1. Introduction

Luminescence thermometry has emerged as a promising alternative for non-invasive, remote temperature sensing and relies on the temperature dependence of the optical signals of luminescent compounds.\(^1\)-\(^3\) Its potential as a local non-invasive temperature probe has been shown in several niche applications ranging from catalysis\(^4\),\(^5\) over biological processes\(^6\) to heat transport phenomena at the micro- and nanoscale.\(^7\)-\(^9\)

Various readout options exist such as the intensity of a signal, the luminescence decay time, width, or position of an emission band. Among the different methodological concepts,\(^10\)-\(^12\) especially the ratiometric intensity approach exploiting the emission from two thermally coupled excited levels has become popular due to its simplicity and possibility for the fast readout (by the usage of sensitive CCD cameras for example). If the two emission bands of interest arise from two thermally coupled excited levels of the same configuration, the luminescence intensity ratio expectedly follows Boltzmann's law and can be linearized if plotted in the correct way.\(^13\) This is particularly appealing for applications as linear calibration laws allow simple identification of systematic biases that are simple, and Boltzmann's law offers the possibility to readily verify the fitting parameter for its physical content.

Boltzmann-type thermalization between two excited levels and thus, the working concept of a ratiometric Boltzmann thermometer requires that the non-radiative transition rate responsible for the coupling of the two excited levels is larger than any radiative or non-radiative depopulation rate of the lower excited level.\(^13\),\(^14\) Otherwise, the excited levels decouple,
and thermometry with them is not possible anymore. Non-radiative transitions in crystalline solids rely on the thermal occupation of phonon modes and become faster with increasing temperature. However, the low-temperature onset for thermal coupling of the two excited levels depends on the ratio between the intrinsic non-radiative transition rate and radiative depopulation rate of the lower excited level. This ratio determines the dynamic working range of a luminescent Boltzmann thermometer.\(^1\)

The lanthanoid ions with their rich spin–orbit energy-level structure arising from the \(4f^n\) (\(n = 2–12\)) open-shell configuration are among the primary candidates for Boltzmann-based luminescence thermometry.\(^1\) Their emission is characterized by high quenching temperatures and narrow linewidths due to the intraconfigurational character of the optical transitions, which offers an intrinsically high resolution of peaks from thermally coupled excited levels. Among the most significant limitations of Boltzmann thermometers are, however, their typically small non-radiative coupling rates that only allow use of energy gaps in the order of the thermal energies of interest \((\Delta E_{23} \sim k_BT)\).

There are several luminescent thermometers that rely on thermalization between excited states with different equilibrium metal-ligand distances, which happens to enhance the non-radiative coupling strength between the thermalized states. One important class is dual-center energy transfer thermometers. Although very flexible, the temperature dependence of the luminescence intensity ratio is typically non-linear and requires more sophisticated (although physically still transparent!) modelling approaches.\(^{15–18}\) Another related class with similar properties to the excited states is so-called thermally coupled excited levels. Among the most significant limitations of Boltzmann thermometers are, however, their typically small non-radiative coupling rates that only allow use of energy gaps in the order of the thermal energies of interest \((\Delta E_{23} \sim k_BT)\).

It was our goal within this work to establish a generalized model for luminescent crossover thermometers and experimental tests that on the representative example of \(\text{SrB}_4\text{O}_7:0.5\% \text{Sm}^{2+}\). It is well-known that this tetraborate stabilizes several lanthanoid dopants in their divalent oxidation state even in the air. \(\text{Sm}^{2+}\) has a \(4f^6\) configuration and can be efficiently excited with blue light into the \(4f^55d^1\) configuration. This configuration is energetically close to the excited \(^3\text{D}_2\) \((J = 1, 2)\) spin-orbit levels,\(^{31,32}\) in contrast to its isoelectronic trivalent analogue \(\text{Eu}^{3+}\), in which the excited \(4f^55d^1\) electronic configuration is located in the vacuum UV range.\(^{33}\) This can be chemically intuitively understood by the much smaller absolute value of the reduction potential of \(\text{Sm}^{3+}/\text{Sm}^{2+}\) \((\Delta E^\circ = -1.55\ \text{V})\) compared to \(\text{Eu}^{3+}/\text{Eu}^{2+}\) \((\Delta E^\circ = +6.20\ \text{V})\).\(^{34}\) The energetic proximity of the \(4f^55d^1\) configuration and the radiatively emitting excited \(^5\text{D}_0\) level offers the desired conditions for a configurational crossover and gives rise to a temperature-dependent change in the appearance of the luminescence spectra of \(\text{Sm}^{2+}\) in \(\text{SrB}_4\text{O}_7\).\(^{31,32}\) We show that our proposed generalized fitting model for luminescent crossover thermometers is physically reasonable, and the parameters can be related to independent time-resolved studies. Based on the calibration model, it is possible to evaluate the performance of the luminescent thermometer and compare it to that obtained on the conventional Boltzmann thermometers.

