The most reliable technique of remote temperature sensing considers either the rise or the decay transient of a luminescent temperature probe. Here, real-time visible (Vis) and near-infrared (NIR) thermal imagings based on the simultaneous measurement of the emission rise and decay of transition or lanthanide metal activator are described. A single pulse time-gated detection method that allows the real-time mode of the temperature measurement, the emission detection at its highest temporal intensity, and the tunability of the emission detection in terms of time delay and gate width is proposed. Cr-ZnGaGeO$_4$/ZnGa$_2$O$_4$, Er, Ho, Yb–Y$_2$O$_3$, and Er, Ho, Yb–K-NaYF$_4$ nanoparticles that display luminescence in the Vis to NIR range (450–1200 nm) with timescales varying from 10 to 100 ms are selected. Maximum relative temperature sensitivity in Vis to Vis and NIR to NIR imaging which exceeds up to a factor of two the values obtained by the standard average lifetime method is achieved. This method applies to any lifetime-based luminescent thermometer, opening a new avenue in designing accurate and straightforward lifetime thermal imaging systems operating in the Vis to NIR range.

1. Introduction

Luminescence thermometry is a growing research field with tremendous potential in noncontact thermometry for micro/nanofluidic, microelectronic, space, nanotechnology, and biomedicine applications. There are three main methods for the temperature reading, which measure 1) the ratio of emission intensity using from thermally coupled levels, 2) luminescence lifetime, and 3) spectral shift of the emission or the integrated intensity of a given transition.

The most common approach is based on the intensity ratio of two thermally coupled (or even nonthermally coupled) transitions (luminescence intensity ratio, LIR), considered to be self-referenced, since there is no need for another reference system. However, the medium-induced optical distortions can significantly affect the temperature readout using the LIR method in the near-infrared (NIR) domain by up to 6 K (∼10% of the expected value). Unlike LIR, the lifetime thermometry method holds the crucial advantage of being virtually unaffected by the size, geometry, and concentration of the luminescent probe. Usually, for lifetime thermometry, the emission decay is monitored either as a rise time or a decay time. Unfortunately, thermal imaging using standard lifetime determination presents some drawbacks. In the case of a short emission lifetime (ns range), the emission is monitored using fluorescence lifetime imaging (FLIM) using a relatively expensive infrastructure. In the case of ms or s range lifetimes, thermal imaging is achieved using a time-gated camera (e.g., ICCD, CMOS, and interline CCD) correlated/synchronized with a modulated pulse excitation source (e.g., LED, laser, and flash lamp), leading to a relatively long acquisition time. Using time-gated camera, the emission decay is reconstructed on each pixel of the camera. Still, reports on thermal imaging using lifetime thermometry using different acquisition methods are starting to emerge.

So far, the most sensitive NIR luminescence thermometer for lifetime thermal imaging is reported in ref. for a hybrid structure composed of upconversion emission PbS quantum dots and NaYbF$_4$:0.5%Tm@NaYF$_4$:10%Yb@NaYF$_4$:50%Nd upconversion nanoparticles. The obtained maximum relative sensitivity is 5.6% K$^{-1}$ at 318 K. For lifetime thermal imaging (or “same wavelength dual emission decoded by time-resolved technique”), the authors monitor the 810 nm upconverted emission upon 865 nm excitation using a time-gated camera to resolve the PbS quantum dots emission from Tm emission. Unfortunately, there is no mention of the used delay/gate or laser pulse width and frequency. Recently, another NIR-to-NIR lifetime thermal imaging method was reported in ref. using a NaYF$_6$:NaYF$_{6}$:20% Yb, 60%Nd@CaF$_2$ inert core/active shell/inert shell nanothermometer with a maximum relative sensitivity of 1.4% K$^{-1}$ at 283 K. Parameters such as the time delay, gate, and acquisition time per image used in monitoring the thermal images are not mentioned. We also note that the chemical complexity induces low repeatability of the proposed nanothermometers.

