ABSTRACT: A new thermographic nanocrystalline Sr₄Al₁₄O₃₅:Mn⁴⁺,Tb³⁺ phosphor was developed, and the concentrations of both dopants and the synthesis conditions were optimized. The combination of the thermally quenched luminescence from the Mn⁴⁺ ions to the almost temperature-independent emission from Tb³⁺ provides a sensitive luminescent thermometer ($S_R = 2.8%/°C$ at 150 °C) with strong emission color variability. In addition, a figure of merit for this luminescence thermochromism was proposed, as the relative sensitivities of the $x$ and $y$ CIE coordinates, which for this phosphor reaches at 150 °C $S_R(x) = 0.6%/°C$ and $S_R(y) = 0.4%/°C$, respectively. Noncontact thermal imaging was demonstrated with this phosphor using a single consumer digital camera and exploiting the ratio of red (R) and green (G) channels of the RGB images, thereby confirming the high application potential of Sr₄Al₁₄O₃₅:Mn⁴⁺,Tb³⁺ nanocrystals for thermal sensing and mapping.

KEYWORDS: manganese, terbium, Sr₄Al₁₄O₃₅ nanocrystals, luminescent thermometer, thermal imaging, thermochromicity, chromatic coordinates, relative sensitivity

INTRODUCTION

Luminescence thermometry (LT) is a class of optical techniques exploiting the temperature dependence of luminescence processes of tracers introduced in transparent fluids or solids or coated onto surfaces to measure their temperature remotely.¹⁻⁶ By allowing spatial, temporal, and spectral discrimination in both laser excitation and luminescence detection processes, luminescence thermometry allows remote sensing with high spatial and temporal resolution and can be applied in environments with high luminosity, which are significant advantages against intrusive probes and infrared thermography.⁷⁻¹⁰ These lend LT a large application potential, in particular for nanothermometry, for example, on microelectronics,¹¹ lab-on-a-chip systems,¹² and in biomedicine;¹³⁻¹⁴ for the study of rapidly varying phenomena, for example, in fluid flows¹⁴ or on rotating parts;¹⁵ and for robust thermometry in harsh environments with significant luminosity, for example, on burning materials¹⁶ or in internal combustion engines.¹⁶ Among luminescence thermometers, inorganic phosphors doped with transition metals (TM) and lanthanides ions are particularly attractive because of their high thermochemical and photo stability.¹⁷

Lanthanide (Ln)-doped thermographic phosphors are some of the most commonly used materials for this type of applications. However, it is well-known that for f–f electronic transitions occurring in Ln³⁺ ions, multiphonon relaxation is usually responsible for thermal quenching of the whole luminescence emission, which occurs only at elevated temperature. This has the advantage of a detectable emission over wide temperature ranges, with measurements reported up to 1400 K,¹⁸ but it also results in the limited temperature sensitivity of this response around ambient temperature when the goal is to detect smaller temperature variations. On the other hand, TM ions are well-known for their strong susceptibility to thermal quenching, which has the additional advantage that it can be tuned by the strong susceptibility of the energy levels positions on the choice of host. However, for robust temperature measurements, monitoring only the absolute intensity of the quenched luminescence emission is not adequate because this signal is also linked to the local excitation intensity, the concentration of the luminescence tracer and losses in the detection systems. Instead, the decrease in the luminescence lifetime as a result of this quenching is
often preferred as it uses temporal separation to achieve self-reference measurement but this requires using pulsed excitation and multiple detection gates.\textsuperscript{19,20} Another approach is to simultaneously detect the luminescence emission from another independent radiative transition, which is temperature insensitive and therefore acts as a reference to extract a temperature dependent ratio of intensities. In the approach presented here, this role is assumed by a codoped trivalent lanthanide ion because Ln\textsuperscript{3+} ions exhibit high quenching temperature, which can then be monitored by a single color sensor of the temperature gradient in a powder stud placed in contact with a hotter body.

Among all TM ions, the Mn\textsuperscript{4+} ion is one of the most promising ones because of its bright red emission. Mn\textsuperscript{4+} ions, which prefer to occupy octahedral sites are characterized by a strong crystal field strength (CFS) caused by their high positive effective charge. This crystal field does not affect the location of the emission band, but it determines the rate of its thermal quenching.