\section{Experimental section}

\subsection{Synthesis}

Microcrystalline powder of \(\text{SrB}_4\text{O}_7:0.5\% \text{Sm}^{2+}\) was prepared by a conventional solid-state method as reported earlier.\(^{35}\) In detail, \(\text{SrCO}_3\) (Alrich, \(\geq 99.9\%\)), \(\text{H}_3\text{BO}_3\) (ChemSolutes, \(\geq 99.5\%\)), and the appropriate fraction of \(\text{Sm}_2\text{O}_3\) (abcr Chemicals, \(99.999\%\)) were intimately mixed in an agate mortar and preheated at 550 °C for 5 h with a ramp of 150 °C h\(^{-1}\) in a corundum crucible. After natural cooling to room temperature, the sintered powder was again intimately ground for 10 min and finally treated at 850 °C with the same heating ramp overnight. This heating step was repeated two more times with intermediate grinding steps. A reducing atmosphere was generated by placing the corundum crucibles on a bed of active charcoal in the
heating steps at 850 °C. The obtained powder was colourless and showed slight red luminescence upon excitation with a 365 nm UV lamp (10 W).

2.2. Characterization and methods

The purity of all microcrystalline samples was verified by powder X-ray diffraction in Debye-Schererrer/transmission geometry (Stoe & Cie STADI P, Cu Kα1 radiation filtered by a focussing Ge(111) monochromator, λ = 1.5406 Å; see Fig. S1 in the ESI†).

Optical measurements were performed on an FLS1000 photoluminescence spectrometer from Edinburgh Instruments equipped with a 450 W Xe arc lamp as an excitation source, double excitation and emission monochromators in Czerny-Turner configuration and a thermoelectrically cooled (−20 °C) photomultiplier tube PMT-980. The emission spectra were corrected with respect to the grating efficiency and PMT sensitivity, while excitation spectra were additionally corrected with respect to the lamp intensity. The decay traces of the intense 5D0 → 7F0-based emission of Sm2+ were measured with a laser diode VPL-420 (Edinburgh Instruments, 70 mW average incident peak power, λ = 423.2 nm) with adjustable temporal pulse width (0.1 μs...1 ms) and variable trigger frequency (0.1 Hz...5 MHz) as the pulsed excitation source. The laser could also be used in a continuous wave excitation mode. The detection mode for the time-resolved measurements was single-photon multi-channel scaling.

Temperature-dependent measurements were performed with a Linkam Scientific THMS600 temperature cell with temperature accuracy of ±0.1 °C in the regarded temperature range between room temperature and 300 °C. The temperature intervals were 25 °C.

3. Results and discussion

3.1. High-resolution luminescence spectra of Sm2+ in SrB4O7

Fig. 1 depicts high-resolution photoluminescence excitation and emission spectra of SrB2O3·0.5% Sm2+ at room temperature. While the excitation spectra are dominated by broad bands due to electric dipole allowed interconfigurational 4f6 → 4f55d1 transitions, the emission spectra at room temperature are dominated by the very narrow line emission due to the intraconfigurational 4f55d1(5D0) → 4f6(7Fj) transitions. The most intense line at 685 nm stems from the actually strongly forbidden 5D0 → 7F0 transition. The strong intensity is in stark contrast to most known cases of Eu3+-activated phosphors, in which that transition is only very weak (a known exception is, however, LaOBr:Eu3+38). This transition has also been considered a potential alternative for optical pressure sensing of the narrow R emission lines of Ca3+ in ruby (Al2O3·Ca3+).36,39

