

# **REMTES** TECHNOLOGY FOR REMOTE TEMPERATURE MEASUREMENTS IN MICROFLUIDIC DEVICES

PROGRAM-PRIZMA-2023-2026 Grant Agreement: 7017



Deliverable 3.1 Model of energy transfer in luminescence thermal probes Version Final

# Project Deliverable Information Sheet

<b>REMTES Project</b>	Project Ref. No. 7017
	Project Title: Technology for remote temperature measurements in microfluidic
	devices
	Project Website: https://www.remtes-
	prizma.org
	Deliverable No.: D 3.1
	Deliverable Type: Report
	Month of delivery: 15
	Actual Delivery Date: 28/03/2025
	Principal investigator: Miroslav DRAMIĆANIN

## **Document Control Sheet**

Document	Title: Model of energy transfer in luminescence thermal probes		
	Version Final		
	Distributed to REMIES Participants and		
	through Project Website		
Authorship	Written by Zoran Ristić		
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	Approved by Miroslav Dramićanin		

# History of Changes

Version	Date	Description	Reviewer	
V0	15.03.2025.	Version 0	Zoran Ristić	
V1	20.03.2025.	Version 1	Miroslav Dramićanin,	
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V2	28.03.2025.	Version Final	Miroslav Dramićanin	

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## **INTRODUCTION**

**REMTES – "Technology for remote temperature measurements in microfluidic devices"** is a Science Fund of the Republic of Serbia funded project (Program PRIZMA, Grant Contract No. 7017) coordinated and completely executed by "Vinča" Institute of Nuclear Sciences – National Institute of the Republic of Serbia, University of Belgrade (VINS). The project will run from December 1<sup>st</sup>, 2023, to November 30th, 2026.

REMTES is a highly ambitious and innovative project aimed at developing a breakthrough system for measuring sample temperatures on the nanoliter scale. The project will create an optical self-referencing thermometer for use in micro- and nanofluidics in the 0–100 °C temperature range by exploiting temperature-induced changes in the luminescence of materials and nanomaterials, specifically by advancing luminescence (nano-)thermometry in a targeted manner. The project seeks to surpass the current state of the art and implement a radically new technology that merges the fields of luminescence thermometry, photothermal spectroscopy, and microfluidics to develop next-generation luminescent thermometry probes using cutting-edge, luminescent, temperature-sensitive, and chemically stable inorganic materials in both bulk and nanomaterial forms. The probes will be embedded in microfluidic chip channels to enable self-referenced remote temperature measurements, and the technology will be validated by a portable microfluidic luminescent thermometer and in situ temperature measurements of fluid flow in nanoliter volume samples. Multiple conceptual breakthroughs can be further envisaged from the proposed technology, extending its impact credibly across various technological areas.

The present document – D.3.1 Model of energy transfer in luminescence thermal probes – is a deliverable of the W3 of the REMTES project. It is a report on microscopic energy transfer and the luminescence model in luminescent thermal probes. This model supports the design of superior luminescent thermal probes in WP1: Synthesis of inorganic luminescence thermometry probes.

# D.3.1 Model of energy transfer in luminescence thermal probes

Work package 3: Modelling, design, and fabrication is defined by the following objectives: modelling, design, and fabrication of all important segments (luminescent probes, microfluidic chips, and microfluidic luminescence probes) for the portable microfluidic luminescent thermometer and the chemical microanalysis system. A specific subactivity (3.1) is designated for microscopic modelling of luminescent processes, to be realized in the first 15 months of the project.

As defined by the project, the subactivity is described as follows: Energy transfer and luminescent processes will be microscopically modeled (Judd–Ofelt, crystal field theory, and others) to understand luminescence dynamics and optimize luminescence efficiency by tuning the sizes, structures, dopant concentrations, and compositions of the luminescence thermometry probes. Temperature readouts from luminescence will be modeled to elucidate the most suitable emissions for exploitation in temperature measurements. Based on microscopic modeling, theoretical optimal concentrations and combinations of phosphor emissions can be determined and compared with experimental results. These efforts will support the design of superior luminescence thermal probes in WP1.

## Judd-Ofelt analysis of Eu<sup>3+</sup> - doped Sr<sub>2</sub>GdF<sub>7</sub> (SGF) colloidal nanoparticles

The report provided in Deliverable 1.1\_Ln3+- and TM-doped luminescence thermal probes informs about the synthesis, structural and morphological characterization, and optical UV-VIS and photoluminescent characterization of a set of seven Sr2Gd1-xEuxF7 (x = 0, 0.05, 0.10, 0.40, 0.60, 0.80, and 1.00, where mol.% of Eu3+ dopant ions were added with respect to Gd3+) colloids. This information and the results are used for calculations and Judd-Ofelt analysis.

