Self-Referenced Temperature Imaging with Dual Light Emitting Diode Excitation and Single-Band Emission of AVO₄:Eu³⁺ (A=Y, La, Lu, Gd) Nanophosphors

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Luminescence thermometers exhibiting ratiometric response in their emission spectrum are widely investigated but to obtain two-dimensional measurements, either the emission spectrum must be slowly scanned over the area of interest or the emission decomposed using two separate detector arrays with spectral filters. Here, the authors propose to exploit instead an excitation-spectrum based ratiometric response. In AVO₄ (A = Lu, Y, Gd, La) nanocrystals doped with Eu³⁺, the 1E(1T₁) → 1B₂(1T₂) absorption band is thermally enhanced with respect to the 1A₂(1T₁) → 1B₂(1T₂) of the V⁵⁺ ion. When observing the Eu³⁺ emission as a result of (VO₄)³⁻ to Eu³⁺ charge transfer, the ratio of intensities recorded upon two different excitation wavelengths is temperature dependent. This response is exploited for transient 2-dimensional temperature imaging using two ultraviolet light emitting diodes (LEDs) for excitation, which are subsequently pulsed, while recording the emission on a single camera. As a demonstration, a YVO₄:Eu³⁺ coated metal plate is subjected to localised heating by a flame. Thanks to the efficient excitation and signal collection, an accuracy of 0.6 °C and a precision of 1.5 °C are achieved at a resolution of 160 μm and a repetition rate of 2.5 Hz, all with peak LED powers below 1 mW and a single low-frame-rate camera.

1. Introduction

Temperature influences the physical properties of materials, whether fluid or solids. As such, its knowledge is key to understand and optimize many of the processes that our life is reliant on, whether the goals are to provide electrical or mechanical power, to transmit information, or to transform materials. Often, remote temperature readout is the only way to provide temperature information with sufficient spatial and temporal resolution and without disturbing the system. Examples include imaging temperature in vivo or in vitro,[1] observing thermal mixing processes in fluids,[2] and monitoring the temperature of microelectronic components[3,4] or that of rotating parts, as in electric motors[5] or gas turbines.[6] Thermal imaging in the infrared range is a well-established remote sensing method but it relies on knowledge of object emissivity, which requires prior characterization and which may change, e.g., during thermal treatment. In addition, infrared radiation is partially absorbed by standard borosilicate glass, water molecules, and polymers. This forbids measurements below liquid films and within biological systems and requires the use of expensive sapphire windows in confined experiments.

One of the promising remote temperature measurement techniques, luminescent thermometry (LT), relies on thermally induced changes of the spectroscopic properties of phosphor materials attached to or embedded into the measured object.[7–10] In addition, luminescence can exploit a wide range of spectral windows to avoid strong water absorption bands, allowing exciting and detecting luminescence through moist gases, liquids, and polymers. Moreover, various luminescent properties depend on temperature, e.g., emission intensity, emission decay time, emission spectrum, and excitation spectrum, but for robust measurements, it is preferable to exploit relative changes, which cancel the artifacts related to spatial and temporal variations in the illumination and detection.[9,11]

The temporal method compares the luminescence emission intensity at different times after the end of an excitation pulse. To obtain a temperature measurement for every excitation pulse, either the emission spectrum must be slowly scanned over the area of interest or the emission decomposed using two separate detector arrays with spectral filters.

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distortions, for example, when imaging through semitransparent materials, e.g., biological tissues.\textsuperscript{1\textsuperscript{8}} However, the disadvantage is that the exposure time must be commensurate with the decay time in the microsecond to millisecond range, which would result in very weak signals in laser-diode-based microscopy experiments.

The method that exploits the temperature dependence of the emission spectrum via a ratio of emission intensities in two separate wavelength ranges is referred to interchangeably as the spectral, intensity ratio, two-color, or ratiometric approach. Unlike the temporal approach, the exposure time is flexible and can be up to several seconds in microscopy experiments. However, two-color detection requires relatively complex imaging systems, and image mapping between the two sensors is critical. When sharp spatial variations in emission intensity are concern, the vast majority of studies use either of the two methods described previously.\textsuperscript{19–23} On the other side, the temperature dependence of the excitation spectrum has been largely unexploited on phosphors. Two excitation light sources but only a single detector would be necessary, avoiding image mapping issues, and the measurement duration would also be flexible. Several combustion diagnostic studies have used excitation strategies with two pulsed lasers at two different wavelengths to excite the fluorescence of ketones,\textsuperscript{23,24} diatomic molecules such as NO,\textsuperscript{25} or OH,\textsuperscript{26} or of indium atoms.\textsuperscript{27} In these studies, the temperature is derived from the ratio of the fluorescence intensities over the whole emission band following each laser pulse. This approach offers a temperature readout that is free of collisional quenching effects, a key consideration in combustion studies. However, beam homogenizers and the close monitoring of the output of the two lasers with an additional camera are necessary and lead to an overall system that is far more complex than the single-excitation two-color detection approach. With progress in light emitting diodes (LEDs), low-cost light sources are available in a wide range of wavelengths with excellent output stability and it is therefore time to explore luminescence thermometry strategies based on probing the excitation spectrum of phosphors with LEDs. In the past few years, our group has demonstrated strategies exploiting two excitation lines within the 4f or 3d manifold of lanthanide and transition metal ions. One wavelength is chosen for absorption into the ground electronic state (GSA), while the second wavelength is matching the absorption from an electronic excited state (ESA). Usually an increase in temperature results in the quenching of the luminescence intensity, but in this latter case, the opposite is observed as the population of the energy state from which absorption takes place is thermally populated. This approach called the single band ratiometric (SBR) approach has been recently intensively investigated in the case of the lanthanide ions due to their unique energy level configuration, which facilitates an efficient ESA process. Therefore, SBR LT of high relative sensitivities has been reported using Eu\textsuperscript{3+} \textsuperscript{28,29} Tb\textsuperscript{3+},\textsuperscript{30} Nd\textsuperscript{3+},\textsuperscript{31} and Pr\textsuperscript{3+}\textsuperscript{32} ions. It was shown that by the intentional activation of the interionic energy transfer processes by the optimization of the dopant concentration it is possible to boost the thermometric properties of the luminescent thermometer and to modify the operating temperature range and the temperature of the highest sensitivity. However, the main limitation of this approach was a relatively low emission signal obtained upon excitation matching the excited state absorption, which was particularly troublesome and inefficient for narrow-band and weak 4f–4f transitions.\textsuperscript{33} On the other hand, the attempt to implement the SBR approach in the Cr\textsuperscript{3+}-doped systems resulted in low relative sensitivities (SR < 0.5% °C\textsuperscript{–1}) due to the low energy separation between the vibronic states of the \textsuperscript{4}A\textsubscript{2} ground state of Cr\textsuperscript{3+} that were involved in the ESA process.\textsuperscript{34}

