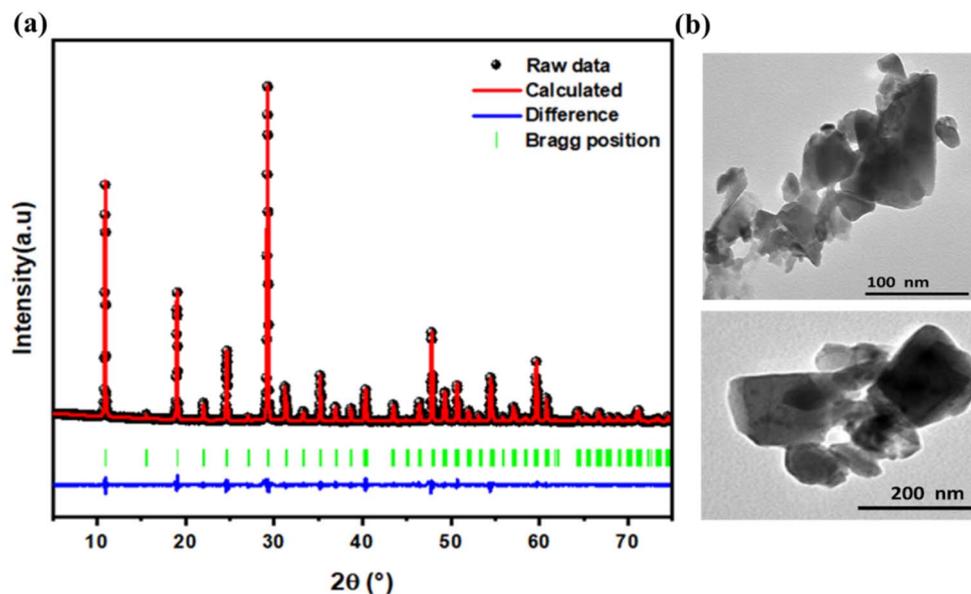


Fig. 1 (a) Rietveld refinement of XRD patterns. (b) TEM images for the NYMO:0.01Tm³⁺/0.15Yb³⁺ sample.

Rietveld structure refinement of the NYMO:0.01Tm³⁺/0.15Yb³⁺ phosphor, conducted using the FullProf Suite software, is presented in Fig. 1a. We performed the Rietveld refinement analysis on Tm³⁺/Yb³⁺-co-doped NYMO samples to enhance visualization of the crystal structure. The refinement results, obtained with the FullProf Suite, demonstrate a strong agreement between the calculated and experimentally observed diffraction profiles.

Table S1 presents the structural parameters obtained from Rietveld refinement of the samples, which were used to determine their crystal structures. Fig. 1a shows the diffraction patterns of the sample, which were used to confirm the phase purity of the synthesized materials. The sample was found to be single-phase, as no additional diffraction peaks were observed. This indicates that the incorporation of Tm³⁺ and Yb³⁺ ions did not result in the formation of secondary phases. While this observation supports the successful incorporation of dopant ions into the NYMO lattice, definitive evidence of their substitution for Y³⁺ ions requires further structural or spectroscopic analysis. To validate this substitution, the percentage difference in the ionic radius (D_r) between Tm³⁺, Yb³⁺, and the host Y³⁺ ion was calculated:²⁹

$$D_r(\%) = \frac{R_s(\text{CN}) - R_d(\text{CN})}{R_s(\text{CN})} \times 100\% \quad (1)$$

Here, CN is the coordination number, R_s (CN) is the radius of the cations in the framework, and R_d (CN) is the radius of the dopant. The ionic radius difference (D_r) should not exceed 30%. The ionic radii of Y³⁺, Yb³⁺ and Tm³⁺ are 0.9 Å, 0.985 Å and 0.994 Å, respectively. The coordination number of both ions is 8. The D_r values in NYMO activated with Tm³⁺/Yb³⁺ were found to be 9.44% and 10.44%, indicating that both Tm³⁺ and Yb³⁺ successfully substitute the lattice positions of the Y³⁺ sites.³⁰

The morphology of the samples co-doped with Tm³⁺/Yb³⁺ in NYMO phosphors was observed by transmission electron

microscopy (TEM), as shown in Fig. 1b. The images reveal noticeable grain aggregation, with particle sizes predominantly ranging from 100 to 200 nm.

