Contents lists available at ScienceDirect



# Sensors and Actuators B: Chemical



journal homepage: www.elsevier.com/locate/snb

# TeSen – tool for determining thermometric parameters in ratiometric optical thermometry



Anna M. Kaczmarek<sup>a,\*</sup>, Rik Van Deun<sup>a</sup>, Mariusz K. Kaczmarek<sup>b,\*</sup>

<sup>a</sup> L<sup>3</sup>—Luminescent Lanthanide Lab., Department of Chemistry, Ghent University, Krijgslaan 281-S3, B-9000 Ghent, Belgium <sup>b</sup> Institute of Mechanics and Applied Computer Science, Kazimierz Wielki University in Bydgoszcz, Kopernika 1, 85-074 Bydgoszcz, Poland

#### ARTICLE INFO

Keywords: Temperature sensors Luminescence Ratiometric thermometers Numerical methods Software

#### ABSTRACT

This work presents the method and numerical program along with graphical user interface (GUI) for calculating the standard parameters necessary to evaluate luminescence ratiometric thermometers – the thermometric parameter  $\Delta$ , absolute sensitivity  $S_a$ , and relative sensitivity  $S_r$ . Despite the high interest in temperature sensing materials, to the best of our knowledge, no such tool has been reported up to date. This is currently usually done by researchers using a trial and error method and is a rather laborious task, with high risk of errors. The undoubtful benefit of employing an optimization technique lies in the very fast and precise determination of the parameters employing different models. The thermometric parameters  $\Delta$ ,  $S_a$  and  $S_r$  are calculated based on the luminescence emission spectra measured over a certain temperature range. Using the TeSen tool the thermometric parameters  $\Delta$  can be calculated based both on the peak maxima and integrated surface areas under the peaks. The tool also allows testing the ratio of multiple peaks, different peak ranges, and different temperature ranges in a very convenient way. In this work TeSen tool was used to study several new sensor materials, presenting new cases of single and dual center luminescent ratiometric theremometers.

# 1. Introduction

The very precise measurement of temperature is becoming progressively important in scientific research and development as well as in technological applications relying on feedback from sensor thermometers [1]. Recent advances in technologies have generated a need for sensing and measuring temperature at the nanoscale (for applications in nanoelectronics, nanophotonics, chemical reactors, and others) [2]. Yet, traditional temperature sensors have many intrinsic constraints and they are not suitable for temperature measurements of objects at the submicron scale as well as fast-moving objects. A wide range of optical methods have been researched for use in new types of thermometers, such as thermography, Raman scattering, thermal reflection and luminescence [3]. Among them luminescence-based thermometry is proving to be a very promising alternative. The luminescence-based thermometry method exploits the relationship between temperature and luminescence behavior in a material. In general, due to the Boltzmann distribution, at exalted temperatures higher energy excited states are thermally occupied and this makes luminescence of all materials temperature-dependent [4]. There is a large variety of temperaturedependent luminescence phenomena that can be used for temperature sensing. The most basic phenomenon that can be used is thermal quenching of the luminescence. The rate of non-radiative transitions  $(k_{nrt})$  is related to *T via* the Arrhenius equation:

$$k_{\rm nrt} \sim e^{\left(-\frac{\Delta E}{k_B T}\right)} \tag{1}$$

where  $\Delta E$  is the energy gap between the lowest excited state and a crossing point to a non-radiatively decaying state, and  $k_B$  is the Boltzmann constant. The non-radiative transition rate increases at higher *T*.

In the last 10–15 years a lot of attention has been given to the research topic of temperature sensors, which has resulted in a numerous amount of very interesting and useful data [5–29]. There are several different parameters for accessing the temperature change of a material: band intensity, spectral position, band-shape, polarization, lifetime and bandwidth. Among these parameters the most often selected is recording the steady state intensity of (a) transition(s). It was observed early on, that sensing measurements based on a single transition band can be affected by many factors such as for example alignment, optoelectronic drift of the excitation source and detectors, or quenching processes [1]. In that regard luminescence thermometers based on the intensity ratio of two transitions, so called ratiometric thermometers, were developed. Many of the currently reported ratiometric thermometers involve lanthanide materials (or mixed d–f materials), such as lanthanide Metal Organic Frameworks (LnMOFs), lanthanide inorganic

\* Corresponding authors. E-mail addresses: Anna.Kaczmarek@UGent.be (A.M. Kaczmarek), mkk@ukw.edu.pl (M.K. Kaczmarek).

https://doi.org/10.1016/j.snb.2018.06.086 Received 21 March 2018; Received in revised form 15 June 2018; Accepted 19 June 2018 Available online 20 June 2018 0925-4005/ © 2018 Elsevier B.V. All rights reserved. phosphors, lanthanide complexes, glass ceramics and others [26,29–31]. Other reported materials include  $Mn^{2+}$  doped quantum dots (QDs) and nanopartilces, organic dyes or organic nano-gels [4,32,33].