In this study, we turn our attention to temperature-dependent excitation features in the AVO\textsubscript{4}:Eu\textsuperscript{3+} group of materials (A = Lu, Y, Gd, La). Absorption of the (VO\textsubscript{4})\textsuperscript{3−} group is known to have a high oscillator strength. Although some of the recently published works report the use of VVO\textsubscript{4}:Ln\textsuperscript{3+} phosphors for this approach, the mechanism behind the thermally induced change of spectroscopic transitions has not been discussed in detail.\textsuperscript{35} Moreover, a systematic discussion of the role of the host material composition of the thermometric parameters of this kind of luminescent thermometry is presented. Additionally, in this manuscript for the first time, the application potential of this approach in thermal imaging of a dynamically changing temperature gradient has been verified by experimentation. The main concept of the proposed approach is schematically shown in Figure 1. The analysis of the configurational energy diagram (Figure 1a,c) of the V\textsuperscript{5+} ions in the (VO\textsubscript{4})\textsuperscript{3−} groups reveals that at low temperatures the excitation that matches the \textsuperscript{1}A\textsubscript{2} (\textsuperscript{1}T\textsubscript{1g}) → \textsuperscript{1}B\textsubscript{2} (\textsuperscript{1}T\textsubscript{1u}) followed by the nonradiative processes enables to populate \textsuperscript{1}A\textsubscript{1} (\textsuperscript{1}A\textsubscript{1g}) state of the V\textsuperscript{5+} ions. The (VO\textsubscript{4})\textsuperscript{3−} → Eu\textsuperscript{3+} energy transfer leads to the population of the \textsuperscript{5}D\textsubscript{0} excited state of Eu\textsuperscript{3+} ions and as a consequence, the well-known red emission of Eu\textsuperscript{3+} ions occurs. However, an increase of temperature results in a gradually increased population of the \textsuperscript{1}E (\textsuperscript{1}T\textsubscript{1g}) state of the (VO\textsubscript{4})\textsuperscript{3−} group, from which the absorption may occur. This effect is especially clearly manifested in the change of the contribution of the particular absorption bands in the total excitation spectrum measured at elevated temperatures (Figure 1b). Therefore, by selecting excitation wavelengths that match the absorption from \textsuperscript{1}A\textsubscript{2} (\textsuperscript{1}T\textsubscript{1g}) (Figure 1d) and \textsuperscript{1}E (\textsuperscript{1}T\textsubscript{1g}) (Figure 1e) states, selective thermal monotonicity of the Eu\textsuperscript{3+} luminescence intensity is expected. Therefore, the luminescence intensity ratio (LIR) of a single band upon these two different optical excitations can be used as a thermometric parameter of high thermal variability, which enables performing 2D LIR maps (Figure 1f). Basing on the calibration curve of the temperature dependence of LIR, the luminescence response of the phosphor can then be used to obtain 2D temperature maps (Figure 1g) using a single camera and two low-power LEDs as demonstrated in this article.

2. Results and Discussion

2.1. Structural and Morphological Characterization

In general AVO\textsubscript{4} (A\textsuperscript{3+} = Lu\textsuperscript{3+}, Y\textsuperscript{3+}, Gd\textsuperscript{3+}, La\textsuperscript{3+}) crystallizes in the tetragonal structure of I4\textsubscript{1}/amd space group (141) (zircon type structure, Z = 4). Its crystallographic structures consist of
fourfold-coordinated tetrahedral sites of \( V^{5+} \) and eightfold-coordinated dodecahedral sites of \( A^{3+} \) ions (Figure 2a). Due to the difference in the ionic radii between \( Eu^{3+} \) dopant ions (1.066 Å) and \( A^{3+} \) ions (0.977, 1.019, 1.053, and 1.16 Å for \( Lu^{3+}, Y^{3+}, Gd^{3+}, \) and \( La^{3+}, \) respectively) and \( V^{5+} \) ions (0.355 Å), the \( Eu^{3+} \) ions preferentially occupy the \( A^{3+} \) ions in the \( (AO_8)^{13-} \) crystallographic position. Comparison of the structural parameters of the host under consideration is shown in Table 1. It can be clearly seen that most of the crystallographic parameters decrease with the reduction of the ionic radii of the \( A \) ions.

![Figure 1](image1.png)

Figure 1. The visualization of the concept of the proposed approach: a) simplified energy diagram of \( VO_4^{3-} \) group and \( Eu^{3+} \) ions and transitions involved for excitation at 266 nm; b) thermal evolution of the excitation spectra of \( Eu^{3+} \) ions; c) simplified energy diagram of the \( VO_4^{3-} \) group and \( Eu^{3+} \) ions and transitions involved for excitation at 340 nm; d) thermal evolution of the emission spectra of \( Eu^{3+} \) ions with excitation \( \lambda_{exc} = 266 \) nm; and e) \( \lambda_{exc} = 342 \) nm. f) The 2D map of the LIR on a \( YVO_4:Eu^{3+} \)-coated steel plate and g) the obtained temperature image during local heating of a \( YVO_4:Eu^{3+} \)-coated plate.