3.2. Optical characterization

3.2.1. Up-conversion luminescent properties. Fig. 2a shows the emission spectrum of the NYMO:0.01Tm³⁺/0.15Yb³⁺ phosphor under 975 nm excitation, from which we can observe the typical characteristic emission peaks of Tm³⁺ ions from the f-f transitions ranging from 400 to 900 nm. All the bands identified are attributed to the intra-configuration 4f-4f radiative transition of Tm³⁺: ¹G₄ → ³H₆ (477 nm) and ³H₄ → ³H₆ (796 nm).^{31,32} The excited states of Tm³⁺ (UC emitter) are mainly pumped by UC energy transfer processes when the absorbed NIR-light by Yb³⁺ ions, acting as a sensitizer, transfer their energy to the neighboring Tm³⁺.

A CIE chromaticity diagram of NYMO:0.01Tm³⁺/0.15Yb³⁺ is shown in Fig. 2b, which shows that NYMO:Tm³⁺/Yb³⁺ has a CIE coordinate of (0.2194, 0.2161) and is in the blue region, indicating that it can emit bright blue light. Moreover, from the recorded optical images, we can witness the brilliant red emission when the finished products were treated with the UV light.³³ To further study the color behavior of the created red light, the following equation was used to assess its color purity:³⁴

$$\text{CP} = \sqrt{\frac{(x - x_{\text{eei}})^2 + (y - y_{\text{ee}})^2}{(x_{\text{d}} - x_{\text{ce}})^2 + (y_{\text{d}} + y_{\text{ce}})^2}} \quad (2)$$

Here, $(x, y) = (0.2194, 0.2161)$, $(x_{\text{ee}}, y_{\text{ee}}) = (0.310, 0.316)$ and $(x_{\text{d}}, y_{\text{d}}) = (0.677, 0.322)$ are attributed to the CIE coordinates of the evaluated phosphors (NYMO: white illumination, and dominant wavelength (796 nm)).³⁵ Thus, the color purity of the emitted blue light from the developed phosphors was 93.8%, indicating that the Tm³⁺/Yb³⁺-activated NYMO phosphors can



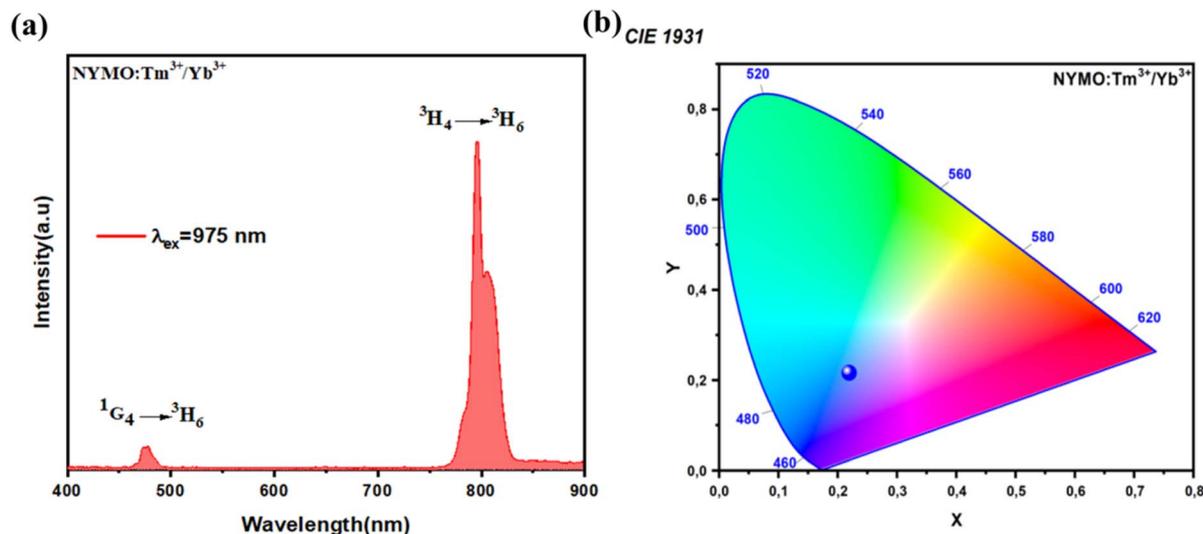


Fig. 2 (a) PL. (b) Chromaticity diagram of NYMO phosphors codoped with 0.01Tm³⁺/0.15Yb³⁺ excited at $\lambda_{\text{ex}} = 975$ nm.

produce high-quality blue light and are suitable for lighting applications.