Herein, we propose a single pulse time-gated detection method for thermal imaging in which both the emission rise and decay...
and decay times of the luminescent activator (either transitional metal or lanthanide) are monitored. Several nanosized optical materials are investigated, such as Cr\(^{3+}\)-ZnGaGeO\(_4\)/ZnGa\(_2\)O\(_4\), Er, Ho, Yb-Y\(_2\)O\(_3\) and Er, Ho, Yb-β-NaYF\(_4\). These materials display emissions spanning the 450 to 1200 nm range under direct excitation into Cr\(^{3+}\) and Yb absorptions with timescales that vary from 10 to 100 ms. The achieved maximum relative temperature sensitivity is 2% K\(^{-1}\) at 490 K for 0.05 Cr-ZnGaGeO\(_4\) (Vis (visible) to Vis thermal imaging) and 0.93% K\(^{-1}\) at 313 K for Ho, Er, Yb-tri-doped Y\(_2\)O\(_3\) and β-NaYF\(_4\) (Er, Ho, and Yb concentrations fixed at 1at%).

2. Results and Discussion

2.1. Summary of Structural and Luminescence Properties

Figure S1, Supporting Information, gather the diffraction patterns and selected TEM images of the investigated nanoparticles. Using Scherrer’s equation, the crystallite sizes were estimated between 29 and 50 nm for Cr\(^{3+}\) (with concentrations of 0.05 and 1at%) in ZnGa\(_2\)O\(_4\) (ZGO) and ZnGaGeO\(_4\) (ZGGO) and Er, Ho, and Yb tri-doped Y\(_2\)O\(_3\) and β-NaYF\(_4\) (Er, Ho, and Yb concentrations fixed at 1at%).

2.1.1. Cr-ZnGaGeO\(_4\)/ZnGa\(_2\)O\(_4\)

The transition metal Cr\(^{3+}\)\(^{[7,18-21]}\) has a maximum absorption around 400–450 nm which matches the available Vis excitation laser, while the emission is centered at 700 nm. The Cr\(^{3+}\) emission in ZGO and ZGGO hosts is monitored selectively using the appropriate bandpass and long-pass filters on a time-gated camera (sCMOS time-gated camera) in the 300–550 K temperature range. The emission timescale varies from 30 to 100 ms.\(^{[7,18-20]}\) The 0.05 and 1 at% Cr\(^{3+}\)-ZGO/ZGGO are denoted as 0.05Cr-ZGO, 1Cr-ZGO, and 1Cr-ZGGO. Figure 1 gathers the excitation and emission spectra of 1Cr-ZGO/ZGGO. The excitation spectra of 0.05Cr-ZGO, 1Cr-ZGO and 1Cr-ZGGO, which monitored the Cr\(^{3+}\) 700 nm emission (\(2\)E\(^{-}\)–\(4\)A\(_{2}\)\(^{g}\) – \(4\)T\(_{1}\)) presents the well-known Cr\(^{4+}\)A\(_{2}\)\(^{g}\) – \(4\)T\(_{2}\) absorptions at 410 and 550 nm, respectively (Figure 1a).\(^{[20,22]}\) Upon 450 nm excitation (\(2\)A\(_{2}\)\(^{-}\)T\(_{1}\) absorption),

Figure 1. Overview of the luminescence properties of a) 0.05/1Cr-ZGO, 1Cr-ZGGO, and b) Ho, Er, Yb-Y\(_2\)O\(_3\), and Ho, Er, Yb-β-NaYF\(_4\). a) excitation spectra monitoring Cr\(^{3+}\) 700 nm emission (\(2\)E\(^{-}\)–\(4\)A\(_{2}\)) and Cr\(^{3+}\) emission spectra excited at 450 nm (\(4\)A\(_{2}\)\(^{-}\)T\(_{1}\)), b) emission spectra of Ho, Er, Yb-Y\(_2\)O\(_3\), and Ho, Er, Yb-β-NaYF\(_4\) excited at 973 nm into Yb absorption.
the samples exhibit the characteristic Cr$^{3+}$ emission ($^2E$–$^4A_2$) around 700 nm (Figure 1b).