![Figure 2](image2.png)

Figure 2. Structural characterization of synthesized materials: a) the X-ray diffraction patterns of \( AVO_4:Eu^{3+} \) powders where \( A^{3+} = Lu^{3+}, Y^{3+}, Gd^{3+}, \) \( La^{3+} \); b) the visualization of the polyhedra of \( A^{3+} \) and \( V^{5+} \) in the \( AVO_4 \) structure for tetragonal \( (A^{3+} = Lu^{3+}, Y^{3+}, Gd^{3+}, La^{3+}) \) phase; the representative TEM images of \( AVO_4 \) for c) \( A^{3+} = Lu^{3+} \), d) \( V^{5+} \), e) \( Gd^{3+} \), and f) \( La^{3+} \).
Table 1. The comparison of structural parameters of the AVO₄ (A = Lu, Y, Gd, La) structures.

| Host material | a [Å] | c [Å] | Volume [Å³] | Ionic radius of A | A-O distance [Å] | A-V distance [Å] | V-O distance [Å] |
|---------------|-------|-------|-------------|------------------|------------------|------------------|------------------|
| LuVO₄         | 7.0254| 6.2347| 107.72      | 0.977            | 2.2516           | 3.117            | 1.7065           |
| YVO₄          | 7.1183| 6.2893| 118.68      | 1.019            | 2.298            | 3.145            | 1.7087           |
| GdVO₄         | 7.1926| 6.3392| 127.95      | 1.053            | 2.3859           | 3.170            | 1.6039           |
| LaVO₄         | 7.4578| 6.5417| 136.84      | 1.116            | 2.4683           | 3.217            | 1.7134           |

cation. This tendency also applies to A-O and A-V distances that will have a significant impact on the luminescent properties of AVO₄ (A³⁺ = Lu³⁺, Y³⁺, Gd³⁺, La³⁺), which will be discussed later in this work (Figure S1, Supporting Information).

To validate the purity of the crystallographic structure of the synthesized AVO₄ nanocrystals (A = Lu, Y, Gd), the X-ray powder diffraction (XRPD) patterns were carefully analyzed (Figure 2b). A perfect match between diffraction reflections and the corresponding crystallographic reference patterns ICSD 152692 for GdVO₄, ICSD 9009764 for YVO₄, and ICSD 78083 for LuVO₄ annealed at 1000°C confirms the phase purity of the material that crystallizes in the tetragonal structure. However, under the same synthesis condition the LaVO₄ nanocrystals of the monoclinic structure of the P2₁/n space group were obtained. To eliminate the effects associated with the change of the crystal structure when studying the influence of the host material within the AVO₄ phosphor, the hydrothermal synthesis method was applied to obtain tetragonal LaVO₄:Eu³⁺ nanocrystals.

The analysis of the XRPD patterns of LaVO₄:Eu³⁺ nanocrystals synthesized in such a way and annealed at different temperatures confirmed that the as-prepared powders are of pure-phased tetragonal phase (Figure S2, Supporting Information). However, to discard the eventual effect of the enlargement of the phosphor particles during the spectroscopic measurements at a higher temperature, the as-prepared LaVO₄:Eu³⁺ nanocrystals were annealed at higher temperatures. The increase of the annealing temperature up to 600°C results in the gradual narrowing of the diffraction reflexes, which can be associated with increase of the particle size. In the case of the samples annealed at 700 and 800°C, additional reflexes from the monoclinic phase of LaVO₄ (ICSD 155240) appear, whereas the pure monoclinic structure was found for annealing temperatures above 900°C. The described structural phase transition that was observed in the LaVO₄ phosphor results most probably from the relatively large ionic size of the La³⁺ cations. At higher temperatures the structures of lower symmetries are energetically more favorable. To compare AVO₄:Eu³⁺ in the tetragonal phase, in the rest of the paper, the LaVO₄ sample annealed at 600°C is compared with the AVO₄ (A = Lu, Y, Gd, La) samples annealed at 1000°C. The transmission electron microscope (TEM) images of AVO₄:Eu³⁺ indicate that the synthesized powders consist of well-crystallized and highly aggregated nanocrystals (Figure 2c–f). The particle size histograms reveal that the average size of the particles is 300, 360, 350, and 63 nm for LuVO₄:Eu³⁺, YVO₄:Eu³⁺, GdVO₄:Eu³⁺, and LaVO₄:Eu³⁺, respectively. The difference in particle size of LaVO₄ with respect to the other members of this group of compounds is associated with the difference in the annealing temperature (Figure S3, Supporting Information). The reflection spots observed in the representative single-area electron diffraction (SAED) patterns that correspond to the particular crystallographic structures are an additional confirmation of the structural purity of the synthesized powders (Figure S4, Supporting Information). However, the diffuse rings noted for the LaVO₄ sample annealed at 600°C are affected by the presence of an amorphous phase; meanwhile the absence of those rings for the AVO₄ (A = Lu, Y, Gd) nanocrystals annealed at 1000°C assures entire crystallization.