3.2.2. Mechanisms of up conversion emission. Fig. S2a illustrates the time-dependent behavior of blue and near-infrared (NIR) upconversion (UC) emissions under pulsed 975 nm excitation. The decay curves exhibit a notable rising component, suggesting the presence of UC energy transfer processes that facilitate population of the emitting energy levels.³⁶

The influence of pump power on UC luminosity was examined at various powers. Fig. S2b shows the log-log curves derived according to the formula $I_{\text{UC}} = P^n$, where n is the number of photons needed for the UC process, P is the power at 975 nm, and I_{UC} is the emission intensity.³⁷ The formula fit indicates that the slope n values of the emission bands at 477 and 796 nm were 2.38 and 1.21, respectively. This indicates that the blue emission band at 477 nm is due to the three-photon absorption UC process, while the red emission is due to the two-photon absorption UC process.³⁸

To further comprehend the energy transfer (ET) process, the ET mechanism in NYMO:0.01Tm³⁺/0.15Yb³⁺ is presented in Fig. 3. Initially, using a 975 nm pump, Yb³⁺ ions with a higher absorption cross section are stimulated from the ²F_{7/2} state to the ²F_{5/2} state *via* ground-state absorption. These ions subsequently relax non-radiatively to the ²F_{7/2} state, delivering energy to the adjacent Tm³⁺ ions.³⁹ The energy obtained excites the Tm³⁺ from the ³H₆ state to the ³H₅ state, and this process may be defined as the ET1 process: ${}^2\text{F}_{5/2}(\text{Yb}^{3+}) + {}^3\text{H}_6(\text{Tm}^{3+}) \rightarrow {}^2\text{F}_{7/2}(\text{Yb}^{3+}) + {}^3\text{H}_5(\text{Tm}^{3+})$. At this stage, part of the non-radiative Tm³⁺ relaxes to the ³F₄ state and subsequently proceeds to absorb photons to the ³F_{2,3} states. This process is termed the ET2 process: ${}^2\text{F}_{5/2}(\text{Yb}^{3+}) + {}^3\text{F}_4(\text{Tm}^{3+}) \rightarrow {}^2\text{F}_{7/2}(\text{Yb}^{3+}) + {}^3\text{F}_{2,3}(\text{Tm}^{3+})$. It then delivers energy to the ³H₆ state in the form of a faint red glow. The other Tm³⁺ ions in the ³H₅ state continually absorb photons and pump them to the ¹G₄ state. It then relaxes to the ³F₄ state.^{40,41} The intense red light at 796 nm is generated by the continuous non-radiative relaxation of Tm³⁺

in the ³F_{2,3} states. In this process, the Tm³⁺ ions, which have relaxed to the ³H₄ state, absorb photons again and are pushed to the ¹G₄ state by the ET3 process: ${}^2\text{F}_{5/2}(\text{Yb}^{3+}) + {}^3\text{H}_4(\text{Tm}^{3+}) \rightarrow {}^2\text{F}_{7/2}(\text{Yb}^{3+}) + {}^1\text{G}_4(\text{Tm}^{3+})$. It then emits energy back to the ³H₆ state in a nonradiative relaxation mode, resulting in blue light at 477 nm.⁴²

3.3. Temperature-dependent UC property of NYMO:Tm³⁺/Yb³⁺

The material investigated as an optical temperature sensor was evaluated by analyzing the temperature-dependent luminescence spectra. The results are illustrated in Fig. 4a. In order to determine the thermometric parameters, we studied the following two transitions of Tm³⁺ ions. Following the UC

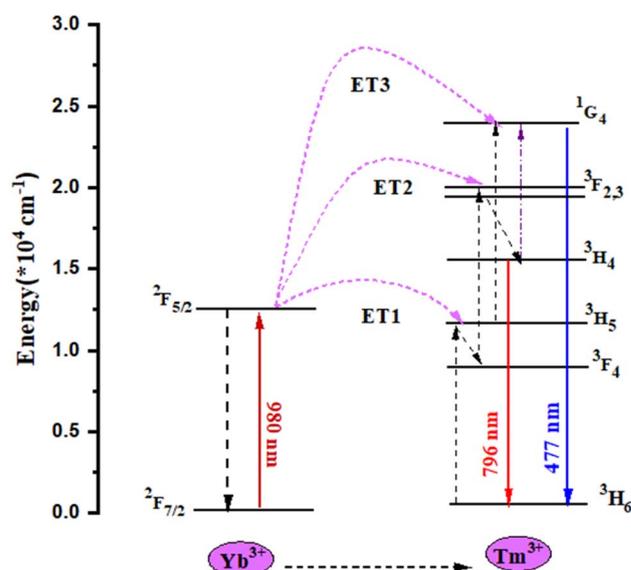


Fig. 3 Proposed energy transfer mechanism of NYMO:0.01Tm³⁺/0.15Yb³⁺.