The high intensity of the 5D0 → 7F0 transition of Sm2+ is not readily explicable within the framework of Judd-Ofelt intensity theory of the 4f5 → 4f6 transitions but can be well-understood with the Wybourne-Downer mechanism instead.40-43 It is attributed to the high intensity of the induced electric dipole character to the 5D0 → 7F0 transition mediated by a spin–orbit interaction between the 4f5 and 4f55d1 levels of Sm2+, which is a third-order perturbative effect only. Since the 4f55d1 configuration is, however, energetically much closer to the 5D0 level in the case of Sm2+ in most inorganic host compounds, the Wybourne-Downer mechanism has a significant contribution. The strong 5D0 → 7F0-related line is accompanied by small peaks with an average separation of 90 cm−1 that can be assigned to vibronic sidebands.31 Their presence, together with the very narrow linewidth of the 4f6–4f6 transitions of Sm2+ indicates very weak vibronic coupling of the 4f6 levels, which is a characteristic feature of all 4f6–4f6 emissions of divalent and trivalent middle lanthanoid ions.44,45

A closer inspection of the luminescence spectra also reveals the presence of weak emission peaks from the higher energetic 5D1 spin–orbit level of Sm2+ in the range between 620 nm and
650 nm (see Fig. 1(b)). The luminescence spectra allow the determination of a $^5D_1 - ^7D_0$ separation of $\Delta E_{10} = 1330 \text{ cm}^{-1}$, in excellent agreement with literature-reported values.\textsuperscript{31,32,46} The presence of the three resolved lines for the $^5D_1 \rightarrow ^7F_0$ and $^5D_0 \rightarrow ^7F_1$ transition, respectively, is compatible with the local $C_5$ symmetry at the Sr sites in SrB$_4$O$_7$.

The luminescence decay traces upon excitation with 423 nm and monitoring the emission from the $^5D_1$ and $^5D_0$ levels are depicted in Fig. 2. Both show purely single exponential decay at room temperature. The energy separation between the $^5D_0$ and lower energetic $^7F_6$ levels is around 10 000 cm$^{-1}$ and the cut-off phonon energy of SrB$_4$O$_7$ is around 1300 cm$^{-1}$. In addition, no 4f$^5$5d$^1$ $\rightarrow$ 4f$^6$ broad-band luminescence is detectable at room temperature. Thus, decay from the $^5D_0 = [1]$ level can be assumed to be purely radiative at 298 K with a radiative decay rate of $k_{\text{rr}} = (0.193 \pm 0.001) \text{ ms}^{-1}$, which agrees perfectly well with previously reported rates.\textsuperscript{31,32,46}

3.2. Model for configurational crossover thermometers over a wide temperature range

Fig. 3 schematically depicts the potential energy curves of the excited $^5D_0$ and 4f$^5$5d$^1$-related electronic levels of Sm$^{2+}$ projected in configurational coordinate space, which are relevant for a thermal configurational crossover. It has been convincingly shown both theoretically\textsuperscript{47-50} and experimentally\textsuperscript{15,51-55} that upon excitation into the lowest energetic states of a 4f$^5$5d$^1$ configuration ($n = 1, 5, 6, 12, 13$), the lanthanoid-ligand distance decreases slightly. However, it should be noted that also a parabola with higher equilibrium distances would not change the following discussion. This is relevant for e.g. organic luminophors displaying thermally activated delayed fluorescence (TADF).

Thus, the potential energy curves of the lowest excited 4f$^5$5d$^1$ and 4f$^6$(5D$_0$) levels will necessarily cross. Moreover, the nature of the chemical metal-ligand bond in both states differs, translating into different curvatures of the potential energy curves. This case has been thoroughly treated theoretically by Struck and Fonger assuming harmonic potentials, which is a reasonable approximation in crystalline solids.\textsuperscript{56} They could show that for the two excited levels $|2\rangle$ and $|1\rangle$ with $\Delta E_{12} \geq 10^3 \text{ cm}^{-1}$ and non-negligible configurational coordinate offset, the non-radiative absorption rate can be described by Mott’s formula,

$$k_{\text{nr}}(T) = k_{\text{nr}}(0) \exp \left( -\frac{\Delta E_{12}}{k_B T} \right)$$

(1)

with $k_{\text{nr}}(0)$ as the intrinsic coupling rate and $\Delta E_{12}$ as the energy gap between the vibrational ground level of the bottom electronic state and the configurational crossover point.

In most typical cases, the activation barrier $\Delta E_{2X}$ from the vibrational ground level of the higher excited electronic state to the configurational crossover point is much lower, typically even $\Delta E_{2X} \ll k_B T$. Consequently, the corresponding non-radiative emission rate from the higher excited to the lower excited level is usually dominated by the intrinsic coupling rate $k_{\text{nr}}(0)$ and has a weak to negligible temperature dependence.