The quantum mechanical, semi-empirical Judd-Ofelt theory [1,2], introduced in the 1960s, serves as a centerpiece in lanthanide spectroscopy [3], being the only theory capable of explaining and predicting the radiative properties of intra-configurational luminescence in ions ranging from  $Pr^{3+}$  to  $Tm^{3+}$ . The theory uses only three intensity parameters to estimate the radiative transition probabilities, radiative lifetimes, branching ratios, and cross-sections. It can also provide quantitative information on the non-radiative de-excitation process and intrinsic quantum efficiency when coupled with time-resolved luminescence measurements [4]. A primary challenge in applying the Judd-Ofelt theory is estimating the intensity parameters,  $\Omega_{\lambda}$ , which is typically achieved by fitting the intensities in the absorption spectrum to theoretical relations [5].

Europium is a unique ion among lanthanides because it has pure magnetic dipole transitions [6]. Magnetic dipole transitions, which are unaffected by the host matrix, can be used to calibrate the emission spectrum [7]. Therefore, in Eu<sup>3+</sup> doped materials, only a single emission spectrum is sufficient for Judd-Ofelt parametrization, using the equation [4]:

$$\Omega_{\lambda} = \frac{D_1}{e^2 U^{\lambda}} \left(\frac{\bar{\lambda}_{\lambda}}{\bar{\lambda}_1}\right)^3 \frac{9n_1^3}{n_{\lambda} \left(n_{\lambda}^2 + 2\right)^2} \frac{I_{\lambda}}{I_1}, \qquad \lambda = 2,4,6$$
(1)

where e is the elementary charge,  $D_1$  is the magnetic dipole strength,  $U^{\lambda}$  are the tabulated values of the squared reduced matrix elements, and n is the refractive index. Transition  ${}^5D_0 \rightarrow {}^7F_1$  is denoted with 1 in the subscript, while induced electric-dipole emissions  ${}^5D_0 \rightarrow {}^7F_{\lambda=2,4,6}$  are denoted with  $\lambda=2,4,6$  in the subscript.  $I_{1,\lambda}$  are the integrated intensities of corresponding emissions.

The asymmetry ratio, a quantitative measure that shows the degree of deviation from the ideal site symmetry of Eu<sup>3+</sup> ion in the host matrix, given by the ratio of integrated intensities of  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  to  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  emission, is directly proportional to the  $\Omega_{2}$  parameter [8]:

$$R = \frac{I_2}{I_1} \propto \Omega_2 \tag{2}$$

The  ${}^{5}D_{0} \rightarrow {}^{7}F_{6}$  emission is of very low intensity and usually lies beyond the sensitive spectral range of most detectors. Thus, this part is most frequently neglected in the Judd-Ofelt analysis, leading to errors in the estimates of derivative radiative quantities. In the recently published method, this Judd-Ofelt parameter can be accurately estimated from the excitation spectrum by [9]:

$$\Omega_6 = 0.459 \frac{n_6 n_1}{(n_6^2 + 2)^2} \frac{\bar{\lambda}_6}{\bar{\lambda}_1} \frac{\Gamma_6}{\Gamma_1} \cdot 10^{-20} \text{cm}^2.$$
(3)

where  $\Gamma$  are the integrated intensities of peaks in the excitation spectrum. Here, 6 abbreviates  ${}^{7}F_{0} \rightarrow {}^{5}L_{6}$ , and 1 in the subscript stands for  ${}^{7}F_{0} \rightarrow {}^{5}D_{1}$  transition.

From the Judd-Ofelt intensity parameters, the radiative transition probabilities for induced electric dipole transitions can be calculated by [13]:

$$A_{\lambda} = \frac{64\pi^4}{3h} \frac{10^7}{\bar{\lambda}_{\lambda}^3} \frac{n_{\lambda} (n_{\lambda}^2 + 2)^2}{9} e^2 \Omega_{\lambda} U^{\lambda}$$

$$\tag{4}$$

and for magnetic dipole transition by:

$$A_1 = \frac{64\pi^4}{3h} \frac{10^7}{\bar{\lambda}_1^3} n_1^3 \cdot$$
(5)