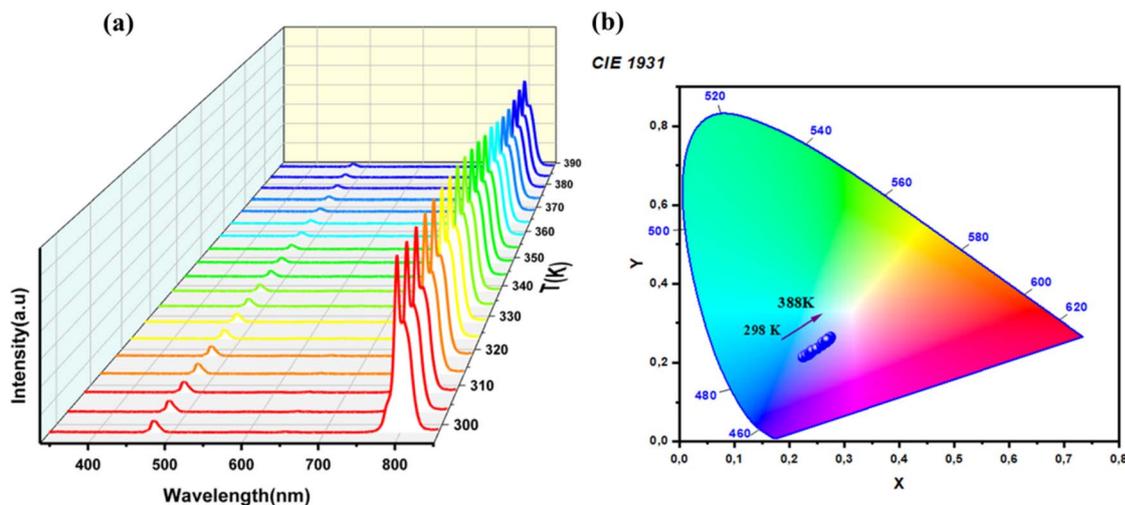


Fig. 4 (a) UC emission spectra. (b) CIE chromaticity diagram of Yb³⁺/Tm³⁺-doped NYMO under 975 nm excitation at various temperatures from 298 to 388 K.

emission studies of NYMO:0.01Tm³⁺/0.15Yb³⁺ samples, the Yb³⁺-codoped samples were investigated for UC emission. Since Yb³⁺, when excited at 975 nm, is effective in producing the UC emission from Tm³⁺ ions, it was chosen as a sensitizer.^{43,44}

As the temperature increases from 298 K to 388 K, the upconversion (UC) emission intensity of the NYMO:0.01Tm³⁺/0.15Yb³⁺ nanoparticles decreases for the ¹G₄ → ³H₆ and ³H₄ → ³H₆ transitions of Tm³⁺ ions. This temperature-dependent reduction in Tm³⁺ luminescence alters the color of the NYMO luminophores under 975 nm excitation. Specifically, the emitted color shifts noticeably from blue to pink as the temperature rises from 298 K to 388 K, accompanied by a continuous decrease in brightness. This color tunability, driven by temperature control, highlights the robust stability of Tm³⁺ ions. These findings suggest that temperature can be qualitatively assessed through the observed thermal bleaching behavior, as depicted in Fig. 4b.

In order to determine the temperature-dependent UC behavior of the converted particles, the FIR (I_{796}/I_{477}) values as a function of T are shown in Fig. 5a. The blue emission band at 477 nm in the fluorescent sample corresponds to the Tm³⁺ energy level transition to ¹G₄. The ¹G₄ level and the other level (³H₄) are not TCELS, and the electronic population does not follow a Boltzmann distribution, and hence temperature cannot be calculated using this rule. Therefore, a polynomial eqn (3) with fitting constants A₁, A₂, A₃ and A₄ is utilized to fit the FIR value of non-TCELS.^{45–47} The experimental data were fitted to a straight line, yielding a good linear fit (R^2 value is 0.999).

$$\text{FIR} = A_1 + A_2 \times T + A_3 \times T^2 + A_4 \times T^3 \quad (3)$$

In practice, absolute and relative sensitivities are often used to quantify the temperature measurement behaviour of thermometers, which can be defined mathematically as follows.^{48,49}

$$S_a = \left| \frac{\delta \text{FIR}}{\delta T} \right| \quad S_r = \frac{1}{\text{FIR}} \left| \frac{\delta \text{FIR}}{\delta T} \right| \quad (4)$$

The values of S_a and S_r can be evaluated as a function of the various un-coupled energy levels. Fig. 5b shows the variations in sensitivity parameters (S_a and S_r) as a function of temperature between 298 K and 388 K. It is worthwhile to study a co-doped sample for optical thermometry because of the availability of different NTCLs with the same or different dopants, which can offer more possibilities for tuning the sensitivity of the thermometer. Moreover, Fig. 5b provides an overview of the estimated maximum value of the sensitivity parameters for each case. It shows that for the selected pair of NTCLs (796/477 nm), the NYMO sample has the highest relative sensitivity ($S_{r \text{ max}} = 2.05\% \text{ K}^{-1}$) in the physiological temperature range.