When selecting the lanthanide dopant to act as the reference emitter, it is important to choose one with emission lines that do not spectrally overlap with the temperature probe band. Additionally, Mn\textsuperscript{4+} emission being in the red region, choosing a reference emission located in the blue or green region would lead to a high variability in the emission color output with temperature, which can then be monitored by a single color sensor array, greatly simplifying the verification of the temperature change. Therefore, in this particular case, the Tb\textsuperscript{3+} ion with its intense green emission was used for this purpose.\textsuperscript{21} Finally, the selection of the host material is also very important in the design of luminescence thermometers. This choice should be oriented toward high thermal and mechanical stability and an appropriate local symmetry around the ionic sites, which will be occupied by the dopant ions. The SrO\textsubscript{−}Al\textsubscript{2}O\textsubscript{3} system seems to be a proper host for TM and Ln\textsuperscript{3+} dopant because the small difference in the ionic radii between strontium (132 and 140 pm for 6- and 8-coordinated Sr\textsuperscript{2+}, respectively) and aluminum ions (53 and 67.5 pm for Al\textsuperscript{3+}) in tetrahedral and octahedral coordination, respectively. Among six different structures, Sr\textsubscript{2}Al\textsubscript{4}O\textsubscript{7} and Sr\textsubscript{2}Al\textsubscript{14}O\textsubscript{25} arouse big interest as bright luminescence emissions from trivalent Ln ions (especially Eu\textsuperscript{3+},\textsuperscript{22−25} Ce\textsuperscript{3+},\textsuperscript{25} and Dy\textsuperscript{3+}\textsuperscript{23,24}) were reported in that matrix. However, when those structures are doped with Mn\textsuperscript{4+} ions, the difference in optical response is noticeable, that is, no emission of manganese in SrAl\textsubscript{2}O\textsubscript{4}:Mn\textsuperscript{4+} was observed\textsuperscript{22} while for Sr\textsubscript{2}Al\textsubscript{14}O\textsubscript{25}:Mn\textsuperscript{4+} intense red luminescence was reported. It indicates that in SrAl\textsubscript{2}O\textsubscript{4} nanocrystals, Al\textsuperscript{3+} ions are substituted by Mn\textsuperscript{3+} ions whose emission is seldom observed rather than by Mn\textsuperscript{4+} ions whose emission is clearly visible in the Sr\textsubscript{2}Al\textsubscript{14}O\textsubscript{25} (hereinafter SAO) host. In the SAO structure, two Sr\textsuperscript{2+} sites that can be found. This great number of possible crystallographic positions enable the significant modification of their spectroscopic properties and makes SAO an especially interesting host for LT applications.

In this work, a detailed structural and luminescence characterization study is presented, which is aimed at optimizing the synthesis conditions and dopant concentrations to obtain a highly sensitive ratiometric LT. The conducted research is devoted to obtain a thermometric phosphor with a high variability of the emission color with temperature. A proof of concept experiment is then presented, which exploits the luminescence thermochromism of SAO:Mn\textsuperscript{4+}, Tb\textsuperscript{3+} nanocrystals with a consumer digital camera to image transient temperature gradient in a powder stud placed in contact with a hotter body.

RESULTS AND DISCUSSION

Structural and Morphological Characterization. The SAO host crystallizes in an orthorhombic system of centrosymmetric Pnma space group (a = 24.785, b = 8.487, and c = 4.866 Å). According to the bond valence theory, the crystal lattice is composed of two double layers made up of (AlO\textsubscript{4})\textsuperscript{5−} tetrahedra, which are similar to a SrAl\textsubscript{2}O\textsubscript{4} unit cell separated by an (AlO\textsubscript{6})\textsuperscript{6−} octahedral layer (Figure 1a). In a single unit cell that is composed of two formula units, there are three inequivalent tetrahedral Al\textsuperscript{3+} sites (Al\textsubscript{1}, Al\textsubscript{2}, and Al\textsubscript{3}) and three octahedral ones (Al\textsubscript{4}, Al\textsubscript{5}, and Al\textsubscript{6}). Strontium ions are
located in two different sites, that is, the Sr and the Al, with 7- and 10-fold coordination to oxygen ions, respectively.22,26,27 Because of the similar ionic radii, the Mn ions occupy the Al sites in this structure (Shannon ionic radius equals 67.5 pm for both Al and Mn in octahedral coordination). However, strong covalent bonds make (AlO₄)²⁻ tetrahedra highly improper for Mn⁴⁺. Therefore, the most likely possibility is that Mn⁴⁺ ions incorporate into the (AlO₆)³⁻ octahedron. Moreover, according to Peng et al.,28 Mn⁴⁺ ions occupy the more covalent Al and Sr sites after doping, rather than the Al₆ site.