The total radiative transition probability, or the rate of spontaneous emission, is then equal to the inverse of the radiative lifetime:

$$A_R = \sum_{i=1,2,4,6} A_i = \frac{1}{\tau_R}$$
(6)

Radiative transition probabilities provide estimates of emission branching ratios by:

$$\beta_{\lambda,1} = \frac{A_{\lambda,1}}{A_R} \tag{7}$$

De-excitation rates, A<sub>obs</sub>, are experimentally measured as the inverse of the observable emission lifetime, which then enables the calculation of the non-radiative rates:

$$A_{NR} = A_{obs} - A_R = \frac{1}{\tau_{obs}} - A_R \tag{8}$$

Radiative transition probabilities enable the calculation of the emission cross-sections, given by

the equation [20]:

$$\sigma_{\lambda}(\lambda_p) = \frac{\lambda_{max}^4}{8\pi c n_{\lambda}^2} \frac{\max I_{\lambda}}{I_{\lambda}} A_{\lambda}$$
<sup>(9)</sup>

where c is the speed of light, and  $\lambda_{max}$  is the position of the peak maximum.

[Eu] (%)	5	10	40	60	80	100
$\Omega_2 \cdot 10^{20}$ (cm <sup>2</sup> )	0.41	0.99	0.98	1.17	1.17	1.08
$\Omega_4 \cdot 10^{20}$ (cm <sup>2</sup> )	3.08	4.19	4.63	4.78	4.79	4.30
$\Omega_6 \cdot 10^{20}$ (cm <sup>2</sup> )	1.91	1.38	1.10	0.88	0.86	0.85
A <sub>1</sub> (s <sup>-1</sup> )	23.0	23.0	23.0	23.0	23.0	23.0
A <sub>2</sub> (s <sup>-1</sup> )	6.3	14.2	14.0	16.8	16.9	15.5
A <sub>4</sub> (s <sup>-1</sup> )	22.6	30.4	33.6	34.7	34.8	31.2
A <sub>6</sub> (s <sup>-1</sup> )	1.1	0.8	0.6	0.5	0.5	0.5
β1 (%)	44	34	32	31	31	33
β <sub>2</sub> (%)	12	21	20	22	22	22
β4 (%)	43	44	47	46	46	44
β <sub>6</sub> (%)	2	1	1	1	1	1
$\sigma_1 \cdot 10^{22}$ (cm <sup>2</sup> )	2.47	1.78	1.67	1.61	1.58	1.66
$\sigma_2 \cdot 10^{22} \text{ (cm}^2\text{)}$	0.74	0.74	0.74	0.84	0.84	0.79
$\sigma_4 \cdot 10^{22}$ (cm <sup>2</sup> )	6.21	4.91	5.55	5.25	5.28	4.91
$\tau_{obs}$ (ms)	12.0	11.7	11.2	10.6	9.3	6.9
A <sub>obs</sub> (s <sup>-1</sup> )	83.2	85.4	89.2	95.4	107.9	144.3
A <sub>R</sub> (s <sup>-1</sup> )	52.9	68.3	71.3	75.0	75.1	70.1
A <sub>NR</sub> (s <sup>-1</sup> )	30.3	17.1	17.9	20.4	32.7	74.1
τ <sub>R</sub> (ms)	18.9	14.6	14.0	13.3	13.3	14.3

 Table 1
 Judd-Ofelt parameters for SrGdF:Eu<sup>3+</sup>

The Judd-Ofelt intensity parameters of SGF with various Eu<sup>3+</sup> concentrations are given in Table 1, together with estimated derived quantities: transition probabilities, branching ratios, cross-sections, and lifetimes. All the quantities for transitions  ${}^{5}D_{0} \rightarrow {}^{7}F_{1,2,4}$  are estimated by JOES software [10], while quantities for  ${}^{5}D_{0} \rightarrow {}^{7}F_{6}$  emission are calculated by JOEX software [9]. Due to the lower emission intensity in the spectra, the analysis for the sample with 5% Eu<sup>3+</sup> content has the largest error.  $\Omega_{2}$  parameter, as the measure of covalency and distortion of symmetry is largest for the samples with 60% and 80% of Eu<sup>3+</sup>. A similar trend is observed with the  $\Omega_{4}$  parameter. Parameter  $\Omega_{6}$ , associated with the rigidity of the matrix, decreases uniformly with an increase in Eu<sup>3+</sup> concentration. The radiative transition probabilities confirm that the emission with the largest photon flux is to the  ${}^{7}F_{4}$  level. Non-radiative component increases with Eu<sup>3+</sup> doping concentration.