2.2. Luminescent Property Characterization

The characteristic luminescence of the Eu³⁺ ions results from intra-configurational 4f–4f electronic transitions between their energy levels (Figure S5, Supporting Information). Upon optical excitation that corresponds to the energy difference between the ground and excited states of the Eu³⁺ ion, its excited states are populated followed by fast nonradiative transitions to the metastable 1D⁰ state. The radiative depopulation of this level to the 2F_j states results in the occurrence of the several narrow emission bands at 595, 619, 653, and 699 nm associated with the 2D⁰→2F_j, 2D⁰→2F_5, 2D⁰→2F_7, and 5D⁰→2F_5 electronic transitions, respectively. The typical excitation spectrum of the Eu³⁺-doped compound consists of characteristic narrow absorption bands and the broad O−→−Eu³⁺ charge transfer absorption band localized in the UV spectral range (Figure S6, Supporting Information). However, in the case of AVO₄:Eu³⁺, the excitation spectra are dominated by the broad absorption band ranging from 250 to 460 nm (Figure 3a and Figure S7, Supporting Information). The deconvolution of this inhomogeneously broadened absorption band indicates that it consists of at least three absorption bands at around 28 000–32 000 cm⁻¹ (≈312–355 nm), attributed to the 1E(Tₐ)→1B₂(T₂) of the (VO₄)³⁻ group, 33 000–35 000 cm⁻¹ (≈285–300 nm), attributed to the 1A₂(T₁)→1B₂(T₂) of (VO₄)³⁻ group, and 36 000–36 500 cm⁻¹ (≈274–278 nm, O²⁻→Eu³⁺ charge transfer band) (Figure 1a–d). The measurement of the excitation spectra of AVO₄:Eu³⁺ nanocrystals reveals that the intensity of these absorption bands as well as their spectral position depends on temperature (Figure 3e, see also Figure S8 and S9, Supporting Information). The contribution of the O²⁻→Eu³⁺ and 1A₂(T₁)→1B₂(T₂) charge transfer bands to the total excitation spectrum decreases with temperature, whereas the intensity of the 1E(T₁)→1B₂(T₂) band is thermally promoted. In addition, a pronounced change of the spectral position of the absorption band can be found as well—when temperature increases, the position of the maximum of the 1E(T₁)→1B₂(T₂) band continuously shifts toward smaller energies in the −190–500°C temperature range (Figure 3f). Only in the case of the LaVO₄:Eu³⁺ nanocrystals, the absorption band intensity remains constant up to around −10°C, above which the band position starts to redshift (Figure 3f). The highest magnitude of this shift was observed for LaVO₄ (ΔE = 3408 cm⁻¹) and GdVO₄ (ΔE = 3397 cm⁻¹), whereas only ΔE = 3230 cm⁻¹ and ΔE = 2860 cm⁻¹ were observed for YVO₄ and LuVO₄, respectively (Figure 3g). This unusual thermal enhancement of the absorption band results from the thermal coupling of the 1A₂(T₁) and 1E(T₁) states of vanadium ions. The thermally pronounced increase of the
The use of Eu$^{3+}$ ions, respectively (Figure 4a,b and Figure S10, Supporting Information). Since the emission band at 619 nm ($(E_{2(1T_{1})}=E_{2})$ is of the highest brightness, its integral intensity will be considered in further studies (Figure S11, Supporting Information). When the temperature increases, the integral emission intensity of Eu$^{3+}$ upon $\lambda_{exc}=266$ nm slightly increases in the temperature range below $-70\,^\circ$C, which is followed by the gradual quenching of luminescence intensity. For all the AVO$_4$Eu$^{3+}$ nanocrystals, the integral intensity reached around 20% of the initial intensity at $470\,^\circ$C (Figure 4a,b). On the other hand, upon $\lambda_{exc}=342$ nm excitation, the emission intensity increases drastically with temperature, reaching maximum at around $220\,^\circ$C followed by the luminescence quenching at higher temperatures. The magnitude of this thermal enhancement of luminescence depends on the stoichiometry of the host material: 58-fold enhancement in YVO$_4$:Eu$^{3+}$, 44-fold in GdVO$_4$:Eu$^{3+}$, 37-fold for LuVO$_4$:Eu$^{3+}$, and 18-fold for LaVO$_4$:Eu$^{3+}$ (Figure S11, Supporting Information) were observed. The magnitude of the enhancement is clearly correlated with the splitting energy $\delta E$, which is in agreement with a Boltzmann distribution of the $E_{1}(T_{1})$ and $A_{2}(T_{1})$ states. The opposite thermal dependence of the same emission band under different excitation wavelengths.
supports the hypothesis that the LIR of these two signals can be used as a thermometric parameter

\[
\text{LIR} = \frac{\int I(\text{Eu}^{3+}:5D_0 \rightarrow 7F_2)_{\lambda_{\text{em}}=342 \text{nm}} \, d\lambda}{\int I(\text{Eu}^{3+}:5D_0 \rightarrow 7F_2)_{\lambda_{\text{exc}}=266 \text{nm}} \, d\lambda}
\]  

(1)