The 0.1% Mn⁴⁺ dopant concentration was based on the research of Peng et al.28 who showed that the most intense emission of SAO:Mn⁴⁺ can be obtained for this concentration. To optimize the synthesis conditions and understand the influence of annealing temperature on the phase purity, the X-ray powder diffraction (XRPD) patterns of SAO/0.1%Mn⁴⁺ samples annealed at 800, 900, 1000, and 1100 °C were measured (Figure 1b). At 800 °C, a wide band, which indicates a highly amorphous phase and only one diffraction peak matched to the ICSD 24249 pattern, which probably corresponds to SrO₂ presence, can be found. When the annealing temperature increases to 900 °C the amount of amorphous phase seems to decrease and XRPD peaks corresponding to Al₂O₃ (ICSD 9770), SrO (ICSD 163625), and SrO₂ appear. Finally, for annealing temperatures above 1000 °C patterns corresponding to a phase pure SAO structure are obtained (ICSD 88527). The broadening of the diffraction peaks in respect to the reference pattern is related to the small size of the SAO particles (Figure S1). For an annealing temperature of 1100 °C, no evidence of phase change or additional peaks were found. However, the significantly narrower diffraction peaks indicate an enlargement of the SAO nanoparticles. The ICP-OES (inductively coupled plasma optical emission spectrometry) measurements conducted for 0.1% Mn⁴⁺ and x% Tb³⁺ (x = 1, 5, 10, 20) codoped SAO powders annealed at 1000 °C confirm close to expected Tb³⁺ concentrations in those samples (Table S1). XRPD studies conducted for 0.1% Mn⁴⁺ and x% Tb³⁺ (x = 1, 5, 10, 20, 50) codoped SAO powders annealed at 1000 °C indicate that the samples with 1 and 5% Tb³⁺ concentration are characterized by pure SAO structure, while for 10 and 20% Tb³⁺ concentration, single peaks originating from SrO₂ (2θ = 51.5°) can be seen (Figure S2). The observed shift of the peak positions by around 0.03–0.08° toward higher angles in comparison to the reference pattern comes from the contraction of the cell size associated with the difference in the ionic radii between the Sr³⁺ ions and the smaller Tb³⁺ activator ions. In the case of the 0.1% Mn⁴⁺, 50% Tb³⁺ codoped powder, additional peaks which correspond to terbium, strontium, and aluminum oxides phases can be found indicating the dephasing of the SAO structure. The transmission electron microscopy (TEM) studies of SAO:Mn⁴⁺ nanocrystals annealed at 800, 900, 1000 and 1100 °C indicate well-crystallized and mostly agglomerated grains which are formed as two-dimensional sheet-like structures, similar to the SEM images obtained by Peng et al.28 (Figure S1c,e,g,i; additional TEM and selected-area electron diffraction (SAED) images for SAO:Mn⁴⁺ annealed at 800, 900, 1000, and 1100 °C can be seen in Figures S3–S6, respectively). The crystallization process that has already begun in samples annealed at 800 and 900 °C is confirmed by the presence of crystalline spots in Figure 1c,e and afterward by reflection spots observed on SAED patterns in Figures S3b and S4b. Diffuse rings noticed for nanoparticles annealed at 800 and 900 °C correspond to the presence of an amorphous phase, meanwhile the absence of those rings for nanocrystals annealed at 1000 and 1100 °C (Figures S5b and S6b) assures entire crystallization. The analysis of reflection spots shown in Figure S2b allows to confirm several crystallographic planes with the strongest intensities (Figure S7). The shape of the nanocrystal resembling flat sheets makes the obtention of a high contrast difficult. For annealing temperatures above 800 °C, the attribution of planes is unclear because of superimposed reflections and a significant amount of theoretical values with similar interatomic spacing d_{hkl} and intensities. It is worth noting that the pattern observed on the 1100 °C sample (Figure S6b) affirms that the created crystal system is orthorhombic.29 The representative TEM images for SAO codoped with Mn⁴⁺ and Tb³⁺ ions annealed at 1000 °C are shown in Figure S8. The histograms for SAO:Mn⁴⁺ (Figure 1d,h,j) for 800, 900, 1000, 1100 °C, respectively) indicate that the average grain size increases with the annealing temperatures from 800 to 1100 °C as follows: 32, 45, 90, and 140 nm, respectively.

**Luminescent Properties Characterization.** In order to understand the spectroscopic properties of Mn⁴⁺ ions of d⁸ electron configuration, a schematic configurational coordinate diagram is performed in Figure 2a. The violet arrows represent λ₄₄ = 266 nm, used here, which enables the transition of the electrons from the ⁴A₂ ground state to the ⁴T₁ excited state.
Table 1. Comparison of Crystal Field Parameters for SAO:Mn⁴⁺

| annealing temperature [°C] | λ_{nm} [nm] | band maximum | Dq | CFS | B |
|---------------------------|------------|--------------|-----|-----|---|
| 1000                      | 652        | lower energy | 2205 | 3.24 | 680 |
|                           |            | 664          | 1968 | 1.71 | 1154 |
| 1100                      | 652        | lower energy | 2204 | 3.01 | 732 |
|                           |            | 664          | 2199 | 1.73 | 1273 |