2.1.2. Er, Ho, and Yb Tri-Doped Y$_2$O$_3$ and β-NaYF$_4$

Figure 1b presents the emission spectra of Ho, Er, Yb-Y$_2$O$_3$ and Ho, Er, Yb-β-NaYF$_4$ upon 973 nm excitation. Upon excitation at 973 nm into Yb $^2F_{7/2}$-$^2F_{5/2}$ absorption, Ho $^5I_{8}$ level is populated via phonon-assisted energy transfer, leading to emission at 1200 nm ($^5I_{8}$–$^5I_{6}$). The Er $^4I_{13/2}$ is populated via resonant energy transfer from Yb $^2F_{7/2}$, and following multiphonon relaxation from $^4I_{13/2}$ to $^4I_{11/2}$. Er emits at 1530 nm ($^4I_{13/2}$–$^4I_{15/2}$ transition). In agreement with the literature,$^{23,24}$ the emission spectra of Ho, Er, Yb-Y$_2$O$_3$ and Ho, Er, Yb-β-NaYF$_4$ show a dual NIR emission corresponding to Ho $^5I_{8}$–$^5I_{6}$ and Er $^4I_{13/2}$–$^4I_{15/2}$ transitions.

2.2. Vis-to-Vis Lifetime Thermometry

We first assess the performance of 0.05Cr-ZGO, 1Cr-ZGO, and 1Cr-ZGGO for Vis lifetime thermometry and Ho, Er, Yb-Y$_2$O$_3$ and Ho, Er, Yb-β-NaYF$_4$ for NIR lifetime thermometry using the average lifetime approach.$^{7,18}$ The average lifetime represents the thermometric parameter being estimated by integrating the area of the emission decays normalized at the maximum intensity.

The relative thermal sensitivity ($S_r$)$^{11}$ is usually used as a figure of merit to compare different thermometers, independently of their nature

\[
S_r = \frac{1}{\Delta \Delta} \left\| \frac{d\Delta}{dT} \right\| \times 100\% \quad (1)
\]
where $\Delta$ is the thermometric parameter, and $d\Delta$ is the variation of the thermometric parameter with temperature ($dT$).

The temperature evolution of the 0.05Cr-ZGO, 1Cr-ZGO, and 1Cr-ZGGO emission in the range of 303–533 K are illustrated in Figures 2a and S3a–c, Supporting Information. We highlight that at 450 nm excitation wavelength, 0.05Cr-ZGO, 1Cr-ZGO, and 1Cr-ZGGO do not exhibit any persistent luminescence. Persistent luminescence requires UV or X-ray excitation$^{[20,22,25]}$ for activating the intrinsic traps. The emission decays are monitored at 700 nm using a laser frequency of 10 Hz with 10 ms pulse width. The Cr$^{3+}$ $^2E\rightarrow{^4}A_2$ transition is spin forbidden, leading to a long emission decay in the ms range. In ZGO/ZGGO hosts, Cr$^{3+}$ $^2E$ level is in thermal equilibrium with the $^4T_2$ level. The $^4T_2\rightarrow{^2}A_2$ transition is spin allowed and is characterized by a shorter lifetime value. With thermal activation, the contribution of the spin allowed transition increases at the expense of $^2E\rightarrow{^4}A_2$ transition, resulting in a reduction of the effective lifetime$^{[26]}$. With increasing temperature from 303 to 533 K, the average lifetime drops from 8.75 to 1 ms for 0.05Cr-ZGO due to the enhanced contribution of the temperature-dependent $^4T_2\rightarrow{^2}A_2$ emission (Figure 2a,b).$^{[26]}$ For 1Cr-ZGO and 1Cr-ZGGO, with increasing temperature from 303 to 533 K, the average lifetime drops from 3.34 and 0.87 ms to 0.24 and 0.12 ms, respectively (Figure S2b,c, Supporting Information). From the temperature evolution of the average lifetimes, $S_T$ is calculated using Equation (1) and its temperature evolution is presented in Figures 2c and S2c,f,S4a, Supporting Information. 0.05Cr-ZGO exhibits a maximum $S_T$ of 1.25% K$^{-1}$ at 493 K. This value places 0.05Cr-ZGO on the top two most sensitive lifetime thermometers based on Cr-ZGO/ZGGO.$^{[17,18,26]}$