## Crystal Field analysis of Mn<sup>5+</sup>-doped Ca<sub>6</sub>Ba(PO<sub>4</sub>)<sub>4</sub>O powders

The report given in Deliverable 1.1\_Ln3+- and TM-doped luminescence thermal probes, informs on Synthesis, Structural properties, and Photoluminescent properties of  $Ca_6BaP_{4-4x}Mn_{4x}O_{17}$  (x = 0.005, 0.0075, 0.0125, 0.01, 0.015, 0.02) powder samples. That information and results are used for the Crystal field analysis. Summarised Optical properties of the  $Ca_6Ba(PO_4)_4O:Mn^{5+}$  powder are presented in Figure 1 as summarised results of excitation and emission spectra.



**Figure 1**. Optical properties of the Ca<sub>6</sub>Ba(PO<sub>4</sub>)<sub>4</sub>O:Mn<sup>5+</sup> powder: a) The Kubelka-Munk transformation of the Ca<sub>6</sub>Ba(PO<sub>4</sub>)<sub>4</sub>O:Mn<sup>5+</sup> diffuse reflectance; inset shows photographs of the Ca<sub>6</sub>Ba(PO<sub>4</sub>)<sub>4</sub>O (white) and Ca<sub>6</sub>Ba(PO<sub>4</sub>)<sub>4</sub>O:Mn<sup>5+</sup> (blue) powders, b) Emission spectra measured at -190°C and 10°C, c) Tanabe-Sugano diagram for 3d<sup>2</sup> electron configuration in tetrahedral coordination, d) Emission spectrum of the Ca<sub>6</sub>Ba(PO<sub>4</sub>)<sub>4</sub>O:Mn<sup>5+</sup> measured at room temperature (black line) and the fit to the Gaussian of the <sup>3</sup>T<sub>2</sub>  $\rightarrow$ <sup>3</sup>A<sub>2</sub> emission peak (red line) showing its maximum 1062 nm / 9416 cm<sup>-1</sup>; spectra shown in logarithm scale, e) temperature dependence of the excited state lifetime (symbols – experimental data, solid line – the fit to Eq. (4)); inset: emission decay measured at 208 K, f) Temperature dependence of the <sup>1</sup>E emission peak spectral position (symbols – experimental data, solid line – the fit to Eq. (5)), g) The estimate of configurational diagram based on the spectroscopic data with calculated Stokes shift (E<sub>Stockes</sub>) and Huang-Rhys parameter (S), h) Photoluminescence internal quantum efficiency (QE) of Ca<sub>6</sub>Ba(PO<sub>4</sub>)<sub>4</sub>O:Mn<sup>5+</sup> powders for different concentrations of Mn; inset shows linear dependence of the log<sub>10</sub>(QE/concentration) vs log<sub>10</sub>(concentration) for data equal and above critical concentration (0.75%) with a

slope of -1.97 indicating that a multipolar dipole-dipole mechanism is responsible for the concentration quenching of emission, and i) The linear dependence of  $Ca_6Ba(PO_4)_4O:Mn^{5+}$  emission intensity on excitation power.

Crystal field analysis is a theoretical approach used to understand the behavior of transition metal ions in a crystal lattice. When negatively charged ligands surround a metal ion, the degeneracy of its d-orbitals is lifted due to electrostatic interactions, leading to a specific energy level splitting that depends on the geometry of the surrounding ligands, commonly octahedral or tetrahedral. In addition to the crystal field splitting energy ( $\Delta$ ), the effects of electron–electron repulsion within the d-orbitals are described by Racah parameters (A, B, and C). These parameters quantify inter-electronic repulsion's strength and help refine energy level calculations beyond simple crystal field theory. Among them, B and C are most commonly used, with B often serving as a measure of covalency—the smaller the B value (compared to the free ion), the more covalent the metal-ligand interaction. Crystal field analysis, together with Racah parameters, provides a more complete picture of electronic transitions, magnetic properties, and the spectroscopic behavior of transition metal complexes and doped solid-state materials.