Thermal evolution of the LIR indicates that the usable temperature range in which thermographic phosphor can be used for remote temperature sensing is limited for LaVO4 to the \(-10\) to 450 °C range due to the initial thermal LIR’s independence at lower temperatures (Figure 4c). Independently from the stoichiometry of the AVO4:Eu3⁺ phosphors, two thermal regimes, in which different slopes of LIR are observed, can be distinguished. At temperatures below 150 °C, a rapid LIR increase can be observed, whereas above this threshold the slope decreases. However, above 280 °C, some irregularities in the thermal dependence of the LIR can be seen, which is not entirely clear. Therefore, these types of luminescent thermometers should not be used at temperatures exceeding this limit value. Notably, the smallest irregularities are found for YVO4:Eu3⁺ nanophosphors (Figure 4d). The relative sensitivity \(S_R \) increases at lower temperatures before reaching a maximum at a temperature which varies between \(-40\) and 20 °C depending on the host (Figure 4e). The maximal relative sensitivity \(S_{R_{\text{max}}} \) was found at \(-40 \) °C for YVO4:Eu3⁺. As a performance criterion for luminescence thermometer, the width of the temperature range over which the relative sensitivity is over 1% °C⁻¹ can be used. This range is \(-90\) to 75 °C in the case of YVO4:Eu3⁺, \(-110\) to 50 °C in the case of LuVO4:Eu3⁺, \(-8\) to 130 °C in the case of LaVO4:Eu3⁺, and \(-50\) to 85 °C in the case of GdVO4:Eu3⁺ nanocrystals. The linear correlation between the temperature at which the maximal \(S_R \) is obtained and the A—V distance suggests that to shift the maximum of \(S_R \) toward higher temperatures, longer A—V distances are beneficial (Figure 4f). Despite the fact that in the case of LaVO4:Eu3⁺ maximal \(S_R \) was achieved at higher temperatures with respect to other representatives of the AVO4:Eu3⁺ family of compounds, its value is still relatively low. The calculated temperature determination uncertainties of AVO4:Eu3⁺ nanocrystals in the SBR approach indicate that the YVO4:Eu3⁺ is characterized by the most promising thermometric parameters and enables the remote temperature determination with the uncertainty as low as 0.3 °C in the \(-75\) to 220 °C temperature range (Equation S2–S3, Figure S12, Supporting Information). The high reproducibility of the temperature readout using the YVO4:Eu3⁺ has been confirmed within the 15 heating–cooling cycles as shown in Figure S13, Supporting Information.
The thermometric performance is not only defined by the relative temperature sensitivity but also by the brightness of the materials. The photoluminescence spectra for each phosphor was quantified in terms of photons nm⁻¹ mg⁻¹ for a pulsed 266 nm laser excitation, with a fluence of 8 mJ cm⁻² (peak power density of 1 MW cm⁻²) and is provided in Figure S14, Supporting Information. The total emission intensity of the 531–700 nm band was equal to 4.18 × 10¹⁴, 1.01 × 10¹⁶, 1.06 × 10¹⁴, and 2.69 × 10¹⁴ photons mg⁻¹, for YVO₄, LaVO₄, GdVO₄, and LuVO₄, respectively. YVO₄ is therefore the most promising material from the perspective of both brightness and useful temperature range above which the relative sensitivity stays above 1% K⁻¹. The luminescence emission intensity of YVO₄ nanocrystals is comparable to those of the brightest micron-size phosphors reported in a previous study. For example, the total emission of micron-sized BaMgAl₁₀O₁₇:Eu²⁺, a widely used lamp phosphor, is about 2 × 10¹⁴ at the same fluence of 8 mJ cm⁻². The AVO₄:Eu³⁺ nanocrystals have a significant advantage over the other single band ratiometric thermometric, e.g. based on Tb³⁺, due to the fact that they exploit strong spin-allowed d–d transition, which results in high signal levels.

2.3. Temperature Imaging Experiment

As it offers the highest sensitivity at room temperature and signal level, YVO₄ was chosen as the host material to perform temperature imaging experiments under dual excitation with LEDs emitting at 270 and 340 nm, respectively (Figure 5). The power density of the LED illumination was only 0.3 mW cm⁻²; 270 nm was chosen as the nearest available LED peak wavelength to 266 nm excitation. A comparison of the excitation spectrum of YVO₄:Eu³⁺ with the spectral characteristics of the LEDs used for excitation is shown in Figure S15, Supporting Information. The thermometric performance is not only defined by the relative temperature sensitivity but also by the brightness of the materials. The photoluminescence spectra for each phosphor was quantified in terms of photons nm⁻¹ mg⁻¹ for a pulsed 266 nm laser excitation, with a fluence of 8 mJ cm⁻² (peak power density of 1 MW cm⁻²) and is provided in Figure S14, Supporting Information. The total emission intensity of the 531–700 nm band was equal to 4.18 × 10¹⁴, 1.01 × 10¹⁶, 1.06 × 10¹⁴, and 2.69 × 10¹⁴ photons mg⁻¹, for YVO₄, LaVO₄, GdVO₄, and LuVO₄, respectively. YVO₄ is therefore the most promising material from the perspective of both brightness and useful temperature range above which the relative sensitivity stays above 1% K⁻¹. The luminescence emission intensity of YVO₄ nanocrystals is comparable to those of the brightest micron-size phosphors reported in a previous study. For example, the total emission of micron-sized BaMgAl₁₀O₁₇:Eu²⁺, a widely used lamp phosphor, is about 2 × 10¹⁴ at the same fluence of 8 mJ cm⁻². The AVO₄:Eu³⁺ nanocrystals have a significant advantage over the other single band ratiometric thermometric, e.g. based on Tb³⁺, due to the fact that they exploit strong spin-allowed d–d transition, which results in high signal levels.

Results of the temperature imaging experiments in which an aluminum plate coated with YVO₄:Eu³⁺ was subjected to heating from a flame are shown in Figure 5c. The flame was turned on at t = 0 s and turned off at t = 6 s. As soon as the burner is turned on, the temperature at the center of the image (point A), where the heat transfer rate from the flame to the plate is the highest, rapidly increases (Figure 5d). Due to the cylindrical symmetry of the burner, isotherms have a circular shape. As time progresses, a larger area of the plate is heated up due to lateral conduction through the highly conductive aluminum (≈ 200 W m⁻¹ K⁻¹). As a result, the cooling heat transfer rate from the plate to the surroundings by natural convection becomes more significant and the rate of increase of the temperature at point A on the sample slows down. Finally, after the burner is turned off, the temperature difference between the center and the edge of the field of view drops rapidly due to lateral conduction in the absence of localized heating, and then the plate cools down slowly and uniformly starting from t = 7 s until t = 13 s when the recording is
stopped. To show the importance of an experiment capable of spatially and temporally resolved temperature maps, a similar experiment was also performed on a stainless steel coated plate that has a lower conductivity (\(\lambda \approx 20 \text{ W m}^{-1} \text{ K}^{-1}\)) and the same thickness and a temperature field obtained during flame heating is shown in Figure 5e. For a peak temperature of 100 °C, measured in the area corresponding to the flame impingement, the temperature measured 15 mm away from that point is still below +40 °C for the steel plate compared to +70 °C at the same distance for the aluminum plate when its peak temperature was +95 °C. Due to the lower heat transfer rate of lateral conduction in the steel plate than in the aluminum plate, the heating is much more localized.