Subsequently, nonradiative relaxation processes lead to the population of the ⁴E state which radiative depopulation leads to the generation of a red emission (the red arrow). The lack of distortion of the ⁴E state in respect to the ⁴A₂ one results in the occurrence of the narrow emission line at around 650 nm. That emission line, as well as the broad band centred at 664 nm, are ⁴E Stokes-like phonon sidebands which originate from electric dipole vibronic transitions induced by lattice vibrations.³⁰,³¹ Meanwhile, in accordance with the magnetic dipole nature, the zero-phonon line emission intensity is very weak and observed only in emission spectra measured below 40 K.³⁰,³² However, for the samples annealed at 800 and 900 °C, inhomogeneously broadened emission bands are observed, which results from the fact that emission from Mn⁴⁺ ions localized in different crystallographic sites contribute to the emission. This indicates a high fraction of amorphous phase and the presence of additional oxide phases. The two broad excitation bands, observed for SAO annealed at 1000 and 1100 °C (Figure 2b), are related to ⁴A₂ → ⁴T₂ (centred in 449–460 nm range) and ⁴A₂ → ⁴T₁ (312–338 nm) spin-allowed transitions. The spectroscopic properties of SAO powders were examined in a wide temperature range from −150 to 270 °C (Figure 2c) in which, as a consequence of the presence of an intersection point between the ⁴E and ⁴T₂ parabolas, a luminescence thermal quenching process occurs. At elevated temperatures, the electronic population of higher vibronic levels of ⁴E state gradually increases. When the provided thermal energy is sufficient to overcome the intersection point (higher than ΔE₂) the ⁴T₁ state becomes populated which is followed by its rapid nonradiative depopulation to the ground state.³³,³⁴ Therefore, ΔE₂ is a crucial parameter from the thermometric point of view. Its value can be directly determined from the emission intensity versus temperature plot (Figure S9) according to the eq 1

\[
\frac{-\Delta E_2}{k} = \frac{1}{T} \ln \left( \frac{I_0}{I_{em}} - 1 \right)
\]

where I₀ is the initial emission intensity (in this case at T = −150 °C) and k is Boltzmann constant. At low temperatures ΔE₂ ≈ 0.31 eV (2466 cm⁻¹) was found.

The activation energy ΔE₂ depends on the relative positions of the ⁴T₂ and ⁴E parabolas. However, since the spectral position of the ⁴E → ⁴A₂ emission band does not change, the location of the ⁴T₂ state determines ΔE₂ which in turn is associated with the CFS. Empirical equations for Dq, local CFS and the Racah parameter B (eqs 2–4) were applied³⁵–³⁷ and compiled in Table 1.

\[
Dq = \frac{E_2(⁴A₂ → ⁴T₂)}{10}
\]

\[
x = \frac{E_2(⁴A₂ → ⁴T₁) - E_2(⁴A₂ → ⁴T₂)}{Dq}
\]

\[
\text{CFS} \equiv \frac{Dq}{B} = \frac{15(x - 8)}{x^2 - 9x}
\]

The spectral positions of particular bands were determined based on the excitation spectra (Figure 2b) obtained for λ_{nm} = 652 and 664 nm for SAO:Mn⁴⁺ annealed at 1000 and 1100 °C, respectively. The broadening of the excitation bands related with ⁴A₂ → ⁴T₂ and ⁴A₂ → ⁴T₁ electronic transitions results from the fact that they are superpositions of those bands for different Al³⁺ sites (octahedral Al₆, Al₄ and Al₃) occupied by Mn⁴⁺ ions.³⁸ To examine that, the CFS values for both samples are compared as a function of R_{av}⁻ and R_{min}⁻ (where R_{av} and R_{min} are average and minimum metal–oxygen distance, respectively) for Al₆, Al₄ and Al₃ sites (Figure S10). According to the band assignment theory of Peng et al., the correlation observed for the 1000 °C sample would indicate that the excitation bands at 19683 cm⁻¹ (~508 nm) and at 29842 cm⁻¹ (335 nm) can be ascribed to the Mn⁴⁺ ion in the Al₃ position and those at 2204 cm⁻¹ (453.5 nm) and at 29226 cm⁻¹ (342 nm) to the Al₆ site. In accordance with the Tanabe–Sugano diagram for the configuration of the minimum of ⁴T₁, is localized beyond the ⁴E parabola [16] [25] in the case of strong CFS approximation (namely, above 1.7), due to the fact that ⁴E is t₂₂ electronic orbital derivative whereas ⁴T₁ originates from t₁₂.

The thermal evolution of the integral emission intensities of Mn⁴⁺ ions for SAO annealed at 1000 and 1100 °C presented in Figure 2d (see also Figure S11) indicates that up to 90 °C no significant difference in the luminescence thermal stability between these two samples can be found. However, above 90 °C, faster thermal quenching was noticed for the sample annealed at 1000 °C. In this case at 210 °C, the emission is totally quenched, while for the sample annealed at 1100 °C, the emission can still be observed until 290 °C. Because of the fact that sidebands at 654 nm are quenched faster than the sideband at 670 nm, the integral intensity of the whole Mn⁴⁺ emission intensity was considered in further studies. The difference in the thermal dependence between these two signals can be explained by their thermal coupling, which was confirmed by the fitting procedure using the Boltzmann equation (see Figure S12).

Additionally, for a better understanding of de-excitation processes, the impact of the annealing temperature on the quantum yield (QY) was measured (Figure 2e) and an evident enhancement of the QY value with the increase in annealing temperature was noted. The values of QY were QY⁹⁰ = 0.11%, QY⁹⁰⁰ = 2.56%, QY¹⁰⁰⁰ = 3.81%, QY¹¹⁰⁰ = 11.95%, respectively. It can clearly be seen that the reduction of the nonradiative losses associated with the high fraction of surface effects results in an enhancement of the QY by about one order of magnitude.