The TeSen Calculator tool can be used to calculate thermometric parameters for any kind of ratiometric sensor material based on the steady state intensity change of two transition peaks. The examples studied in this work are based on various lanthanide materials, presenting different lanthanide systems. The choice of lanthanide materials for testing is linked to the research work carried out by some of the authors of the papers, yet does not limit the TeSen Calculator tool in any way only to this class of thermometric materials.

There are different strategies to design ratiometric luminescence thermometers: 1) luminescence can be generated from two independent emitting centers; as the two luminescent centers are electronically independent and there is no energy transfer between them, the changes in luminescence intensities arise from the different thermal quenching behavior of each luminescent center; 2) dual emissions can be obtained from two closely related luminescent centers in which one (donor) sensitizes the other (acceptor) via energy transfer; 3) dual emissions can arise from the two thermally coupled energy levels of a single luminescent center [1]. Different systems have been tested using the TeSen Calculator tool.

Materials showing temperature sensor behavior are of very high interest, which is supported by the large number of publications and reviews published on this topic in the last years, some of them mentioned in the earlier referred papers and reviews. To the best of our knowledge there is no existing widely available tool for calculating the thermometric parameters of luminescence thermometers. This is usually currently done by researchers using a trial and error method and is a rather laborious task, with high risk of errors. An easy to use program, such as the proposed TeSen Calculator tool allows quick analysis of the data when taking into consideration both the peak maxima as well as the surface areas under the peak, as well as testing the ratio of multiple peaks, different peak ranges, and different temperature ranges. The tool enables using simultaneously the different  $\Delta$ equations for identification of model parameters that guarantee the best fit to experimental data and comparing the results (including R<sup>2</sup> errors), and calculating the absolute sensitivity S<sub>a</sub> and relative sensitivity S<sub>r</sub> values. The  $S_r$  indicates the relative change of the thermometric parameter per degree of temperature change (%  $K^{-1}$ ). Compared with  $S_a$ ,  $S_r$ has the important advantage of being independent of the nature of the thermometer and allows direct and quantitative comparison to different materials. Although usually it is recommended to calculate the ratio between the integrated surface areas under the peaks, in some cases e.g. when peaks overlap, using the peak maxima is very useful. As the Matlab environment was used to write the program, emission maps and graphs for  $\Delta$ ,  $S_a$  and  $S_r$  are generated by Matlab and can be easily customized to a chosen style available in the Matlab software.

In this work the TeSen Calculator tool was tested, its use described in detail and discussed showing its usefulness and relevance for researchers working in the field of luminescent temperature sensors. The TeSen tool can be downloaded free of charge from the following website: http://www.tesen.ugent.be. We ask that this publicaton be cited when using our TeSen software.

# 2. Discussion

# 2.1. Assumptions

It was assumed that for a material considered as a ratiometric optical sensor experimental data of luminescence emission spectra over a certain temperature range and constant temperature increment are given. The calculator, which enables determining thermometric parameters, should facilitate a simple windowing of two data sets related to peaks of emission spectra for the whole range of temperature. For each temperature it calculates thermometric parameters  $\Delta$  based on the ratio of the maximum values of peaks (indicated by a user) and the ratio of values of the integrated surface areas under the windowed peaks,  $\Delta_{max}$ ,  $\Delta_{int}$ , respectively. Three models for the thermometric parameter  $\Delta$  as the function of temperature T are considered:

$$\Delta_1 = \alpha \, \exp\left(-\frac{\Delta E}{k_B T}\right) \tag{2}$$

$$\Delta_2 = \frac{\Delta_0}{1 + \alpha \, \exp\left(-\frac{\Delta E}{k_B T}\right)} \tag{3}$$

$$\Delta_3 = \frac{\Delta_0}{1 + \alpha 1 \exp\left(-\frac{\Delta E1}{k_B T}\right) + \alpha 2 \exp\left(-\frac{\Delta E2}{k_B T}\right)}$$
(4)

where  $\alpha$ , .... are the unknown model parameters. The model parameters, which guarantee the best fit of the models (2)–(4) to experimentally determined dependencies  $\Delta_{max}$  and  $\Delta_{int}$  are found using numerical optimization in the minimum mean square root sense. Corresponding goodness of fits are calculated. Sensitivity parameters  $S_a$ and  $S_r$  are evaluated for the whole range of temperature and the maximum values, along with corresponding values of temperatures are found. Each step of the program is controlled from the GUI and a complete visualization of the results is ensured.