The steady-state population density ratio of the two excited levels can be generally derived as\textsuperscript{13,14}

$$\frac{n_2}{n_1} = \frac{z_{a2}k_{\text{rr}} + (z_{a1} + z_{a2})k_{\text{nr}}^{\text{abs}}(T)}{z_{a1}k_{\text{rr}} + (z_{a1} + z_{a2})k_{\text{nr}}^{\text{em}}(T)}$$

(2)

with $z_{a1}$ and $z_{a2}$ as the feeding ratios from a pumped excited auxiliary level $|a\rangle$ to the excited levels $|2\rangle$ and $|1\rangle$ of interest. Using eqn (1) and the previously justified assumption of a temperature-independent non-radiative emission rate,
we obtain

\[ R_{21}(T) = \frac{I_2}{I_1} = C \frac{n_2}{n_1} \left( \frac{\Delta E_{X_1}}{k_B T} \right) \]

with \( C \) as an electronic pre-factor connecting the luminescence intensity ratio (LIR) with the population ratio. \( C \) contains the radiative rates of the excited levels. If the intensities are integrated over all different possible ground levels (to avoid incorporation of emission branching ratios) and upon introduction of \( k_{\text{eff}} = (\omega_{a1} + \omega_{a2})k_{\text{nr}(0)} \), it follows (see ESI† for a detailed derivation),

\[ R_{21}(T) = \frac{I_2}{I_1} = \frac{\omega_{a2}k_{\text{eff}}(0)}{\omega_{a1}k_{\text{eff}}(0)} \left( \frac{\Delta E_{X_1}}{k_B T} \right) \]

\[ \equiv A + B \exp \left( -\frac{\Delta E_{X_1}}{k_B T} \right) \]

(4)

Thus, the LIR simply follows an effective or “quasi”-Boltzmann-type law with constant offset at low temperatures, which was also experimentally found earlier already but was lacking theoretical justification so far.32,57

The relative sensitivity, \( S_r(T) \), is often considered a figure-of-merit for luminescent thermometers. For the case of a configurational crossover thermometer with the LIR obeying eqn (4), \( S_r \) is given by

\[ S_r(T) = \frac{1}{R_{21}(T)} \left( \frac{\Delta E_{X_1}}{k_B T} \right) \left[ 1 + A \exp \left( -\frac{\Delta E_{X_1}}{k_B T} \right) \right]^{-1} \]

(5)

Unlike the relative sensitivity of a conventional Boltzmann thermometer \( S_r(T) = \frac{\Delta E_{X_1}}{k_B T} \), the relative sensitivity of a crossover thermometer goes through a maximum at a specific temperature \( T_{\text{opt}} \) (in this case \( T_{\text{opt}} \sim 400 \) K) dependent on the relative size of the different radiative and non-radiative rates encoded in the ratio \( A/B \). Only at high temperatures \( \omega_aT \gg \Delta E_{X_1} \) and small ratios of \( A/B \) does the relative sensitivity of a crossover thermometer agree with that of a conventional Boltzmann thermometer. It should be noted, however, that it is the interplay between the relative sensitivity and high signal-to-noise ratio that defines the practically actually relevant quantity of statistical precision of a luminescent thermometer.13,58,59

The statistically expected relative temperature uncertainty is given by

\[ \sigma_T = \frac{1}{S_r(T) T} \left( \frac{1}{\sqrt{R_{21}(T)}} + \frac{1}{R_{21}(T)} \right) \]

(6)

with \( R_{21}(T) \) and \( S_r(T) \) as given in eqn (4) and (5), respectively. Formula (6) is valid under the assumption of Poissonian photon counting statistics of the photodetector, which is given for a photomultiplier.

