

## NanoTBTech

# Nanoparticles-based 2D thermal bioimaging technologies

H2020-FETOPEN-1-2016-2017

Grant Agreement: 801305



Deliverable number D1.3 (D3)

First round of nanoheaters and nanoplatforms

**Final Version** 

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## Project Deliverable Information Sheet

NanoTBTech Project	Project Ref. No. 801305
	Project Title: Nanoparticles-based 2D thermal
	bioimaging technologies
	Project Website: <u>http://www.nanotbtech.eu/</u>
	Deliverable No.: D3
	Deliverable Type: Report
	Dissemination Level: Public
	Contractual Delivery Date: 31 Aug 2019
	Actual Delivery Date: 28 Aug 2019
	EC Project Officer: Barbara GERRATANA

## **Document Control Sheet**

Document	Title: First round of nanoheaters and		
Document	nanoplatforms		
	Version: Final		
	Available at: Participant's Portal		
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## History of Changes

Version	Date	Description	Reviewer
V0	07.08.2019.	Version 0	Vinca
V1	20.08.2019.	Version 1	Prof. Luis Carlos
V2	28.08.2019.	Final version	All partners



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## Abbreviations and Acronyms

AuNPs	Gold nanospheres
BW	Biological window
CNRS	Centre National de la Recherche Scientifique
COD	Crystallography Open Database
CSIC	Agencia Estatal Consejo Superior de Investigaciones Cientificas
DLS	Dynamic light scattering
EG	Ethylene glycol
FIBIRYCIS	Fundacion para la Investigacion Biomedica del Hospital Universitario Ramon Y Cajal
GOF	Goodness of fit
GIG	Gadolinium iron garnet (Gd <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> )
ICSD	Inorganic Crystal Structure Database
Ln <sup>3+</sup>	Lanthanide ions
LPO	Lanthanum phosphate (LaPO <sub>4</sub> )
MPA	3-mercaptopropionic acid
NIR	Near Infra-Red
NPO	Neodymium phosphate (NdPO <sub>4</sub> )
NPs	Nanoparticles
OA	Oleic acid
ODE	Octadecene
PL	Photoluminescence
QDs	Quantum dots
Re	Expected weighted profile factor
Rp	Profile factor



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Rwp	Weighted profile factor		
ТС	thermocouple		
TEM	Transmission electron microscopy		
TVC	Thermovision camera		
ТМ	Transition metal		
UAVR	Universidade de Aveiro		
UCNPs	Upconverting nanoparticles		
UU	Universiteit Utrecht		
UV-VIS	Ultraviolet-visible spectroscopy		
VINCA	Institut Za Nuklearne Nauke Vinca		
WP	Work package(s)		
WPAS	Instytut Niskich Temperatur I Badan Strukturalnych Im. Wlo Trzebiatowskiego Polskiej Akademii Nauk	dzimierz	a
XRD	X-Ray Diffraction		
YAG	Yttrium aluminium garnet (Y <sub>3</sub> Al <sub>5</sub> O <sub>12</sub> )		
YIG	Yttrium iron garnet ( $Y_3Fe_5O_{12}$ )		



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## **D1.3 FIRST ROUND OF NANOHEATERS AND NANOPLATFORMS**

The goal of the NanoTBTech project is to develop a 2-D thermal bioimaging technology featuring sub-microscale resolution, based on nanothermometers and heater-thermometer nanostructures. We will design, synthetize, and bio-functionalize nontoxic luminescent nanostructures, operating essentially beyond 1000 nm, for in vivo nanothermometry and nanoheating. Furthermore, to monitor the temperature-dependent nanostructures' luminescence we will develop a novel imaging system. The effective delivery of that major advance in 2D thermal bioimaging will be implemented through two impactful biomedical showcases: highly spatially-modulated intracellular magnetic/optical hyperthermia and in vivo detection and tracking of cancer. Multiple conceptual breakthroughs can be further envisaged from the proposed 2D-thermal imaging system, credibly spreading its impact towards nonbiomedical technological areas.

Work package 1 (WP1) of the project is titled: "Design and synthesis of luminescent NPs and heaterthermometer nanostructures". The report is mainly given by a lead beneficiary of the WP1: Institut Za Nuklearne Nauke Vinca (VINCA); along with other partners:

- Universidade de Aveiro (UAVR)
- Centre National de la Recherche Scientifique (CNRS)
- Agencia Estatal Consejo Superior De Investigaciones Científicas (CSIC)
- Instytut Niskich Temperatur I Badan Strukturalnych Im. Wlodzimierza Trzebiatowskiego Polskiej Akademii Nauk (WPAS)
- Universiteit Utrecht (UU)

This report describes selection of the first round of the most promising nanoheaters and nanoplatforms (up to 5 materials), including the description of the synthesis and the structural, morphological and optical properties. Materials will be divided and presented under Tasks given in the Grant. At the end, further plans will be summarized in the final paragraph.



## 1. TASK 1.1: SYNTHESIS OF Ln<sup>3+</sup> and TM-doped NANOTHERMOMETERS

Four key aspects of the luminescence characteristics of NPs are engineered per the requirements of the application: i) desired excitation and emission wavelengths (BW-II and BW-III), ii) NIR electronic transitions that can be used for temperature reading, iii) quantum efficiency (q) >10% and iv) non-toxicity.

Desired excitation and emission wavelengths (BW-II and BW-III) and NIR electronic transitions that can be used for temperature reading are controlled by the selection of the dopant: lanthanide activators (Ln<sup>3+</sup>) and transition metals (TM) covering 1000-1500 nm range. Quantum efficiency and non-toxicity is considered by the host material chemistry. Host-dopant combinations are attempted using combinatorial chemistry.