#### 2.2. TeSen tool and GUI description

The Matlab environment (Version 7.11) was used to write the TeSen Calculator program for determining the thermometric parameters ( $\Delta$ ,  $S_a$  and  $S_r$ ) based on emission intensity changes at different temperatures. The program includes a GUI (see Fig. 1), which is intuitive and easy to use even for users who are not familiar with the tool. The best fit of the three models to experimental data is found using *lsqnonlin* function from Matlab's Optimization toolbox.

In order to calculate the thermometric parameters the compiled emission spectra, measured over a certain temperature range, are required. The temperature minimum and temperature maximum, as well as step size need to first be inserted into the "Input Data" section (see field 1 in the GUI). Next, the "upload emission spectra" button (field 2 in GUI) is pressed to select the correct data file. One txt file consisting of the compiled emission spectra, with no headers at the top of document, needs to be uploaded. Once this has been done Figs. 1 and 2 immediately pop up (Fig. 2 in this paper). Figs. 1 and 2 are two different emission maps over the measured temperature range showing a change in the intensity of the emission peaks. Next, the user moves on to field 3 in the GUI. Here, the peaks, which the user wants to use for the determination of the thermometric parameters, are selected. After pressing the button "Peak 1" the first peak is selected - first the area range for calculating the integrated surface area under the peaks is selected with a cursor, and last the peak maximum. The same is done for peak 2 after selecting the "Peak 2" button (Figs. 3-5 in the program, see Fig. 3 in this paper). TeSen calculates the ratio between "Peak 1"/ "Peak 2". After the peak range and maxima have been selected Figs. 6 and 7 appear (Fig. 4 in this paper). The  $\Delta$  data points (experimental  $\Delta$  = Peak 1/Peak 2) are presented as a function of 1/T (Fig. 6) and T (Fig. 7). The  $\Delta$  data points are shown for both the integrated surface areas under the peaks and peak maxima. The experimental  $\Delta$  data points can next be fitted using one of the 3 available models "Finding Fitting Parameters". In the TeSen Calculator, due to limitations in the formation of the GUI in Matlab environment, the Greek letters  $\Delta$  and  $\alpha$ have been substituted with D and a/A, respectively. Also for simplification  $\frac{\Delta E}{k_{\rm p}}$  is referred to as e/E in the equation (small letters are used in model 1 and capital letters in models 2 and 3). The data fit with one of the models can be selected in field 4 in the GUI (circled for model 1). The user presses the "Fit" button under the selected equation and the a/ A and e/E parameters as well as R<sup>2</sup> fit show up on the screen, calculated



Fig. 1. GUI of the TeSen Calculator. The numbers referring to the particular fields of the GUI are described in the text.

for peak maxima ("for D\_max") and for integrated surface area under the peaks ("for D\_int"). Additionally in the Command Window RMSE\_max and RMSE\_int can be found, but are not included in the interface of the program. The choice of the model is mostly based on the users knowledge about thermometer materials. If a single luminescent center material is considered model 1 is selected, if two luminescent centers are available either model 2 or 3 can be used depending on the amount of deactivation energies in the material; this can be evaluated based on knowledge of the material and on the goodness of fit between the  $\Delta$  data points and the equation. After this step Figs. 8 and 9 are obtained (Fig. 5 in this paper). Fig. 8 shows the  $\Delta$  data points as a function of 1/T fitted with the chosen equation. Fig. 9 shows the  $\Delta$  data points as a function of T fitted with the chosen equation. Last, the user moves on to calculating the "Sensitivity Parameters" - the absolute sensitivity  $S_a$  and relative sensitivity  $S_r$ . There the "Calculate" button under the correct model is selected. As marked in field 5 in the GUI the maximum values of  $S_a$  and  $S_r$  (indicated for which temperature the maximum values are reached) are given "for D\_max" and "for D\_int". Fig. 10 presents the absolute sensitivity  $S_a$  [1/K] values as a function of T. Fig. 11 presents the relative sensitivity  $S_r$  [%/K] values as a function of T (Fig. 6 in this paper). In field 6 in the GUI one can choose to "close figures with fits and S", "close figures with data & D" or "close program". One can also go back to field 4 of the GUI and chose to fit the  $\Delta$  data points with a different model or go back to field 3 to select other peaks or peaks windows.

In order to verify the TeSen Calculator independent codes were written for each of the DELTA models (Eqs. (2)–(4)), which generated synthetic data files. The data files included a number of mimicking emission spectra composed of two families of Gaussian peaks predefined by the user. The independent variable (vector) of the Gaussian peaks, corresponding to wavelength, was selected arbitrary and had no influence on the results. The maximum values of the peaks were defined in such a way that their ratio depended on the specified vector of temperature and parameters present in one of the Eqs. (2)–(4). The TeSen Calculator was tested using the synthetic data for different models and range of model parameters.