3.2. Case study: configurational crossover thermometry with Sm\(^{3+}\) (4f\(^5\))

We demonstrate the concept of a configurational crossover thermometer on SrB\(_2\)O\(_7\) : 0.5% Sm\(^{3+}\). Fig. 4(a) depicts the temperature-dependent steady-state luminescence spectra (normalized to the intensity of the most intense \( 5\mathrm{D}_0 \rightarrow \mathrm{F}_6 \) transition) of SrB\(_2\)O\(_7\) : 0.5% Sm\(^{3+}\). At higher temperatures, a broad band due to the \( 4f^55d^1 \rightarrow 4f^6 \) transition is clearly visible, in good agreement with earlier findings. The evolution of the LIR with temperature is shown in Fig. 4(b) and can be fitted very accurately by the model (4). An energy gap of \((3810 \pm 90) \, \text{cm}^{-1}\) between the \( 5\mathrm{D}_0 \) level and crossover point of the \( 4f^55d^1 \)-related level is obtained. This appears reasonable as it is assumed that the zero-phonon energy of the broad-banded \( 4f^55d^1 \rightarrow 4f^6 \)-related emission \((E_{0,0} \approx 17700 \, \text{cm}^{-1})\) according to
the crossing point between emission and excitation spectrum) should be at the slightly lower energies than the actual crossover point ($E_x \approx 4000$ cm$^{-1}$).

The fitting parameters $A$ and $B$ can also be evaluated in terms of their physical context. According to eqn (4), $A$ basically represents the ratio between the radiative rate of the higher excited level and an effective overall rate containing both the radiative and intrinsic non-radiative crossover transition rate. In a crossover thermometer, it is usually $k_{nr}(0) \gg k_{2\tau r}$, as estimated from the temperature dependence of the $^4D_0$ related decay time (see Fig. S2 in the ESI†) or reported for other Sm$^{3+}$-activated compounds such as the matlockite-type fluoroindochlorides MFCI ($M = \text{Ca, Sr, Ba}$). Thus, $A$ is expectedly to be very small ($A \ll 1$). This is also found from the fit of the temperature-dependent luminescence data in SrB$_4$O$_7$:0.5% Sm$^{3+}$, for which $A = (4.78 \pm 0.66) \times 10^{-3}$. The parameter $B$ consists of two factors according to eqn (4). On the one hand, it contains the ratio of the radiative rates of the two excited levels coupled with the crossover process. While $k_{2\tau r} = (0.192 \pm 0.001)$ ms$^{-1}$, the radiative rate of the $4f^6$ state also dominated by the $4f^5$-activated emission could not be reliably determined with our equipment as it only gains appreciable intensity at higher temperatures and the overall decay is dominated by the non-radiative relaxation rate then. However, it is known for most Sm$^{3+}$-doped phosphors that the radiative rate of a $4f^6$ $\rightarrow$ $4f^5$ transition is in the order of $1 \sim 10^4$. Thus, the order of magnitude of the factor $k_{2\tau r}/k_{nr}(0)$ is expectedly $10^3$–$10^4$. The second factor contained in $B$ relates the intrinsic non-radiative crossover coupling rate $k_{nr}(0)$ to the effective total relaxation rate of the $4f^5$ level also dominated by $k_{nr}(0)$. This factor should be expected to be of the order of 1. Thus, $B$ is overall expected to be in the order of $10^3$–$10^4$. From the least-squares fit of the model (4) to the temperature-dependent LIR, a value of $B = (2.70 \pm 0.66) \times 10^4$ is derived, which perfectly agrees with the previous estimates. The presented calibration model for crossover thermometers allows the physical interpretation that can be independently verified by time-resolved measurements and thus, in principle, simulated independently from the experiment.

The expected relative sensitivity and relative temperature uncertainty of the luminescent crossover thermometer SrB$_4$O$_7$:0.5% Sm$^{3+}$ are depicted in Fig. 5. The relative sensitivity of the tetraborate shows a maximum at around 400 K with a value of 2.98% K$^{-1}$, similar to earlier reports. Both the temperature and the value of the relative sensitivity depend on the interplay between $\Delta E_X$ and the ratio $A/B$ and thus, basically intrinsic electronic properties of the emitting luminescent centre. The practically more relevant quantity of a (relative) temperature measurement uncertainty can be particularly controlled by the emission intensity $I_1$ of the lower excited level. Since Sm$^{3+}$ is a very bright emitter in SrB$_4$O$_7$ that can be even efficiently excited due to the electric-dipole allowed nature of the $4f^6$ $\rightarrow$ $4f^5$ transition, the statistically expected relative temperature uncertainty is typically below 0.1% even for integrated intensities of the $^5D_0 \rightarrow ^7F_J$-based emission as low as $10^5$ counts (see Fig. 5(b)).