**Optimization of the Co-dopant Concentration.** If another emission presenting a different thermal quenching behavior than that from the Mn⁴⁺ ions could be probed simultaneously, then the ratio of the intensities of the two emissions could be used as a robust temperature readout.
Here, Tb$^{3+}$ ions, which emission typically only quenches at high temperatures, were selected to provide the reference emission. In order to optimize the Tb$^{3+}$ concentration, spectroscopic properties of a series of SAO:0.1% Mn$^{4+},x$% Tb$^{3+}$ powders ($x = 1; 5; 10; 20$) annealed at 1000 °C were examined in a wide temperature range. The emission spectra of the obtained nanocrystals exhibit beside the previously described Mn$^{4+}$ emission bands, three additional bands at 490 nm, 545 nm, and 587 nm associated with the $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, and $^5D_4 \rightarrow ^7F_4$ electronic transitions of Tb$^{3+}$ ions (Figure 3a). Excitation spectra were also measured for Tb$^{3+}$ ions, by monitoring at 545 nm (Figure S13a). Among others, the peaks correspond to transitions between the ground state $^7F_6$ and subsequent levels $^5H_5$ (301 nm), $^5H_7$ (318 nm), $^5L_6$ (340 nm), $^5G_4$ (355 nm), $^5G_5$ (362 nm), and $^5L_{10}$ (370 nm) states. A broad excitation band with maximum intensity (centered in the range 373–378 nm) originates from the $^7F_6 \rightarrow ^5D_4$ electronic transition of Tb$^{3+}$ ions. Interestingly, the Mn$^{4+}$ excitation bands previously described are absent in the excitation spectra for Tb$^{3+}$, which indicates that there is no Mn$^{4+} \rightarrow$ Tb$^{3+}$ energy transfer (Figure S13a). Analogously, excitation spectra measured for $\lambda_{em} = 654$ nm (Mn$^{4+}$ emission) consist only of Mn$^{4+}$ absorption bands (Figure S13b). The lack of interionic energy transfer reveals that the f states of Tb$^{3+}$ ions are directly excited confirming their high performance as a luminescent reference.

It is noteworthy that the contribution of the Tb$^{3+}$ luminescence in the emission spectra of SAO:Mn$^{4+}$,Tb$^{3+}$ depends on the Tb$^{3+}$ concentration. The room temperature emission spectra clearly indicate that with the increase of the Tb$^{3+}$ amount up to 10% of Tb$^{3+}$ ions, an enhancement of the Tb$^{3+}$ emission intensity in respect to the Mn$^{4+}$ one can be observed (Figure 3b). In the case of SAO:Mn$^{4+}$,20% Tb$^{3+}$, a slight lowering of the Tb$^{3+}$ emission intensity can be found, which can be explained in terms of either structural changes for this sample or by the energy migration among the excited states of Tb$^{3+}$ ions toward the surface quenchers. This concentration effect has natural implications in the change of the emission color. Chromatic coordinates (CIE 1931) for all samples are located in the red region, wherein the impact of the Tb$^{3+}$ concentration is substantial. The enhancement of the Tb$^{3+}$ concentration causes a shift of the emission color toward the orange region (Figure 3c).

The analysis of the kinetics of the excited states of Mn$^{4+}$ and Tb$^{3+}$ ions provides additional insight into the process of light generation in the SAO:Mn$^{4+}$,Tb$^{3+}$ nanocrystals (Figures 3d and S14). Surprisingly the lifetime of the $^2E$ state of Mn$^{4+}$ increases from 1.65 ms for SAO:Mn$^{4+}$,1% Tb$^{3+}$ to 2.08 ms for SAO:Mn$^{4+}$,5% Tb$^{3+}$. The origin of this effect is not clear but is probably related to the modification of the Mn$^{4+}$ local ions symmetry by the introduction of the Tb$^{3+}$ ions causing a lowering of the probability of radiative depopulation of the $^2E$ state. As seen, above 5%, increasing the Tb$^{3+}$ concentration does not affect the decay constant of the $^2E$ excited state of Mn$^{4+}$, which would agree with the lack of the interionic energy transfer between Mn$^{4+}$ and Tb$^{3+}$ ions previously discussed basing on the excitation spectra analysis.

The thermal evolution of the emission spectrum of the SAO:0.1% Mn$^{4+}$,5% Tb$^{3+}$ phosphor, representative of the behavior, is shown in Figure 4a (the thermal evolution of the emission spectrum for all Tb$^{3+}$ concentration can be found in Figure S15). Similarly to outcomes observed in SAO:Mn$^{4+}$,
powders, in codoped nanoparticles, the intensity of the manganese emission is also gradually quenched up to about 210 °C, which guarantees a high temperature sensitivity. On the other hand, the Tb³⁺ emission intensity is temperature independent, which results from the high energy gap between emitting ⁵D₄ and the next lower laying ⁷F₀ state (above 14,000 cm⁻¹). This sufficiently prevents the ⁵D₄ state depopulation via the multiphonon processes and thus thermal quenching of Tb³⁺ luminescence. Surprisingly, a high Tb³⁺ dopant concentration increases the rate of thermal quenching of the ⁷F⁻→⁵D₂ electronic transition at temperatures above 150 °C. The most significant changes of the Mn⁺⁺⁺ luminescence were found in the case of SAO:Mn⁴⁺,5% Tb³⁺ ions, for which a decrease by three orders of magnitude was noted. On the other hand, the emission intensity of Tb³⁺ at 545 nm becomes almost temperature-independent in a wide range, namely, from −150 to 300 °C, which facilitates the ratiometric temperature readout. To verify this thesis, the luminescence intensity ratio (LIR) defined as follows