# 2.3. Example

In order to present the usefulness of the TeSen Calculator tool we demonstrate and discuss below a step by step analysis of a 5%Dy:YVO<sub>4</sub> material prepared in the Luminescent Lanthanide Lab ( $L^3$ ) at Ghent University. The structure and morphology of the YVO<sub>4</sub> microparticles and Ln:YVO<sub>4</sub> have been pulished in one of our previous works [34].



Fig. 2. Emission maps obtained in the TeSen Calculator tool for the 5%Dy:YVO4 material.



Fig. 3. The range and peak maxima selection presented for "Peak 1" for the 5%Dy:YVO<sub>4</sub> material.

Dy<sup>3+</sup> materials are very interesting as they show efficient emission in the blue/green spectral region, where the contribution from black body radiation at elevated temperature is minimal. In Dy<sup>3+</sup> materials two thermally coupled energy levels  ${}^4\!F_{9/2}$  and  ${}^4\!I_{15/2}\!,$  and therefore two emission peaks  ${}^{4}I_{15/2} \rightarrow {}^{6}H_{15/2}$  and  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$  can be monitored for temperature sensor applications [35,36]. With temperature increase, the higher energy level  $({}^{4}I_{15/2})$  becomes populated and hence its emission intensity increases gradually. This is at the expense of the population of the lower state  $({}^{4}F_{9/2})$ , which gradually decreases in emission intensity. The energy difference between the barycenters of the two states is around  $900-1000 \text{ cm}^{-1}$ , which is small enough to reach thermal coupling between the states, yet large enough to ensure well-resolved emission peaks and good sensitivity of temperature measurements in a higher temperature range [37]. Analysis of two other systems, consisting of different lanthanides, is discussed in detail in the Supporting Information of the paper.

We studied the temperature-dependent luminescence properties of the 5%Dy:YVO<sub>4</sub> material in the 310–380 K range, with a step size of 10 K. This information is first inserted into the "Input data" (field 1 in GUI): Tmin = 310, Tmax = 380, Tstep = 10. Next, the compiled emission spectra are uploaded ("Upload emission spectra", field 2). Figs. 1 and 2 are obtained (see Fig. 2 in this paper). These emission map figures can be easily tuned (color, rotation, font size, etc.) with various tools available in the Matlab environment. When the buttons "Peak 1" and "Peak 2" (field 3 in GUI) are selected the specific peaks, which will be used for the calculations, and their exact range and maxima, are chosen (Figs. 3–5 in TeSen Calculator). Selecting the range and maximum of "Peak 1" has been shown in Fig. 3 in this paper. After the peak range for both peaks have been selected the TeSen Calculator calculates the experimental  $\Delta$  points for each temperature.

The  $\Delta$  data points are presented as a function of 1/T (Fig. 6) and T (Fig. 7), see Fig. 4 in this paper. The experimental  $\Delta$  data points are next fitted using one of the 3 available models under "Finding Fitting Parameters". For this material, as we are dealing with a single luminescent center material, it is appropriate to use model 1 for the fitting. The user presses the "Fit" button under the selected model 1 to obtain Figs. 8 and 9 showing the fit of the  $\Delta$  data points with Eq. (2) (see Fig. 5 in this paper).

Using this tool we calculated the  $\Delta$  data points along with the fit for model 1 taking into consideration both the ratio of the peak maxima as well as the ratio of the surface areas under the peaks. Both approaches can be found in literature, but as already mentioned in the introduction usually it is recommended to use the surface areas under the transition peaks. Only in cases, where for example the peaks overlap, this might be a very useful approach (for example in Yb<sup>3+</sup>/Tm<sup>3+</sup> co-doped upconversion materials, where the  ${}^{1}G_{4/3} \rightarrow {}^{3}F_{4}$  and  ${}^{3}F_{2,3} \rightarrow {}^{3}H_{6}$  Tm<sup>3+</sup> transitions partially overlap or in Yb<sup>3+</sup>/Ho<sup>3+</sup>/Tm<sup>3+</sup> co-doped samples where the  ${}^{5}F_{3} \rightarrow {}^{5}I_{8}$  transition peak of Ho<sup>3+</sup> overlaps with the  ${}^{1}G_{4} \rightarrow$ <sup>3</sup>H<sub>6</sub> transition peak of Tm<sup>3+</sup>). For this material there is no peak overlap, that is why exploiting the results obtained for surface areas under the peaks in recommended. For both cases we calculated  $\Delta E$ , for D\_max  $\Delta E = 1174.6 \text{ cm}^{-1}$  and for D\_int  $\Delta E = 996.9 \text{ cm}^{-1}$ . The  $\Delta E_{int}$  is closer to the theoretical calculated value (energy difference between  ${}^{4}F_{9/2}$  and  ${}^{4}I_{15/2}$  energy levels), which is 900–1000 cm<sup>-1</sup>. This confirms the appropriatness of using the ratio of the integrated surface areas under the two peaks for this thermometer material.