The accuracy and precision of the measurement system were also assessed. The maximum deviation of the fit was determined to be 0.6 °C over the 20–140 °C temperature range and can be considered as a measure of the accuracy. Finally, the precision was assessed from a single temperature image measured in the calibration unit at a temperature of 78 °C shown in Figure S18, Supporting Information. The measured plate temperature is not perfectly homogeneous, which quantitatively agrees with the temperature determined by infrared thermal imaging measurements using a plate of the same material sprayed with a high-emissivity coating. Statistics in a uniform temperature region (5 mm by 1 mm) indicate a single pixel standard deviation of 1.5 °C for a spatial resolution of 160 µm, as determined from an image of a 1951 United States Air Force (USAF) resolution target with the same processing applied.

Here the imaging system had a low magnification (0.3) as the emphasis was placed on measuring a wide temperature field to visualize the flame heating rather than achieving resolution in the submicrometer range as in impressive thermal imaging studies using scanning thermal microscopy,\textsuperscript{[180]} confocal microscopy,\textsuperscript{[134]} or a fiber scanning system.\textsuperscript{[139]} Such a resolution yields 2D maps of 340 × 260 independent temperature measurements per image over a 34 mm by 26 mm region. Another estimate for the spatial resolution can also be derived from the temperature resolution (1.5 °C) and the maximum gradient in the measurement (12 °C in Figure 5f), as in Antić et al.\textsuperscript{[40]} yields a value of 130 µm. Spatial averaging can be applied to increase the temperature resolution at the expense of spatial resolution. Several factors contribute to obtaining such a high level of precision/spatial resolution with only low-power LED illumination (\(\approx 0.3 \text{ mW cm}^{-2}\)) and a single slow-frame-rate camera. First, excitation in the two thermally coupled levels of \(\text{V}^3\) is efficient due to the spin-allowed nature of the transition. Second, this radiometric response has a high temperature sensitivity (>1%/°C). Finally, with this scheme, light is collected from the phosphor material with a high duty cycle (25%), which is key to harvesting luminescence photons from low-power LEDs. Notably, the high brightness of the proposed phosphor and the easiness in the practical implementation of the proposed technique mean this approach is suitable for use with smartphone-based detection.\textsuperscript{[41]}

3. Conclusion

In this article, a mechanism of thermally induced changes in the excitation spectrum of AVO\(_{4}\)Eu\(^{3+}\) (\(A = Y, La, Lu, Gd\)) was studied and explained in detail. It was found that the thermal coupling of the \(^3\text{A}_2(\text{T}_{1g})\) and \(^1\text{E}(\text{T}_{1g})\) states of the (VO\(_4\))\(^{3-}\) group enhances the intensity of the \(4\text{f}^7\text{E}(\text{T}_{1g}) \rightarrow 1\text{B}_2g(\text{T}_{2g})\) with respect to the \(^3\text{A}_2(\text{T}_{1g}) \rightarrow 1\text{B}_2g(\text{T}_{2g})\) bands at elevated temperatures. The energy separation between those two states depends on the stoichiometry and increases from 1974 cm\(^{-1}\) for the LuVO\(_4\) to 2689 cm\(^{-1}\) for LaVO\(_4\), which correlates with the Y–O distance. The high-absorption cross-section of the vanadate group with respect to the 4\text{f}–4\text{f} absorption of Eu\(^{3+}\) and the resulting thermal susceptibility of the emission intensity enables us to demonstrate a ratiometric luminescent thermometer based on the single \(5\text{D}_{0} \rightarrow 7\text{F}_1\) emission band intensity of Eu\(^{3+}\). The relative sensitivity and the temperature at which its maximal value is reached can be altered by modification of the host material composition. Using estimation of the luminescence absolute brightness and the relative sensitivity \(S_R = 3%/{^\circ C}\) at \(-40^\circ C\) as figures of merit, the YVO\(_4\) Eu\(^{3+}\) phosphor was selected for further studies and thermal imaging.

A novel temperature imaging system based on two low-power LEDs for excitation and a single camera imaging the integral Eu\(^{3+}\) emission for detection was used. This system allows mapping the 2D transient surface temperature with a single pixel precision of 1.5 °C at a resolution of 160 µm, using an LED with a peak power of only 0.8 mW. Such a performance results from the brightness and high temperature sensitivity of the YVO\(_4\) Eu\(^{3+}\) phosphor at room temperature as well as the high photon budget of the detection scheme. Unlike the two-emission-color ratiometric imaging, this single-camera method does not require correction of the image pair for distortion before division, so image processing is very straightforward and systematic errors from misalignment are kept to a minimum. On the other hand, this approach allows a higher photon budget than lifetime-based thermometry as photon harvesting is not limited by the luminescence lifetime. This method does not require accurate camera timing or fast frame readout and detection can therefore be performed with a smartphone. A measurement kit combining two external UV LEDs to a smartphone would be a new addition to the emerging portfolio of smartphone-based temperature imaging techniques, for example\textsuperscript{[41]} It may even be possible to shift the material composition for absorption in the visible. In that case, excitation could even be performed by applying color filters to the dual LEDs with which some smartphone are equipped. Due to the low power of the LED photoexcitation used here, the current repetition rate does not go beyond 2.5 Hz, which limits its temporal resolution. Nevertheless, the approach is flexible and the phosphors are ultra-photostable. Therefore, more powerful UVB LEDs should improve frame rates tenfold and enable investigations of even faster heat transfer transients.