As illustrated in Fig. S3, the experimental temperature uncertainty was determined by measuring 100 spectra at 298 K under similar conditions since the sensor operation additionally depends on the temperature resolution estimate. Temperature resolution values show typically a Gaussian distribution around ambient temperature.^{50,51} In this case, the standard deviation is 0.54 K. To give a complete comparison with the previously published FIR thermometers, the thermal sensing features of different materials, including sensitivity and operating spectral range, are presented in Table 1. The sensitivity of NYMO is substantially greater than that of previously reported similar materials, suggesting that it is an excellent candidate material for luminous temperature monitoring.

To test the accuracy of the temperature measuring technique, the thermometric parameters (FIR values) were regularly measured. This was done by cycling the sample between low and high temperatures. The results are shown in Fig. S4. Repeatability (R) was defined as the average of the absolute differences between the repeated measurements.

$$R_p(100\%) = \left(1 - \frac{\max |M_i(T)_c - M(T)_c|}{\text{FIR}_c} \right) \times 100 \quad (5)$$

$M_i(T)_c$ is the measurement parameter (FIR or band centroid) in the i th cycle and $M(T)_c$ is the average value of $M(T)$ over seven cycles. The FIR values showed reversible variations in response to



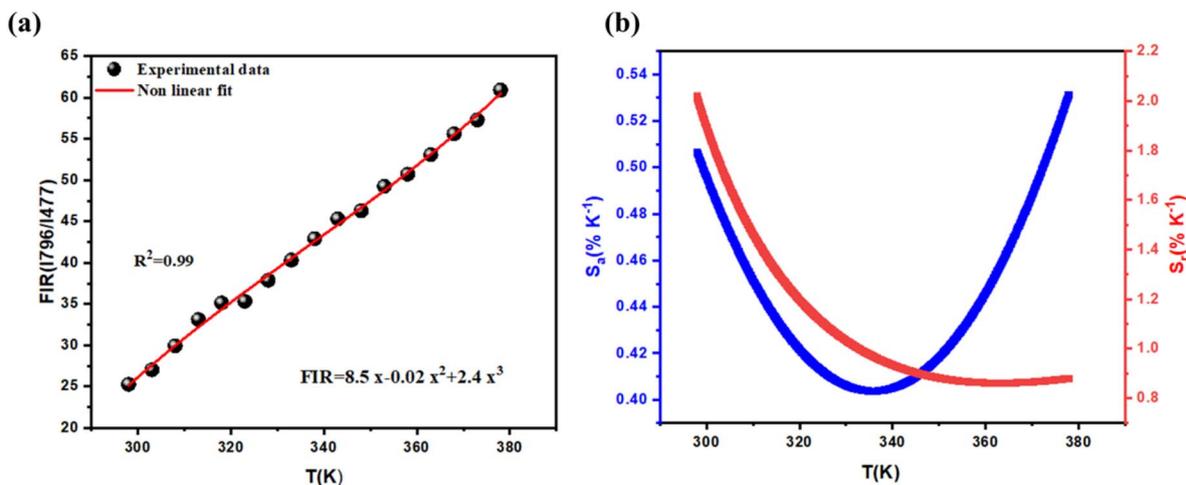


Fig. 5 (a) Experimental data and the fitted line of the FIR. (b) Curves of relative sensitivity, S_r , and absolute sensitivity, S_a , of NYMO co-doped $\text{Yb}^{3+}/\text{Tm}^{3+}$ in the temperature range of 298–388 K.