After this the sensitivity parameters ( $S_a$  and  $S_r$ ) are calculated. In field 5 of the GUI the "Calculate" button is pressed under model 1. This



**Fig. 4.** The graphs present the experimental  $\Delta$  data points for each measured temperature (for peak maxima – round blue dot and integrated surface areas under the peaks – red stars). The data points are presented as a function of 1/T [1/K] in Fig. 6 and as a function of T [K] in Fig. 7 in the TeSen Calculator. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 5. The graphs present the experimental  $\Delta$  data points for each measured temperature (for peak maxima – round blue dot and integrated surface areas under the peaks – red stars) fitted with model 1 in the TeSen Calculator tool. The data points are presented as a function of 1/T [1/K] in Fig. 8 and as a function of T [K] in Fig. 9 in the TeSen Calculator. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

results in Figs. 10 and 11 popping up as well as the maximum  $S_a$  and  $S_r$  showing up in the calculator window (for appropriate temperature); see Fig. 6 in this paper. The maxima  $S_a$  and  $S_r$  values are indicated on the graphs. For D\_max the maximum value of  $S_a = 0.000439$  (at 380 K) and the maximum value of  $S_r = 1.7586$  (at 310 K). For D\_int the maximum value of  $S_r = 1.5264$  (at 310 K). Fig. 7 presents the GUI with the imputed data and calculated thermometric parameters. Fig. 8 presents a snap shot of the command window where additionally RMSE values can be found.

#### 3. Conclusions

Here we have presented a developed method along with a GUI for finding the thermometric parameters for ratiometric luminescent thermometers. This program allows simple and very fast determination of  $\Delta$ ,  $S_a$  and  $S_r$  based on emission intensity change at different temperatures. Currently no such tool, which would be widely available, exists. Therefore, such calculations need to be done manually (trial and error method), which is a laborious process, prone for errors. The undoubtful benefit of employing an optimization technique lies in the very fast and precise determination of the parameters of different models. The program allows calculating the thermometric parameters based on the peak maxima as well as integrated surface areas under the peaks. Also it is possible to quickly test the ratio of multiple peaks, different peak ranges, and different temperature ranges and compare the results. This is a very strenuous task in the trial and error method. Very importantly it also allows comparing the thermometric parameters when selecting different models. The program provides graphs, which can be used in their current form, or customized with all the available tools in the Matlab environment. Due to the large interest in ratiometric luminescent thermometers, we strongly believe this will be a very useful tool for many scientists (e.g. chemists, physicist and engineers) working in this field of luminescent ratiometric thermometers. The TeSen tool can be downloaded free of charge from the following website: http://www. tesen.ugent.be. We ask that this publicaton be cited when using our TeSen software.

#### Acknowledgments

A.M.K. thanks Ghent University's Special Research Fund (BOF) for a Postdoctoral Mandate (project BOF15/PDO/091). The authors thank Pat Borra for making the TeSen website as well as Prof. Kristof Van



**Fig. 6.** The graphs present  $S_a$  (left, Fig. 10) and  $S_r$  (right, Fig. 11) values calculated for the investigated temperatures (calculated for peak maxima – round blue dot and integrated surface areas under the peaks – red stars). The solid lines are a guide for the eyes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

🕢 TeSenCalculator									
	TeSenCalculator								
INPUT DATA: Tmin= 310 Tmax= 360 Tstep= 10 upload emission spectra									
PEAKS' SELECTION & D CALC .:	Peak 1 Peak 2	Jan Tesen							
FINDING FITTING PARAMETERS: (calculation of D_max and D_int)>									
Model 1: D= a exp (-e/T))	Model 2: D= Do / (1 + Aexp (-E/T))	Model 3: D= Do / (1 + A1exp (-E1/T)+A2 exp(-E2/T))							
FIT	FIT	FIT							
a= e= goodness of fit r^2=	Do= A= E= goodness of fit r*2=	Do= A1 E1= A2= E2= goodness of fit r*2=							
for D_max: 3.2089 1690 0.9874									
for D_int: 1.4605 1466.8 0.99087									
calculate	calculate	calculate							
for D_max: 0.000439 380 1.7586 310									
for D int: 0.000312 380 1.5264 310	- i - i - i - i - I								
CLOSE FIGURES OR PROGRAM:	close figures with fits & S close figures w	ith data & D close program							

Fig. 7. TeSen Calculator GUI with inputted data and calculated thermometric parameters.