\[
\text{LIR} = \frac{\text{⁷F} \rightarrow \text{⁵D₄}(\text{Mn}^{4+})}{\text{⁵D₄} \rightarrow \text{⁷F₅}(\text{ Tb}^{3+})}
\]  

was used as a thermometric parameter (Figure 4b). Below 50 °C only a slight change of LIR can be found independently of the Tb³⁺ concentration. However, above 50 °C, a drastic decrease of the LIR by over two orders of magnitude can be observed, which results from the significant quenching of Mn⁺⁺⁺ emission intensity. To quantify the observed thermally induced changes, the relative sensitivity of SAO:Mn⁴⁺,Tb³⁺ nanomaterials powder to temperature changes was calculated as follows

\[
S_r = \frac{1}{\text{LIR}} \times \frac{\Delta \text{LIR}}{\Delta T} \times 100\%
\]  

where ΔLIR represents change of LIR corresponding to ΔT change of temperature (Figure 4c). Independently on Tb³⁺ concentration, at temperatures below 50 °C the S_r ~ 0.5%/°C was found. Above this critical temperature the enhancement of S_r up to 2.8%/°C at 150 °C was noticed. For a Tb³⁺ concentration of 5%, a relative sensitivity over 2%/°C was maintained over a temperature range as wide as 150 °C (80–230 °C). The further increase of the Tb³⁺ amount to 20% results in the gradual narrowing of the temperature range, in which this high relative sensitivity was obtained to only 90 °C (the range from 80 to 170 °C). Excitation spectra measured over the −150 to 300 °C temperature range for the representative SAO:0.1% Mn⁴⁺,5% MnTb³⁺ powder when monitoring the Tb³⁺ (Figure S16a) and Mn⁺⁺⁺ (Figure S16b) emissions do not show any thermally induced change in the band position and shape. This indicates the CFS does not change with temperature. Moreover, the thermometry performance of SAO:Mn⁴⁺,Tb³⁺ powder in terms of stability was confirmed by measurements of the LIR readout within 10 heating-cooling cycles (Figure S17), which showed excellent repeatability (maximum deviation of 1.9%). In order to determine the useful temperature range, the signal to noise ratio-based LIR uncertainty at each temperature was converted using the relative temperature sensitivity into a temperature uncertainty (Figure S18). A value of δT = 0.5 °C within the 50–210 °C temperature range promises a high performance in that range. An additional advantage of the SAO:Mn⁴⁺,Tb³⁺ thermographic phosphor is the great variability of its emission color with temperature (Figure 4d). The emission color shifts from bright red at 0 °C to green at 300 °C. These changes, visible to the naked eye, are confirmed by the strong shift of the chromatic CIE coordinates from red to green shown in Figure 4c. Thermographic phosphors with a high variability in their emission colors are of great importance as their temperature can be measured with a single color array, which makes for an easy to use and inexpensive temperature sensor, which can be used, for example, for the early detection of overheating spots on different surfaces. Several studies have reported using a CIE diagram a strong color response of some luminous compounds for thermometry. In order to, in the future, compare the thermochromic performance of these materials, we, for the first time, suggest to consider the relative sensitivity of the emission color CIE coordinate as figure of merit parameters \[S_χ(x), S_χ(y) calculated using eq 6\]. These parameters would be the chromatic counterpart of the relative sensitivity, which is an accepted figure of merit for the ratio of intensities between transitions from thermalized levels. In the case of SAO:0.1% Mn⁴⁺,5% Tb³⁺ nanocrystals, chromatic relative sensitivities as high as \[S_χ(x) = 0.6%/°C and S_χ(y) = 0.4%/°C\] were found at 150 °C. In addition, as shown in Figure S19, the Mn⁴⁺ and Tb³⁺ emission are located in regions where there is very little overlap between the color filter curves of consumer digital cameras, so that the two emission can be almost completely separated between the red and the green channel.