![Fig. 5](image_url) (a) Plot of the relative sensitivity, $S(T)$, of the anticipated luminescent crossover thermometer SrB$_4$O$_7$:0.5% Sm$^{3+}$ using the fitting values from the plot in Fig. 4(b). The expected relative sensitivity of a purely Boltzmann-based luminescent thermometer with energy gap $\Delta E_X = 3810$ cm$^{-1}$ is also indicated in grey colour. (b) Expected relative statistical temperature uncertainties of SrB$_4$O$_7$:0.5% Sm$^{3+}$ with different integrated intensities of the $^5D_0 \rightarrow ^7F_J$ transitions.

It should not be misinterpreted, however, that crossover thermometers can be readily used for wide ranges. Due to the configurational coordinate shift of one of the excited state potentials, not only a crossover to an excited level of interest but also to the ground-level potential is possible. Given the high non-radiative coupling rates $k_{nr}(0)$ between the $4f^5$ and $4f^6$-based levels, thermal quenching of the luminescence is a
serious problem at high temperatures (see also Fig. 3), as was already demonstrated several times for transition metal ions by the Marciniak group\textsuperscript{54,65} or in dual-centre luminescent thermometers by e.g. Kaczmarek \textit{et al.}\textsuperscript{66} Thus, despite the promising relative sensitivities and high measurement precision, crossover thermometers are usually reasonably applicable in a limited temperature range only. This is different from conventional luminescent Boltzmann thermometers based on two excited levels thermally coupled by multiphonon transitions. This type of thermometer does not usually suffer from high-temperature quenching, but the slower thermal coupling processes limit the low-temperature threshold above which thermometry with a Boltzmann-type thermometer would be possible. In that regard, luminescent crossover thermometers offer a practical alternative to classical Boltzmann-type luminescent thermometers.

**Conclusions**

In this work, we discussed the class of ratiometric luminescent crossover thermometers and derived a physically-interpretable calibration model for them. We showed that the luminescence intensity ratio of such a thermometer generally follows a “quasi”-Boltzmann-type behaviour with constant offset at low temperatures and how to physically interpret the different fitting parameters. Such verifiability is important for critically judging the quality and physical content of a thermometric calibration model.

The concepts were explicitly demonstrated on experimental data of synthesized microcrystalline SrB$_4$O$_7$:0.5% Sm$^{3+}$. Sm$^{2+}$ (4f$^5$) has a low energetic excited 4f$^6$5d$^1$ configuration that allows a configurational crossover from the excited 5D$_0$ level of the 4f$^6$ configuration. While the luminescence of SrB$_4$O$_7$:0.5% Sm$^{3+}$ at room temperature is dominated by narrow line emission due to the 5D$_0$ $\rightarrow$ 7F$^J$ ($J$ = 0–6) transitions of Sm$^{3+}$ with a particularly strong 5D$_0$ $\rightarrow$ 7F$_0$-based emission line at 685 nm, a broadband 4f$^6$5d$^1$ $\rightarrow$ 4f$^7$-based emission with a maximum at 585 nm emerges at temperatures above 400 K. The temperature-dependent luminescence intensity ratio defined by the integrated intensities of the 4f$^6$5d$^1$ $\rightarrow$ 4f$^7$ and 5D$_0$ $\rightarrow$ 7F$_0$-based emission can be fitted very well with the presented model and the fitting parameters related to the excited state kinetic data. A maximum relative sensitivity of almost 3% K$^{-1}$ at around 400 K was derived. Together with the high luminescence intensity of the 5D$_0$ $\rightarrow$ 7F$_0$-based emission of Sm$^{3+}$ in SrB$_4$O$_7$, relative statistical temperature measurement uncertainty below 0.1% can be retained above 400 K. However, despite the promising performance values, crossover thermometers suffer from severe thermal quenching of the luminescence at high temperatures ($T > 548$ K), which poses an upper threshold to the dynamic working range of this type of luminescent thermometers. This is different from classic Boltzmann thermometers, which usually do not suffer from this limitation but are rather insensitive and thus, less precise at high temperatures. Nonetheless, the presented calibration model with the possibility of explicit verification of the physical content offers a way to design luminescent thermometers with desirable performance properties.

**Author contributions**

B. B. performed the synthesis, characterization, and optical measurements. M. S. supervised the project, analysed the data, and wrote the manuscript. All authors agreed on the final version of the manuscript.

**Conflicts of interest**

There are no conflicts to declare.

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