-) MATLAB R2017b - dassroom use															
HOME	PLOTS	S	4	PPS						à <b>th</b> 'o (		Search Docum	entation	Q	Log In
New New Script Live Script	New of	Dpen	Final	d Files mpare	Import Data	Save Workspace	New Variable	ace •	Analyze Code	Simulink	Layout	<ul> <li>Preferences</li> <li>Set Path</li> <li>Parallel •</li> </ul>	Add-Ons	RESOURCES	-
FILE VARIABLE CODE SIMULINK ENVIRONMENT															
Image: Second															
Current Folder			•	Comm	and Wind	low B2 See recour	rees for Celling Star	ted						Works	pace ()
10-100K M	ulti Scans.tx	t		>:	> TeSe	nCalcula	tor	<u>teu</u> .							~
Dy_YVO4 3	10-380K.tx	t		RI	ISE_ma	x =									
er3.m er31.m	.ona				0.0	011									
TeSenCalo TeSenCalo	ulator.fig ulator.m			RI	ASE_in	t =									
					7.25	87e-04									
				R	2i =										
					0.9	909									
				R	2m =										
					0.9	874									
Details			^	fx >:	>										•

Fig. 8. Snapshot of the Command Window showing the RMSE values.

Hecke for designing the TeSen logo.

# **Conflicts of interest**

There are no conflicts to declare.

### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.snb.2018.06.086.

#### References

[1] L.D. Carlos, F. Palacio, Thermometry at the Nanoscale: Techniques and Selected Applications, Royal Society of Chemistry, Oxfordshire, 2016.

- [2] D. Jaque, F. Vetrone, Luminescence nanothermometry, Nanoscale 4 (2012) 4301-4326.
- [3] C.D.S. Brites, P.L. Lima, N.J.O. Silva, A. Millan, V.S. Amaral, F. Palacio, L.D. Carlos,
- Thermometry at the nanoscale, Nanoscale 4 (2012) 4799–4829.
  [4] X.-d. Wang, O.S. Wolfbeis, R.J. Meier, Luminescence probes and sensors for temperature, Chem. Soc. Rev. 42 (2013) 7834–7869.
- [5] Z. Wang, D. Ananias, A. Carne-Sanchez, C.D.S. Brites, I. Imaz, D. Maspoch, J. Rocha, L.D. Carlos, Lanthanide-organic framework nanothermometers prepared by spraydrying, Adv. Funct. Mater. 25 (2015) 2824–2830.
  [6] L. Li, Y. Zhu, X. Zhou, C.D.S. Brites, D. Ananias, Z. Lin, F.A. Almeida Paz, J. Rocha,
- W. Huang, L.D. Carlos, Visible-light excited luminescent thermometer based on single lanthanide organic frameworks, Adv. Funct. Mater. 26 (2016) 8677-8684.
- [7] R.G. Geitenbeek, P.T. Prins, W. Albrecht, A. van Blaaderen, B.M. Weckhuysen, A. Meijerink, NaYF<sub>4</sub>: Er<sup>3+</sup>,Yb<sup>3+</sup>/SiO<sub>2</sub> core/shell upconversion nanocrystals for luminescence thermometry up to 900 K, J. Phys. Chem. C 121 (2017) 3503–3510.
- [8] X. Liu, S. Akerboom, M. de Jong, I. Mutikainen, S. Tanase, A. Meijerink, E. Bouwman, Mixed-lanthanoid metal-organic framework for ratiometric cryogenic temperature sensing, Inorg. Chem. 54 (2015) 11323-11329.
- [9] D. Ananias, F.A. Almeida Paz, D.S. Yufit, L.D. Carlos, J. Rocha, Photoluminescent

thermometer based on a phase-transition lanthanide silicate with unusual structure disorder, J. Am. Chem. Soc. 137 (2015) 3051–3058.