Table 1 Comparison of the sensitivity (S_r) of varied materials

Samples	Temperature range (K)	S_r max (% K^{-1})	Ref.
$\text{Tm}^{3+}:\text{Y}_2\text{O}_3$	303–753	0.35	52
$\text{Yb}^{3+}/\text{Tm}^{3+}:\text{Sr}_2\text{GdF}_7$	293–563	1.97	53
$\text{Yb}^{3+}/\text{Tm}^{3+}:\text{Y}_2\text{O}_3$	303–573	1.5	54
$\text{Yb}^{3+}/\text{Tm}^{3+}:\text{NaY}_2\text{F}_7$	307–567	1.63	55
$\text{Yb}^{3+}/\text{Tm}^{3+}:\text{GdVO}_4$	297–673	0.87	56
$\text{Yb}^{3+}/\text{Tm}^{3+}:\text{NaBiF}_4$	303–443	1.1	57
$\text{Yb}^{3+}/\text{Tm}^{3+}:\text{Y}_2\text{Ti}_2\text{O}_7$	300–400	0.87	58
$\text{Yb}^{3+}/\text{Tm}^{3+}:\text{Na}_3\text{GdV}_2\text{O}_8$	298–565	2.01	59
$\text{Yb}^{3+}/\text{Tm}^{3+}:\text{LiNbO}_3$	400–773	0.7	60
$\text{Yb}^{3+}/\text{Tm}^{3+}:\text{NLMO}$	300–650	1.16	61
$\text{Yb}^{3+}/\text{Tm}^{3+}:\text{PbF}_2$ GC	300–700	0.30	62
$\text{Yb}^{3+}/\text{Tm}^{3+}:\text{NaYF}_4$	300–510	1.53	63
$\text{Yb}^{3+}/\text{Tm}^{3+}:\text{NYMO}$	298–388	2.05	This work

temperature, with all observed FIRs above 98% throughout the tested temperatures. This result demonstrated the high reproducibility and dependability of the thermometric methods used.

3.4. Photothermal conversion performance of $\text{Tm}^{3+}/\text{Yb}^{3+}$ codoped NYMO phosphors

To evaluate the photothermal conversion performance of the NYMO:0.01 Tm^{3+} /0.15 Yb^{3+} nanophosphor under 975 nm laser excitation, upconversion (UC) emission spectra were measured across a range of excitation power densities (90.8 to 194.9 W cm^{-2}), as shown in Fig. 6a. Variations in the population distribution of the energy levels result in differing intensity changes for the $^1\text{G}_4 \rightarrow ^3\text{H}_6$ and $^3\text{H}_4 \rightarrow ^3\text{H}_6$ transitions of Tm^{3+} ions within the sample. This differential intensity variation causes a shift in the fluorescence intensity ratio (FIR), defined as I_{796}/I_{477} , with increasing excitation power density. The FIR as a function of excitation power density is plotted in Fig. 6b, revealing a gradual increase in FIR as the power density rises from 90.8 to 194.9 W cm^{-2} . This trend indicates a corresponding rise in the sample's internal temperature with higher laser power, as illustrated in

Fig. 6c. A greater change in FIR values signifies more pronounced heating of the material.^{64,65}

The temperature increase in the NYMO:0.01 Tm^{3+} /0.15 Yb^{3+} phosphor is primarily due to energy absorption by the crystal-line powder, which is then dissipated as heat *via* nonradiative processes. This thermal energy propagates from the crystal, raising the temperature of the surrounding volume. Concurrently, enhanced electron–phonon interactions further contribute to heating within the crystal, with these interactions becoming more significant at higher temperatures. These findings highlight the efficient conversion of NIR laser excitation power density into heat by the $\text{Tm}^{3+}/\text{Yb}^{3+}$ co-doped NYMO phosphor, positioning it as a promising material for photothermal therapy applications.^{66,67}

3.5. Investigation of the depth of penetration under tissue

To assess the suitability of the NYMO:0.01 Tm^{3+} /0.15 Yb^{3+} nanophosphor for biological experiments, a vertical setup was designed to excite the sample using a method similar to those reported in the literature.^{68–70}

Using the experimental setup schematically illustrated in Fig. 7a and described in detail in the Experimental section, we investigated the optical attenuation experienced by the two emission bands of NYMO:0.01 Tm^{3+} /0.15 Yb^{3+} nanoparticles (NPs). This configuration enabled us to quantify the progressive attenuation of Tm^{3+} luminescence as it propagates through a blood layer of controlled thickness. The NPs were excited with a 975 nm laser, and the resulting upconversion emission was collected by a microscope objective positioned opposite the sample. Blood, known for its high absorption and scattering coefficients in the NIR-I region, is widely used as a tissue-mimicking phantom to approximate the optical response of human skin.^{71,72} Its extinction coefficient spectrum, measured using a Lambda 1050 PerkinElmer double-beam absorption spectrometer, is shown in Fig. 7b.