4. Experimental Section

Pechini Method of AVO\(_{4}\)Eu\(^{3+}\) (\(A = La, Lu, Y, Gd\)) Synthesis: The powders of AVO\(_{4}\)Eu\(^{3+}\) (\(A = Lu, Y, Gd\)) nanocrystals were synthesized with a modified Pechini method. NH\(_4\)VO\(_3\) (>99.99% purity, Alfa Aesar), Eu\(_2\)O\(_3\) (99.999% purity, Stanford Materials Corporation), Cu\(_2\)H\(_4\)O\(_7\) (>99.9% purity, Alfa Aesar), HO\(_4\)(CH\(_2\))\(_3\)OH, (PEG-200, \(n = 200\), Alfa Aesar), Lu\(_2\)O\(_3\) (99.999% purity, Stanford Materials Corporation), Y\(_2\)O\(_3\) (99.999% purity, Stanford Materials Corporation), and Gd\(_2\)O\(_3\) (99.999% purity, Alfa Aesar) were used as starting materials. Stoichiometric amounts of
ammonium vanadate was dissolved in deionized water. Lutetium/yttrium/gadolinium and europium oxides were dissolved in deionized water with the addition of a small amount of HNO₃ (65% purity, Avantor) and then recrystallized three times to remove the excess nitrogen and added to the water solution of ammonium. After that, an anhydrous citric acid and polyglycol were added to the mixture. The molar ratio of citric acid to all metals was set up as 6:1; meanwhile PEG-200 and citric acid were used in a molar ratio of 1:1. Subsequently, the obtained solution was dried for 24 h at 150°C until a resin was formed. The produced resins of the samples with 1% Eu³⁺ concentration with respect to the number of A⁻³⁻ moles ions were annealed in porcelain crucibles for 2 h in air at 1000°C.

Hydrothermal Synthesis of LaVO₄:Eu³⁺ Nanocrystals: Tetragonal LaVO₄: Eu³⁺ nanocrystals were synthesized with the hydrothermal method according to the modified protocol presented in a previous study.[42] Lanthanum and europium oxides were dissolved in deionized water with the addition of ultrapure nitric acid to obtain suitable lanthanane nitrates. 1 mmol of ethylenediaminetetraacetic acid (EDTA) was added to 15 ml of deionized water and under vigorous stirring the 0.5 m of NaOH was added dropwise until a clear solution was obtained. Subsequently, 0.99 mmol of La(NO₃)₃·6H₂O and 0.01 mmol Eu(NO₃)₃·6H₂O were dissolved in 5 ml of deionized water and then added into the obtained solution of EDTA sodium salt to form a chelate lanthanum and europium complexes. Na₂VO₄ (1 mmol) was dissolved in 15 ml deionized water and added into the lanthanane complex solution under vigorous stirring. During the synthesis the pH was adjusted to 8–9 by the use of 0.5 m of NaOH. After establishing the desired pH range, the final color of the solution changed to light orange. Finally, the solution was transferred into a 100 ml stainless steel autoclave and maintained at 180°C for 24 h. The obtained precipitates were separated by centrifugation, followed by washing with deionized water and ethanol several times. The final product was dried for 12 h in air and afterward annealed for 2 h at 600, 700, 800, 900, and 1000°C.

Characterization: All of the synthesized materials were examined by X-ray powder diffraction (XRD) measurements conducted on a PANalytical X’Pert diffractometer, equipped with an Anton Paar TCU 1000 N temperature control unit, using Ni-filtered Cu Kα radiation (λ = 40 kV, I = 30 mA). TEM images were taken using a Philips CM-20 SuperTwin TEM. The samples were dispersed in methanol, and a droplet of such a suspension was put on a microscope copper grid. Next, the samples were dried and purified in a plasma cleaner. Studies were performed in a conventional TEM procedure with 160 kV parallel beam electron energy. The sizes were determined manually using ImageJ software by measuring the longest linear size (Peret diameter) of each particle.

The emission spectra were measured using a Silver-Nova Super Range TEC spectrometer from Stellarnet (1 nm spectral resolution) as a detector and the 266 nm (2, peak power density of 0.5 MW cm⁻²) and the 342 nm (with a fluence of 5 mJ cm⁻², peak power density of 0.6 MW cm⁻²) excitation lines from an OPOLITE 355 LD Tunable Optical Parametric Oscillator. The temperature of the sample was controlled using a THMS 600 heating–cooling stage from Linkam (0.1°C temperature stability and 0.1°C set point resolution).

The excitation spectra and luminescence decay profiles were recorded using a FLS1000 fluorescence spectrometer from Edinburgh Instruments with a 450 W xenon lamp and a µFlash lamp as excitation sources and a R928P side window photomultiplier tube from Hamamatsu as a detector.

Due to obtaining the results of relative sensitivity with lower uncertainty, all of the LIR values were fitted according to the Mott–Seitz equation (Equation S1, Supporting Information).

Along with the temperature sensitivity, the brightness of the phosphor material is also crucial to the thermometric performance. Quantifying signal levels on powder samples is ambiguous as the optical state is not well defined and therefore a method based on probing phosphor particles dispersed in liquid was recently developed.[44] This method was applied here to the four AV₅O₄ samples. For each sample, 10 mg of the phosphor powder was dispersed in 20 mL deionized water, yielding a standard dispersion with concentration 500 mg L⁻¹. An ultrasonic homogenizer (Bandelin Sonopuls HD 2200) was used to disperse and break agglomerated particles. As a result, milky dispersions of Lu₂VO₄, YVO₄, and GdVO₄ were obtained. In the case of the LaVO₄ dispersion, large agglomerates could be observed with the naked eye. Therefore, the latter dispersion was left stirring for 24 h, after which a milky solution was obtained. Each mixture was further diluted to obtain a dispersion with a mass load of 20 mg L⁻¹, prepared in a 30 mL fused silica cuvette. The cuvette was stirred continuously using a small magnetic stirring bar during the spectroscopic measurements.