- [10] A.M. Kaczmarek, Y.-Y. Liu, C. Wang, B. Laforce, L. Vincze, P. Van Der Voort, R. Van Deun, Grafting of a Eu<sup>3+</sup>-tfac complex on to a Tb<sup>3+</sup>-metal organic framework for use as a ratiometric thermometer, Dalton Trans. 46 (2017) 12717–12723.
- [11] A.M. Kaczmarek, D. Esquivel, J. Ouwehand, P. Van Der Voort, F.J. Romero-Salguero, R. Van Deun, Temperature dependent NIR emitting lanthanide-PMO/silica hybrid materials, Dalton Trans. 46 (2017) 7878–7887.
- [12] A.M. Kaczmarek, J. Liu, B. Laforce, L. Vincze, K. Van Hecke, R. Van Deun, Cryogenic luminescent thermometers based on multinuclear Eu<sup>3+</sup>/Tb<sup>3+</sup> mixed lanthanide polyoxometalates, Dalton Trans. 46 (2017) 5781–5785.
- [13] J. Liu, R. Van Deun, A.M. Kaczmarek, Optical thermometry of MoS<sub>2</sub>:Eu<sup>3+</sup> 2D luminescent nanosheets, J. Mater. Chem. C 4 (2016) 9937–9941.
- [14] L. Marciniak, A. Bednarkiewicz, D. Kowalska, W. Strek, A new generation of highly sensitive luminescent thermometers operating in the optical window of biological tissues, J. Mater. Chem. C 4 (2016) 5559–5563.
- [15] L. Marciniak, A. Bednarkiewicz, J. Drabiak, K. Trejgis, W. Strek, Optimization of highly sensitive YAG:Cr<sup>3+</sup>,Nd<sup>3+</sup> nanocrystal-based luminescent thermometer operating in an optical window of biological tissue, Phys. Chem. Chem. Phys. 19 (2017) 7343–7351.
- [16] L. Marciniak, K. Prorok, A. Bednarkiewicz, Size dependent sensitivity of Yb<sup>3+</sup>, Er<sup>3+</sup> up-converting luminescent nanothermometers, J. Mater. Chem. C 5 (2017) 7890–7897.
- [17] Y. Ciu, R. Song, J. Yu, M. Liu, Z. Wang, C. Wu, Y. Yang, Z. Wang, B. Chen, G. Qian, Dual-emitting MOF⊃ dye composite for ratiometric temperature sensing, Adv. Mater. 27 (2015) 1420–1425.
- [18] Y. Ciu, H. Xu, Y. Yue, Z. Guo, J. Yu, Z. Chen, J. Gao, Y. Yang, G. Qian, B. Chen, A luminescent mixed-lanthanide metal-organic framework thermometer, J. Am. Chem. Soc. 134 (2012) 3979–3982.
- [19] F. Huang, D. Chen, Synthesis of Mn<sup>2+</sup>:Zn<sub>2</sub>SiO<sub>4</sub>-Eu<sup>3+</sup>:Gd<sub>2</sub>O<sub>3</sub> nanocomposites for highly sensitive optical thermometry through the synergistic luminescence from lanthanide-transition metal ions, J. Mater. Chem. C 5 (2017) 5176–5182.
- [20] X. Fan, S. Freslon, C. Diaguebonne, L. Le Polles, G. Calvez, K. Bernot, X. Yi, G. Huang, O. Guillou, A new family of lanthanide-based coordination polymers with boronic acid as ligand, Inorg. Chem. 54 (2015) 5534–5546.
- [21] J.M. Lupton, A molecular thermometer based on long-lived emission from platinum octaethyl porphyrin, Appl. Phys. Lett. 81 (2002) 2478–2480.
- [22] F. Ye, C. Wu, Y. Jin, Y.-H. Chan, X. Zhang, D.T. Chiu, Ratiometric temperature sensing with semiconducting polymer dots, J. Am. Chem. Soc. 133 (2011) 8146–8149.
- [23] C. Pietsch, A. Vollrath, R. Hoogenboom, U.S. Schubert, A fluorescent thermometer based on a pyrene-labeled thermoresponsive polymer, Sens.-Basel 10 (2010) 7979–7990.
- [24] V.A. Vlaskin, N. Janssen, J. van Rijssel, R. Beaulac, D.R. Gamelin, Tunable dual emission in doped semiconductor nanocrystals, Nano Lett. 10 (2010) 3670–3674.
- [25] A.P. Herrera, M. Rodriguez, M. Torres-Lugo, C. Rinaldi, Multifunctional magnetite nanoparticles coated with fluorescent thermo-responsive polymeric shells, J. Mater. Chem. 18 (2008) 855–858.
- [26] J. Zhong, D. Chen, Y. Peng, Y. Lu, X. Chen, X. Li, Z. Ji, A review on nanostructured glass ceraminc for promising application in optical thermometry, J. Alloys Compd. 763 (2018) 34–48.
- [27] D. Chen, S. Liu, Z. Wan, Z. Ji, EuF<sub>3</sub>/Ga<sub>2</sub>O<sub>3</sub> dual-phase nanostructural glass ceramics with Eu<sup>2+</sup>/Cr<sup>3+</sup> dual-activator luminescence for self-calibrated optical thermometry, J. Phys. Chem. C 120 (2016) 21858–21865.
- [28] D. Chen, Z. Wan, S. Liu, Highly sensitive dual-phase nanoglass-ceramics self-calibrated optical thermometer, Anal. Chem. 88 (2016) 4099–4106.
- [29] D. Chen, Z. Wan, Y. Zhou, X. Zhou, Y. Yu, J. Zhong, M. Ding, Z. Ji, Dual-phase glass ceramic: structure, dual-modal luminescence, and temperature sensing behaviors, ACS Appl. Mater. Interfaces 7 (2015) 19484–19493.
- [30] Y. Ciu, F. Zhu, B. Chen, G. Qian, Metal-organic frameworks for luminescence

thermometry, Chem. Commun. 51 (2015) 7420-7431.