Fig. 7c presents the measured emission intensity of $\text{Tm}^{3+}/\text{Yb}^{3+}$ co-doped NYMO NPs (emission at 796 nm) as a function of



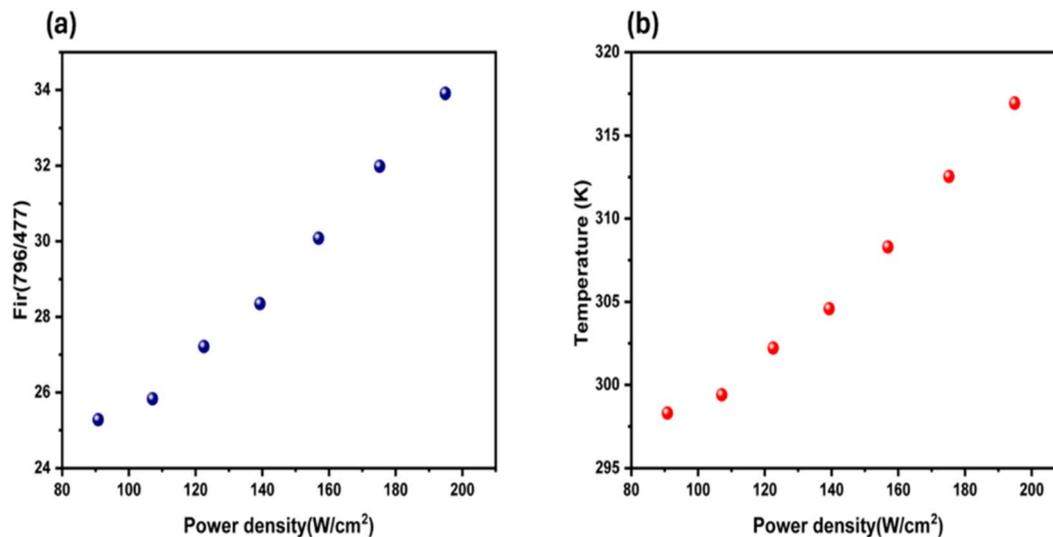


Fig. 6 Power dependence of NYMO:0.01Tm³⁺/0.15Yb³⁺ ions. (a) The fitted line of FIR (796/477) and (b) calibration temperature.