The particle dispersions were illuminated with the fourth harmonic 266 nm of a Nd:YAG laser (Quanta-Ray, Spectra-Physics) with 10 ns pulse duration, and operated at 10 Hz. The luminescence emitted by the dispersed phosphors was collected using a 50 mm f/4 camera objective lens (Nikon) focused at infinity. The collected light was spectrally dispersed using a 300 mm focal length spectrometer (Superpro: HRS-300, Princeton Instruments) with a grating groove density of 300 g mm⁻¹ blazed at 300 nm, and a 200 µm entrance slit width. To avoid scattered laser light entering the spectrometer, a long pass filter (WG295) was placed in front of the lens. Emission spectra were recorded using an intensified CCD camera (LaVision IRO and Imager Intense) set to a gate of 990 µs to collect the whole luminescence decay. The transmission efficiency of the collection system was calibrated using the reference spectrum of a tungsten halogen lamp (LS-1, Ocean Optics). To convert the recorded emission spectrum to quantitative luminescence emission in terms of photons nm⁻² ms⁻¹, the method described in Fond et al.[45] was applied.

Temperature Imaging System: A two-LED single-camera temperature imaging system was set up. For this, a metal plate coated with YVO₄: Eu was illuminated by light pulses from two LEDs at 275 and 340 nm, respectively, which were separated in time. The luminescence emission was captured by a camera, and the ratio of the two emissions recorded for each of the two illumination wavelengths was extracted to derive the temperature map. The ratio response of the temperature imaging system was first calibrated by recording data when the plate was homogeneously heated or cooled with a temperature-controlled unit. A demonstration experiment was performed by heating the plate from the back using a burner while measuring the transient temperature maps on the plate.

Phosphor Coating Procedure: To prepare a phosphor paint which can be applied to a large area, 150 mg of YVO₄:1% Eu³⁺ phosphor powder was diluted in 24 mL of distilled water and 7 mL of coating binder (HPC, ZVP Coatings). The solution was mixed for 5 min using the ultrasonic homogenizer. The prepared mixture was then air sprayed onto a 1 mm thick aluminum plate using an in-house-built automatic spraying system consisting of an airbrush and a 3D printer frame. The plate was dried at ambient temperature for 48 h. A homogeneous coating with dimensions of 4 × 4 cm was achieved with a thickness of 30 µm as measured with a gauge micrometer.

To calibrate the response of the system at a prescribed temperature, the plate was placed on heating–cooling stage consisting of an aluminum body with internal channels through which silicon oil flows at a prescribed temperature, which is described in Dragomirov et al.[46] The temperatures of the aluminum body and of the fluid were monitored with thermocouples in the solid body and in the oil flow and the accuracy of temperature determination at the center of the plate was of the order of 1°C. To heat up the plate nonuniformly, the outlet of a 2 mm diameter premixed flame burner was directed toward the back of the coated plate.

To exploit temperature-dependent excitation dynamics of AV₅O₄:Eu³⁺ phosphors for temperature measurements, two low-power LEDs, emitting at 275 nm (Roithner Lasertechnik UVTOP270-HL-T039, 0.6 mW) and 340 nm (Roithner Lasertechnik DUV340-HL5N, 1.0 mW), both fitted with a hemispheric lens were used. The two diverging LED beams were placed at 90° and overlapped using a UV beam splitter to homogenously illuminate a 3 cm × 3 cm area of the phosphor coating plate from a single direction. The luminescence emission was imaged onto a 12 bit CCD camera (LaVision, Imager Intense) using a 50 mm f/1.4 lens.

The plate was sequentially illuminated by the 275 and 340 nm LED, so that two consecutive frames correspond to two separate illumination wavelengths. For this, each LED was therefore triggered at 2.5 Hz, which is half the recording frequency of the camera (5 Hz) by utilizing an SRS.
pulse/delay generator (Model DG535, Stanford Research Systems). Thus, the phosphor emission signal from two precisely controlled excitation pulses could be recorded sequentially in two consecutive exposures. The duration of each LED pulse was set at 50 ms, corresponding to a quarter of the recording period, as limited by the readout time of the camera of 150 ms for the full-resolution image (1.4 megapixel). A long pass 570 nm filter (Schott OG570) was used to collect the Eu$^{3+}$ luminescence and reject excitation light.

The luminescence images were background subtracted using images with the LED off, and 4 x 4 software binned using MATLAB to yield a spatial resolution of 100 μm. It was chosen to bin the images in posttreatment and not in hardware to maximize the camera dynamic range. Ratio images were derived from each image pair. As shown in Figure S17a, Supporting Information, raw images of the plate at room temperature have a slightly different intensity distribution due to differences in the LED emission pattern. This results in the nonuniform ratio shown in Figure S17b, Supporting Information. To correct for this, ratio images obtained under an arbitrary condition were divided by an average ratio image obtained at room temperature where the temperature of the plate was uniform.

Finally, the corrected ratio images were converted to temperature using calibration data obtained when the phosphor plate was maintained at prescribed temperatures. At each temperature, the ratios obtained from 75 image pairs were temporally and spatially averaged. A power law was fitted to this ratio ($\phi$) versus temperature (T) curve to extract the function $f = T(\phi)$ used to convert the corrected-ratio image to the temperature in the burner experiment.

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

The data that support the findings of this study are available on request from the corresponding author.

Keywords

europium, lanthanide ions, luminescent thermometry, sensitization by transition metals, temperature-sensitive paints, vanadate group

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