- [31] J. Rocha, C.D.S. Brites, L.D. Carlos, Lanthanide organic framework luminescent thermometers, Chem. Eur. J. 22 (2016) 1–15.
- [32] E. Glais, V. Dordevic, J. Papan, B. Viana, M.D. Dramicanin, MgTiO<sub>3</sub>:Mn<sup>4+</sup> a multireading temperature nanoprobe, RSC Adv. 8 (2018) 18341–18346.
- [33] M.D. Dramicanin, Luminescence Thermometry, first edition, Woodhead Publishing, 2018.
- [34] A.M. Kaczmarek, D. Ndagsi, R. Van Deun, Dopant and excitation wavelength dependent color tunability in Dy<sup>3+</sup>:YVO<sub>4</sub> and Dy<sup>3+</sup>/Eu<sup>3+</sup>:YVO<sub>4</sub> microparticles towards white light emission, Dalton Trans. 45 (2016) 16231–16239.
- [35] Z. Antic, M.D. Dramicanin, K. Prashanthi, D. Jovanovic, S. Kuzman, T. Thundat, Pulsed laser deposited dysprosium-doped gadolinium-vanadate thin films for noncontact, self-referencing luminescence thermometry, Adv. Mater. 28 (2016) 7745–7752.
- [36] T. Xia, Y. Cui, Y. Yang, G. Qian, A luminescent ratiometric thermometer based on thermally coupled levels of a Dy-MOF, J. Mater. Chem. C 5 (2017) 5044–5047.
- [37] W.T. Carnall, P.R. Fields, K.J. Rajnak, Electronic energy levels in the trivalent lanthanide aqua ions. I. Pt<sup>3+</sup>, Nd<sup>3+</sup>, Pm<sup>3+</sup>, Sm<sup>3+</sup>, Dy<sup>3+</sup>, Ho<sup>3+</sup>, Er<sup>3+</sup>, and Tm<sup>3+</sup>, Chem. Phys. 49 (1968) 4424–4442.

**Dr. Anna M. Kaczmarek** received her master's degree in chemistry from the Adam Mickiewicz University in Poznan, Poland in 2010. In 2015 she defended her PhD in Ghent University, Belgium under the promotorship of Prof. Rik Van Deun. During her PhD, she studied the luminescence properties of nano- and micro-sized materials such as rare-earth tungstates, vanadates and carbonates. Currently she is a post-doctoral researcher in the L<sup>3</sup> group of Prof. Van Deun (Ghent, Belgium) and studies lanthanides based ratiometric optical temperature sensors based on MOFs, POMs, and inorganic phosphors, as well as other applications for luminescent POM and MOF materials e.g. anticounterfeiting purposes.

**Prof. dr. Rik Van Deun** obtained a master in chemistry at the Katholieke Universiteit Leuven (KU Leuven) in Belgium. He subsequently acquired a PhD in the Molecular Design and Synthesis group of the same university under guidance of prof. dr. Koen Binnemans and prof. dr. Christiane Görller-Walrand, on lanthanide-containing liquid crystals. During a seven-year postdoctoral term he specialized in (near-infrared) lanthanide luminescence, as well as the use of X-ray Absorption Spectroscopy (XAS) to study the coordination chemistry of lanthanide complexes. He therefore conducted a research stay at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, at both the Dutch-Belgian Beamline (DUBBLE, BM26A) under the guidance of dr. Wim Bras, and the Rossendorf Beamline (ROBL, BM20) under the guidance of dr. Andreas Scheinost and dr. Christoph Hennig. In October 2008 he obtained a permanent position at the Inorganic and Physical Chemistry Department of Ghent University (Belgium), where he created the Luminescent Lanthanide Lab (L<sup>3</sup>, www.L3.ugent.be) where his research on 4*f*-elements focuses on the development of lanthanide-containing luminescent materials, both in the visible, near- and mid-infrared spectral range.

**Prof. Mariusz Kaczmarek** received his master's degree in mechanical engineering from University of Technology in Poznan, Poland in 1982, his Ph.D. and the D.Sc. in applied mechanics from the Institute of Fundamental Technological Research PAS in Warsaw in 1990, and 2002. He started his research career at the Polish Academy of Sciences in Poznan, then has held postdoctoral positions at Ruhr University in Bochum in Germany (1991) and Duke University in USA (1992–1995). Then he joined Kazimierz Wielki University in Bydgoszcz (Poland) in 1997. He was also working as visiting professor at Centrale de Lille (France). His principle research interests lie in modelling and computer simulations of porous materials filled with fluid (soils, rocks, tissues etc.). He develops software for solution of direct and inverse problems related to deformations, transport, wave propagation and other phenomena in porous media. His current projects deal with identification of hydro-mechanical parameters of soft tissues and saturated soils as well as non-destructive evaluation methods of cement based materials.