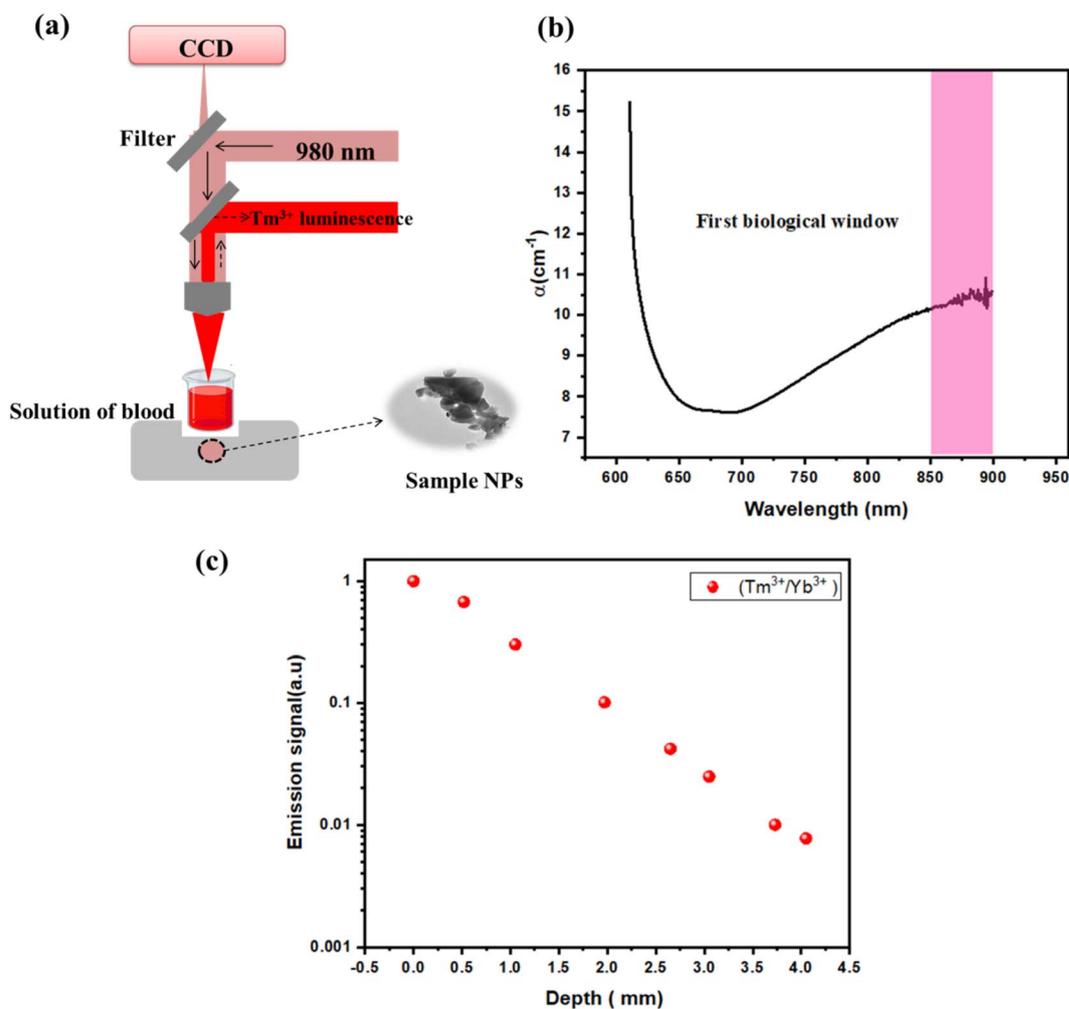


Fig. 7 (a) Schematic representation of the experimental setup for the determination of the penetration depth of two photon-excited NYMO nanoparticles. (b) Wavelength dependence of blood extinction coefficient. (c) Intensity of photon-excited luminescence emitted by Tm³⁺ nanoparticles: NYMO as a function of blood thickness under 975 nm excitation.



phantom thickness. As expected, the luminescence signal decreases monotonically with increasing depth, consistent with attenuation dominated by absorption and scattering processes.⁷³ The attenuation profile was quantitatively analyzed, allowing us to estimate the depth at which the signal drops to the detectable limit under our measurement conditions. Based on this analysis, the effective *in vitro* penetration depth for the 796 nm emission is approximately 4 mm in the blood phantom. It should be noted that this value represents an inferred penetration depth from the attenuation curve rather than a direct imaging demonstration. Nevertheless, the observed attenuation behavior aligns well with reported NIR propagation characteristics in biological tissues and confirms that the Tm³⁺-based emission exhibits enhanced transmission through strongly scattering media. These results highlight the potential of NYMO:0.01Tm³⁺/0.15Yb³⁺ nanoparticles for applications requiring improved light penetration in biological environments.

4. Conclusion

In this study, we successfully synthesized Tm³⁺/Yb³⁺-co-doped NYMO nanoparticles using the sol-gel method and comprehensively characterized their structural, morphological, and luminescent properties. Under a 975 nm laser excitation, the upconversion (UC) emission spectra displayed two distinct bands at 477 nm and 796 nm, corresponding to the ¹G₄ → ³F₆ and ³H₄ → ³H₆ transitions of Tm³⁺ ions, respectively. By applying the fluorescence intensity ratio (FIR) method between these emission bands, the nanoparticles exhibited a maximum relative sensitivity (*S_r*) of 2.05% K⁻¹ at 298 K and a maximum absolute sensitivity (*S_a*) of 0.53% K⁻¹ at 388 K, demonstrating their potential for high-precision optical thermometry. To evaluate photothermal conversion performance, the UC emission spectra were measured across a range of excitation power densities (90.8–194.9 W cm⁻²). The observed variation in emission intensity was attributed to changes in the population distribution among energy levels, resulting in a gradual increase in FIR (*I*₇₉₆/*I*₄₇₇) with increasing excitation power. This indicates a rise in internal temperature driven by laser-induced energy absorption and subsequent nonradiative heat dissipation, further amplified by enhanced electron-phonon interactions at elevated temperatures. Additionally, under 975 nm excitation, the near-infrared (NIR) emission from the NYMO nanoparticles remained detectable at tissue depths of up to 4 mm, confirming their exceptional tissue penetration capabilities. Operating within the biological optical window, these Tm³⁺-sensitized NYMO nanoparticles enable effective deep-tissue imaging and enhanced detection of subtle biological signals. In conclusion, the Tm³⁺/Yb³⁺ co-doped NYMO nanoparticles exhibit outstanding optical sensitivity, efficient photothermal conversion, and robust tissue penetration, positioning them as highly promising candidates for integrated applications in optical temperature sensing, photothermal therapy, and deep-tissue *in vivo* imaging.

Conflicts of interest

There are no conflicts to declare.

Data availability

All data underlying the results are available as part of the article and no additional source data are required.

Supplementary information (SI) is available. See DOI: <https://doi.org/10.1039/d5ra08947f>.

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