**Proof-of-Concept Temperature Imaging Experiment.**

The applicative potential of SAO:0.1% Mn⁴⁺,5% Tb³⁺ nanocrystals for noncontact temperature sensing was verified by a proof-of-concept experiment (Figure 5). A quartz tube (5 mm in diameter) was filled with the SAO:0.1% Mn⁴⁺,5% Tb³⁺ powder and placed on a heating plate at a temperature of 25 °C. At \(t = 0\) the set point temperature of the heating plate was increased up to 250 °C and from there on, every 5 s, digital color camera images (Figure 5a) and infrared thermography
camera images (Figure 5b) were recorded. It can clearly be seen that upon 256 nm excitation light, the emission of the powder, which is intense red at the start of the experiment gradually changes with time into green, as heat diffuses from the plate into the power. The profile of the color change along the line shown in Figure 5c was analyzed (see also Figure S20). Because of the fact that CIE coordinates of SAO Mn$^{4+}$, Tb$^{3+}$ nanocrystals changes from red to green in the analyzed temperature range, the noncontact temperature readout using a digital camera may be simplified to the analysis of the intensity of red (R) and green (G) channels of RGB color images (Figure 5d–g). This allows to obtain two-dimensional LIR images, from which a profile as a function of the distance from the heating plate was plotted at different t (Figure 5h). This profile is then converted to temperature using a calibration curve obtained by measuring the LIR at different controlled temperatures (monitored by the thermal imager) under steady state conditions (Figure S21), and is shown in Figure 5h. As shown, with time, the maximum thermal gradient decreases while its spatial extent increases, which is a textbook demonstration of 14 line pairs per mm.

Figure 5h. As shown, the maximum thermal gradient decreases while its spatial extent increases, which is a textbook demonstration of the one-dimensional time-dependent heat equation. To assess the measurement uncertainty, the temperature profile obtained from the luminescence and from the IR imager were compared. Until t = 70 s, the maximum deviation between the profiles is about $5{^{\circ}}$C, which demonstrates excellent accuracy in the range 25–150 °C (Figure S22). At t = 90 s, larger deviations are observed, which may be explained by two factors. As the plate temperature increases, the amount of thermal radiation emitted from the plate and reflected by the tube, which has a reflectivity of (1 − $\varepsilon$), where $\varepsilon$ is the emissivity, grows with the fourth power of the plate temperature. This can lead to an overestimation of the tube temperature. Reflection radiation interference is a well-known issue of IR thermography, which is also discussed in ref 46. The emissivity of quartz, which is measured as 0.93 at 40 °C, decreases with temperature. It is also worth noticing that the thermal imager measures mainly the tube temperature while luminescence thermometry measures the powder temperature, which thermal profiles may differ. In addition, above 200 °C, the signal in the red channel approaches the noise floor so that nonlinearity and signal interference may alter the temperature reading of the luminescence thermometry. However, as reported in ref 49, the camera includes an IR blocking filter, which may be lead to a 75% signal loss in the red channel. Removing this filter should allow to increase the temperature range of this thermal imaging concept. Finally, using an RGB image of the powder on the heated plate under steady state conditions, the deviation from a uniform temperature field was used to estimate the random uncertainty or precision of the technique for single exposures, which was found to be better than 1.6 °C at 150 °C and for a resolution of 14 line pairs per mm.

This experiment clearly confirms the high application potential of SAO:Mn$^{4+}$,Tb$^{3+}$ nanocrystals for temperature imaging using a simple and cheap digital camera. Additionally, it is worth noticing that in contrary to the thermovision camera, no information concerning the emissivity of the object is required.

### CONCLUSIONS

In this work, step-by-step optimization of the synthesis condition and Tb$^{3+}$ dopant concentration of SAO:Mn$^{4+}$,Tb$^{3+}$ nanocrystals was presented in order to obtain a highly sensitive ratiometric luminescent thermometer. It was found that above 100 °C the intense red emission of SAO:Mn$^{4+}$,Tb$^{3+}$ nanocrystals associated with the $^4E \rightarrow ^4A_2$ electronic transition of Mn$^{4+}$ ions was drastically quenched while the $^5D_4 \rightarrow ^7F_5$ emission of Tb$^{3+}$ stayed almost thermally independent. The SAO-0.1% Mn$^{4+}$,5% Tb$^{3+}$ nanocrystals displayed a thermal sensitivity above 2%/°C over the range 80–250 °C with a maximum of $S_\text{T} = 2.8%/{^{\circ}}$C at 150 °C. Because of the distinct spectral location of the emissions from the two ions, the thermal quenching of the Mn$^{4+}$ emission was associated with a pronounced change in emission color, which can be captured by a consumer digital camera, as shown in the proof-of-concept experiment. For future comparison, a chromatic temperature sensitivity was quantified as a figure of merit on the basis of the x and y coordinates.

The developed nanophosphors were demonstrated to provide sensitive temperature measurements in the range of 25–150 °C, which includes the boiling point of liquids used for spray cooling and the glass transition temperature of polymers used in 3D printing, and which is also relevant to the thermal management of batteries, fuel cells, and electric motors. Those applications demand the observation of complex thermal phenomena which impacts the performance but the implementation of IR thermography is not possible because of the opacity of liquids and polymers, and to reflections of thermal radiation by inner surfaces of battery, fuel cell, and motor assemblies.6 This combined to the flexibility of the ratiometric approach and the simplicity of detection of color change with consumer cameras holds great promises for widespread use as a temperature imaging sensors in key industrial processes.