### 2.3. NIR to NIR Lifetime Thermometry

For Ho, Er, Yb–Y$_2$O$_3$, and Ho, Er, Yb–NaYF$_4$ nanoparticles (Figures 2b and S3, Supporting Information), the emission decays monitored the Ho emission ($^5I_{15/2}\rightarrow^5I_{11/2}$) at 1200 nm upon 973 nm excitation at 50 Hz. Since the main application of the NIR lifetime thermometer is for bio-imaging, the temperature assessment range was limited to the physiological range (303–323 K). As shown in Figure 2e the average lifetime decreases from 0.5 to 0.27 ms when heating from 303 to 533 K. Ho, Er, Yb–Y$_2$O$_3$ nanoparticles showing the best $S_T$ value of 0.2% K$^{-1}$. For Ho, Er, Yb–NaYF$_4$ case, the Ho average lifetime decreases from 4.5 to 2.8 ms, respectively (Figure S3, Supporting Information). The maximum $S_T$ value in the same physiological temperature range is 0.17% K$^{-1}$ for Ho, Er, Yb–NaYF$_4$ (Figure S4, Supporting Information).

### 2.4. Real-Time Imaging Using Single-Pulse Time-Gated Detection

In single pulse time-gated detection, parameters such as the laser pulse width, frequency, as well as delay and gate parameters are optimized to enhance the thermometer performance. This method requires a relatively simple experimental setup: a laser diode, a time-gated camera synchronized with a signal generator, and appropriate optical filters (Figure 3).
Figure 4. Temperature evolution of the integrated emission rise and decay times using different Gate 1/2 values of 1 a), 5 b), 10 c), and 15 ms d) of 0.05Cr-ZGO upon 450 nm excitation (15 ms pulse width). The emission was monitored at 700 nm from 303 to 533 K. Gate 2 monitors the emission with no delay and 1 ms delay after the laser pulse. Temperature evolution of thermometric parameter as the ratio between the integrated intensity of Gates 1 and 2 (e,f) and their estimated relative thermal sensitivity, S_r (g,h).
where $\tau_0$ is the radiative lifetime, $C = \frac{\tau_0}{\tau_{NR0}}$, and it is assumed that the rate of radiative processes is independent of temperature ($A_{NR}(0) = \text{const.} = \frac{1}{\tau_{NR0}}$), while the probability of nonradiative process has a temperature dependence described by a Boltzmann factor of the form $A_{NR}(0) \times \exp(-\Delta E/kT)$, and $A_{NR}(0) = \frac{1}{\tau_{NR0}}$ is the nonradiative transition rate when $T = 0$ and $\Delta E$ is the activation energy of the nonradiative process.\(^{12}\) Similar processes occur in the Ln counterpart with different time scales.