The Tanabe-Sugano model describes the 3d<sup>2</sup> electronic configuration of Mn5+ in a tetrahedral environment for 3d<sup>8</sup> electronic configuration in octahedral symmetry [11], see Figure 6c). The crystal field and Racah parameters are calculated from the following equations using data from diffuse reflection and emission spectra [12, 13]:

$$Dq = \frac{E({}^{3}A_{2} \rightarrow {}^{3}T_{2})}{10} = \frac{10604.5}{10} \text{ cm}^{-1} = 1060 \text{ cm}^{-1}$$
(10)

$$x = \frac{E({}^{3}A_{2} \rightarrow {}^{3}T_{1}) - E({}^{3}A_{2} \rightarrow {}^{3}T_{2})}{Dq} = \frac{15649.5 - 10604.5}{1060.45} = 4.757$$
(11)

$$B = \frac{x^2 - 10x}{15 \cdot (x - 8)} \cdot Dq = 544 \text{ cm}^{-1} \quad \rightarrow \quad \frac{10Dq}{B} = 19.5$$
(12)

$$C = \frac{1}{2} \cdot \left( E \left( {}^{3}A_{2} \rightarrow {}^{1}E \right) - 10Dq - 8.5B + \frac{1}{2}\sqrt{400Dq^{2} + 40DqB + 49B^{2}} \right)$$
(13)  
= 2292 cm<sup>-1</sup>

$$\frac{C}{B} = 4.21\tag{14}$$

By comparing the obtained Dq, B and C parameters with literature data, given in Table 2, one can observe that Ca<sub>6</sub>Ba(PO<sub>4</sub>)<sub>4</sub>O provides the smallest Dq and the largest B parameters amongst all phosphate hosts, and that Li<sub>3</sub>VO<sub>4</sub> is the only host with a smaller Dq (considering available data).

Host material	<i>Dq</i> [cm <sup>-1</sup> ]	<i>B</i> [cm <sup>-1</sup> ]	<i>C</i> [cm <sup>-1</sup> ]	Reference
Li <sub>3</sub> PO <sub>4</sub>	1208	475	2556	[14]
Ca <sub>2</sub> PO <sub>4</sub> Cl	1162	455	2657	[14]
Y <sub>2</sub> SiO <sub>5</sub>	1133	550	2255	[15]
Sr5(PO4)3Cl	1100	500	2320	[16]
YAlO <sub>3</sub>	1100	485	2256	[17]
Sr10(VO4)6F2	1088	518	2321	[18]
$Ca_6Ba(PO_4)_4O$	1060	544	2292	This work
Li <sub>3</sub> VO <sub>4</sub>	1049	646	2006	[19]

**Table 2** Comparison of the Dq, B and C parameters for the tetrahedrally<br/>coordinated Mn<sup>5+</sup> ions in different crystalline solids

By considering the obtained parameters and the configuration coordinate diagram, Figure 1g), the relatively small value of Huang-Rhys parameter S=0.53 is found for the assumed coupling to the  $v_{1+}v_L/v_{3+}v_L$  vibrational mode with energy  $\hbar\omega = 1128.5$  cm<sup>-1</sup>.

The Slater parameters are calculated from Racah parameters by the simple relations [20,21]:

$$F^{(2)} = 49F_2 = 7(7B + C) = 42271 \text{ cm}^{-1}$$
, (15)

$$F^{(4)} = 441F_4 = 441\frac{C}{35} = 28877 \text{ cm}^{-1}.$$
 (16)

Both values are considerably reduced from the free-ion values of  $F^{(2)} = 91427 \text{ cm}^{-1}$  and  $F^{(4)} = 56625 \text{ cm}^{-1}$ .

As follows from the Tanabe-Sugano diagram for the  $3d^2$  configuration in the tetrahedral crystal field (Figure 6c)), the energy separation between the ground state  ${}^{3}A_{2}$  and the first excited state  ${}^{1}E$  (in the strong crystal field) is practically independent on the crystal field strength (both states are parallel to each other). At the same time, this energy interval is very close to the energy interval between the  ${}^{3}F$  and  ${}^{1}D$  states of the free ion, which is determined by the Racah parameters B and C, which vary from host to host because of the covalent effects. As a result, the nephelauxetic effect is dominating in this case.

The combination of Judd–Ofelt theory, crystal field theory, and Tanabe–Sugano formalism, along with the estimation of Racah parameters (B and C) and crystal field splitting (Dq), enables fine-tuning of emission properties. These theoretical insights, bolstered by experimental validation, inform the rational design of luminescent thermal probes with enhanced sensitivity, spectral selectivity, and thermal stability. Ultimately, this deliverable advances the core objective of WP3 by establishing predictive, microscopic models that strongly correlate with the observed luminescence behavior, paving the way for their implementation in the microfluidic thermometer prototype and broader sensor applications envisioned within the REMTES project.

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