### MATERIALS AND METHODS

The SAO powders can be obtained using various synthesis procedures such as combustion, solid state reaction, or ceramic methods; however, a modified Pechini method was applied in this case because of its simplicity and the lower annealing temperatures in respect to other methods.47 $\text{Sr(NO}_3\text{)}_2$ (99.996% purity, Puratronic), $\text{Al(NO}_3\text{)}_3\cdot x\text{H}_2\text{O}$ ($x \approx 9$, 99.999% purity, Alfa Aesar), Mn(NO$_3$)$_2$·4$\text{H}_2\text{O}$ (99.999% purity, Sigma-Aldrich), Tb$_2$O$_3$ (99.999% purity, Stanford Materials Corporation), $\text{C}_2\text{H}_4\text{O}_2$ (>99.5% purity, Alfa Aesar), and H(OCH$_2$CH$_2$)$_2$OH, (PEG-200, Alfa Aesar) were used as starting materials. Stoichiometric amounts of aluminum, strontium, and manganese nitrates were dissolved in deionized water in separate glasses and then mixed together. Terbium oxide was dissolved in deionized water with the addition of a small amount of HNO$_3$ (65% purity, Avantor), then recrystallized three times to remove the excess nitrogen and added to the water solution of nitrates. After that, an anhydrous citric acid and polyglycol were added to the mixture of nitrates. The molar ratios of citric acid to all metals, and that of PEG-200 to citric acid were set to 6:1 and 1:1, respectively. Subsequently, the obtained solution was dried for 24 h at 100 °C until a resin was formed. The produced resin of the sample with 0.1% molar Mn$^{4+}$ concentration in respect to Al$^{3+}$ ions was annealed in porcelain crucibles for 12 h in air at 800, 900, 1000, and 1100 °C. The samples with 0.1% Mn$^{4+}$ and x % Tb$^{3+}$ ($x = 1, 5, 10, 20$) concentration in respect to the number of Sr$^{2+}$ ions were annealed for 12 h in air at a temperature of 1000 °C. All of the synthesized materials were examined by XRPD measurements carried out on a PANalytical X’Pert diffractometer, equipped with an Anton Paar TCU 1000 N temperature control unit, using Ni-filtered Cu $K\alpha$ radiation (V = 40 kV, I = 30 mA). The ICP-EOS measurements were taken using a Thermo Scientific ICAP 7000 spectrometer with a charge injection device detector.

Transmission electron microscope (TEM) images were taken using a Philips CM-20 SuperTwin TEM microscope. The samples were...
dispersed in methanol, and a droplet of such 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 (Feret diameter) of each particle. The emission spectra were measured using the 266 nm excitation line from a laser diode (20 mW) and a Silver-Nova Super Range TEC spectrometer from StellarNet (1 nm spectral resolution) as a detector. 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 FL980 Fluorescence spectrometer from Edinburgh Instruments with a 450 W xenon lamp and recorded using a FLS980 Fluorescence spectrometer from Edinburgh. The same procedure.

The quartz tube. No smoothing was applied to the image. LIR pro placed on the heating plate and LIR was calculated using the above-mentioned system equipped with an integrating sphere and Al₂O₃ powder as a reference. Average decay constant of the excited states was calculated as follows

\[ \tau = \frac{\int I(t) \cdot dt}{\int I(t) dt} \]  

(M1)

where \( I(t) \) represents the emission intensity at time \( t \). Thermovision images were collected using a T540 camera from FLIR.

The digital images were taken using a Canon EOS 400D camera with a EFS 60 mm macro lens using a 1 s integration time, 14.3 lp/mm spatial resolution. After capturing color images of the quartz cuvette filled with SAO:Mn⁴⁺,Tb³⁺ powder the emission maps for red and green channels (RGB) were extracted using IrfanView 64 4.51 software. After that obtained pictures were divided by each other using OriginLab 2019 Software in order to obtain LIR profiles along the quartz tube. No smoothing was applied to the image. LIR profiles were converted into temperature profiles using the calibration curve. To obtain this calibration curve, the SAO:Mn⁴⁺,Tb³⁺ powder was placed on the heating plate and LIR was calculated using the above-described procedure as a function of temperature. The temperature of the powder was controlled by the thermovision camera. The emissivity of the SAO:Mn⁴⁺,Tb³⁺ powder was estimated by the comparison of the temperature of the powder placed on the heating plate of constant temperature (40 °C monitored by IR camera) with the temperature of the Scotch 130C tape of standardized emissivity (0.95). The emissivity of the quartz tube has been estimated using the same procedure.

**ASSOCIATED CONTENT**

1. Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c11730.

Results of ICP-EOS, XRPD, TEM, and SAED measurements for different samples, graphs of CFS versus metal–oxide bond, emission intensity versus 1/T, thermal evolution of band integral intensities, graphical representation of the Boltzmann distribution through 1/T, excitation spectra in function of Tb³⁺ concentration and temperature, luminescent decays for Tb³⁺ concentration, comparison of the emission spectra with the color filter curves of consumer digital camera, photographs from digital and thermovision camera, and calibration curve as the LIR versus temperature (PDF)

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**Notes**

The authors declare no competing financial interest.

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