The pulse width varied from 1 to 15 ms. The 15-ms pulse width was found to be the optimum value allowing us to achieve signal saturation during the excitation pulse while measuring the complete timescale of the emission rise (Figure 4a). Since $\text{Cr}^{3+}$ emission displays a long emission timescale of up to 75 ms, the chosen laser frequency was 10 Hz. Next, to find the optimum detection gate-width in which both integrated emission rise and the decay times are most sensitive to temperature, we varied the gate-width from 1 to 15 ms (the pulse width limits the maximum gate-width) and calculated the respective relative thermal sensitivity (Figure 4). Gate 1 represents the integrated area of the emission during the excitation pulse within the selected widths (1–15 ms) at 0 ms delay from the start of the laser pulse (the dark grey rectangle labelled as G1 in Figure 5). Gate 2 represents the integrated area from 0 and 1 ms delay after the laser pulse within the 1–15 ms selected widths (the dark grey rectangle labelled as G2 in Figure 5).

Since both the emission rise and decay accelerate with temperature, the value of Gate 1 increases while the value of Gate 2 decreases. We define the thermometric parameter ($\Delta$) as the ratio between the selected Gates 1 and 2.
Figure 4g,h compares the obtained $S_r$ evolutions for 1, 5, 10, and 15 ms widths for Gates 1 and 2 with Gate 2 starting from 0 and 1 ms delay after the laser pulse. When integrating the Gate 2 at 0 ms delay after the laser pulse, the maximum $S_r$ is 1.2\% K$^{-1}$ for 15 ms optimal width at 450 K. A value of 1 ms delay after the laser pulse (Gate 2) boosts the variation of the emission decay time with temperature keeping the signal to noise ratio (S/R) above 100 (Figure 4e,f) increasing the maximum $S_r$ to 2\% K$^{-1}$ at 465 K. If the gate-width is too narrow, the temperature dependence of Gates 1 and 2 cannot be accurately measured. For 0.05Cr-ZGO, the optimum width that generates the best relative thermal sensitivity is 15 ms, with Gate 1 at 0 ms delay from the start of the laser pulse and Gate 2 at 1 ms delay after the laser pulse (Figure 4h).

Figure 5a illustrates the temperature evolution of Cr$^{3+}$ emission dynamics within and after the 450 nm excitation pulse. Increasing the temperature from 303 to 533 K, Gate 1 increases from 10.1 to 13.9 ms while Gate 2 diminishes from 5.7 to 0.2 (Figure 5a). The thermometric parameter (Equation (5)) increases from 1.77 to 67 using the single-pulse time-gated detection method. The single pulse time-gated method yields the highest $S_r$ value of 2\% K$^{-1}$, compared to 1.25\% K$^{-1}$ obtained using the average lifetime method (Figure 5a).

Using a similar procedure as described for 0.05Cr-ZGO (Figure 4), we determined an optimum width of 0.5 ms (Gate 1 = Gate 2 = 0.5 ms) with 0 ms delay from the start and after the laser pulse when monitoring the Ho emission dynamics at 1200 nm. For Ho, Er, Yb-Y$_2$O$_3$, the excitation source was a 973 nm laser with 4 ms pulse width at 50 Hz frequency, allowing us to achieve signal saturation during the excitation pulse while measuring the complete timescale of the emission rise. The maximum $S_r$ is 0.5\% K$^{-1}$ which is twice the $S_r$ value of 0.25\% K$^{-1}$ obtained using the average lifetime method as the thermometric parameter (Figure 5b).

As illustrated in Scheme 1, in real-time thermal imaging using 0.05Cr-ZGO and Ho, Er, Yb-Y$_2$O$_3$, the time-gated camera records the images denoted as Frames 1 and 2 for every excitation pulse. Both emission rise and decay are monitored at their highest temporal intensity.

Figure 5, Supporting Information, shows the calculated $\Delta$ value and the calibration curve $\Delta(T)$ for 0.05Cr-ZGO, Ho, Er, and Yb-Y$_2$O$_3$. The obtained $\Delta$ offers excellent stability over 1000 pulses excitation, and the method repeatability is around 99.2\% for 0.05Cr-ZGO and 98.5\% for Ho, Er, Yb-Y$_2$O$_3$. The acquisition system does not affect the thermometer performance; since either a PMT or a time-gated camera presents similar thermometer performance (Figure S6, Supporting Information).

Figure 6 shows the real-time thermal images monitored using the single-pulse time-gated detection for 0.05Cr-ZGO and Ho, Er, Yb-Y$_2$O$_3$ samples (video files are included in Supplementary Information). The thermal stage temperature varied from 300 to 500 K, and a selection of three thermal images was used to show the change of temperature across the sample.

The best temperature resolution (or temperature determination uncertainty) obtained for 0.05Cr-ZGO is $\approx$0.1 K for temperature between 350 and 450 K. For Ho, Er, Yb-Y$_2$O$_3$, the best temperature resolution is obtained at 373 K and is $\approx$0.2 K. (Figure S7, Supporting Information). The accuracy of the method was tested by placing water media in the excitation and emission path of 0.05Cr-ZGO and Ho, Er, Yb-Y$_2$O$_3$ at 333 K (Figure S8, Supporting Information).

When the water cuvette is placed in either the excitation or emission optical path, we observe that the temperature readout over 1000 pulses varies by a maximum of 2 K for 0.05Cr-ZGO and 4 K for Ho, Er, Yb-Y$_2$O$_3$ (Figure S8, Supporting Information). The temperature readout differences are generated by the light scattering and absorption in water that increases the background and thus reduces the signal to noise ratio. The proposed single-pulse time-gated thermal imaging is an accurate
temperature readout method as the absorption of the medium does not seem to distort the temperature readout significantly.

A comparison of thermal imaging approaches reported in the literature based on luminescence lifetime thermometry and their thermometers performance are summarized in Table S1, Supporting Information.

Previously reported methods for lifetime thermal imaging present a few drawbacks: 1) long acquisition (0.6 s in ref. [14]) time, 2) long processing time (35 s for evaluation time using decay slope analysis in ref. [17]), and 3) low excitation frequency (from 1 to 4 Hz[5,30] with no details regarding the acquisition time). So far, the dual-frame lifetime method was employed to monitor the luminescence decay to get a single pulse thermal image.[15] Upon excitation at 355 nm with 10 ns pulse, the authors recorded two frames of the Bi$^{3+}$-ScVO$_4$ thermographic phosphor at 610 nm emission using an interline CCD camera, achieving a maximum $S_r$ of 6% K$^{-1}$ at 333 K.[15]

The proposed single-pulse time gated thermal imaging presents a short processing time (depending on the image resolution, pixel depth, and processing power, it should be less than 1–10 ms) and reduces the equipment cost necessary due to the lower frame rate (<100 Hz). The method is not limited to thermal imaging as it can be adapted to any lifetime dependent luminescent sensors or even for multiplexing and anticounterfeiting applications.[31] In short, these advantages refer to the real-time mode of the temperature measurement, the emission detection at its highest temporal intensity and the tunability of the emission detection in terms of time delay and gate width.

3. Conclusions

We present a new real-time Vis and NIR thermal imaging method based on the simultaneous measurement of the emission rise and decay of a transition metal or lanthanide activator. A single pulse time-gated detection method is described, allowing a real-time mode of the temperature measurement, the measurement of emission at its highest temporal intensity, and the tunability of the emission detection in terms of time delay and gate width. The method is validated using Cr-ZnGaGeO$_4$/ZnGa$_2$O$_4$, Er, Ho, Yb–Y$_2$O$_3$ and Er, Ho, Yb–NaYF$_4$ nanoparticles, which display a significant variation of luminescence timescales (10–100 ms) in the Vis to NIR range (450–1200 nm).

To the best of our knowledge, this is the first report on real-time thermal NIR imaging using lifetime thermometry, presenting clear advantages over the existing thermal imaging approaches.

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/transitional metal-doped nanoparticles, lifetime thermometry, luminescence thermometry, real-time thermal imaging, time-gated detection, Vis/NIR imaging

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