## 1.1 Nd<sup>3+</sup>-doped LaPO<sub>4</sub> and NdPO<sub>4</sub> nanopowders

**Introduction:** In the previous deliverable (D1.1\_Del1\_First Generation of Nanoparticles) conventional hydrothermal synthesis of LaPO<sub>4</sub> (LPO) doped with Nd<sup>3+</sup> (2, 5, 25 mol%) and NdPO<sub>4</sub> (NPO) in nanopowder form is presented together with detail structural, UV-VIS, transmission electron microscopy and photoluminescent characterization.

*Additional nanopowder synthesis:* Additional nanopowder sample, LPO doped with 10mol% Nd<sup>3+</sup>, was synthesized according to the procedure given in D1.1\_Del1\_First Generation of Nanoparticles. 10mol% is often the concentration best suited for detection of physiological temperatures. Moreover, one more sample in the set would be beneficial in comparing theoretical and experimental results. Detailed precursor quantities for additional 10mol% Nd<sup>3+</sup> sample is given in the Table 1.

<b>Table 1</b> Detailed precursor quantities used for 16	0 mol% Nd <sup>3+</sup> -doped LaPO <sub>4</sub> nanopowder synthesis
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	La(NO3)3*6H2O (g)	Nd(NO3)3*6H2O (g)	(NH4)2HPO4 (g)	NaOH (ml)	H2O (ml)
LaPO4: 10mol%Nd	0.7794	0.0890	0.2695	7.4	12.6

*Structural analysis:* In the previous deliverable (D1.1\_Del1\_First Generation of Nanoparticles) LaPO<sub>4</sub> crystal structure is given and discussed. Figure 1 shows X-ray diffraction patterns of the additional 10mol% Nd<sup>3+</sup>-doped LPO sample. The absence of impurity phases indicates that dopant Nd<sup>3+</sup> ions were successfully and uniformly incorporated into the LaPO<sub>4</sub> matrix due to the equal valence (+3) and similar ionic radii between the Nd<sup>3+</sup> (*a* = 0.116 nm) and La<sup>3+</sup> ions (*a* = 0.122 nm)



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[1]. Relevant results of nanopowders structural analysis (unit cell parameter, crystal coherence size, microstrain values and data fit parameters) obtained by using built-in software are presented as inset in Figure 1. The starting parameters for the structural analysis were taken according to the reference [2]. Crystallite size is similar to the whole set (6-9 nm).

*UV-VIS characterization:* UV-Vis-NIR diffuse reflectance spectra of additional 10mol% Nd<sup>3+</sup>-doped LaPO<sub>4</sub> nanopowder recorded at room temperature is given in Figure 1b. There are several characteristic bands placed around: 329 nm ( ${}^{4}I_{9/2} \rightarrow {}^{4}D_{7/2}$ ), 355 nm ( ${}^{4}I_{9/2} \rightarrow {}^{4}D_{3/2, 5/2}$ ), 474 nm ( ${}^{4}I_{9/2} \rightarrow {}^{4}G_{11/2}$ ), 513 nm ( ${}^{4}I_{9/2} \rightarrow {}^{4}G_{9/2}$ ), 525 nm ( ${}^{4}I_{9/2} \rightarrow {}^{4}G_{7/2}$ ), 579 nm ( ${}^{4}I_{9/2} \rightarrow {}^{4}G_{5/2}$ ), 624 nm ( ${}^{4}I_{9/2} \rightarrow {}^{2}H_{11/2}$ ) 680 nm ( ${}^{4}I_{9/2} \rightarrow {}^{4}F_{9/2}$ ), 746 nm ( ${}^{4}I_{9/2} \rightarrow {}^{4}F_{7/2}$ ), 800 nm ( ${}^{4}I_{9/2} \rightarrow {}^{4}F_{5/2}$ ), 871 nm ( ${}^{4}I_{9/2} \rightarrow {}^{4}F_{3/2}$ ) that correspond to Nd<sup>3+</sup> transitions.



**Figure 1** a) Powder X-ray diffraction patterns (Cu  $K_{\alpha}$  radiation) of additional 10mol% Nd<sup>3+</sup>-doped LaPO<sub>4</sub> nanopowder in comparison to the diffraction patterns simulated from single crystal structure data. Relevant results of nanopowders structural analysis are given as Inset, b) Diffuse reflectance spectra of the 10mol% Nd<sup>3+</sup>-doped LaPO<sub>4</sub> nanopowder.

**Transmission electron microscopy:** In the previous deliverable (D1.1\_Del1\_First Generation of Nanoparticles) the preliminary TEM images (Tecnai 12, U = 100 kV) of LaPO<sub>4</sub>:2%Nd<sup>3+</sup> and LaPO<sub>4</sub>:5%Nd<sup>3+</sup> nanopowders were given stating that TEM images of all samples will follow + optimized images for selected ones (Figures 2 and 3). Optimized images of the selected LaPO<sub>4</sub>:2mol%Nd<sup>3+</sup> sample show ellipsoidal particles with 2:1 aspect ratio and around 20 nm in length.



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**Figure 2** TEM images of (a) LaPO<sub>4</sub>: 2% Nd<sup>3+</sup>, (b) LaPO<sub>4</sub>: 5% Nd<sup>3+</sup>, (c) LaPO<sub>4</sub>: 25% Nd<sup>3+</sup> and (d) NPO nanopowders with 20 nm scale given at the bottom.



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Figure 3 Optimized TEM images of the selected LaPO<sub>4</sub>: 2% Nd<sup>3+</sup> sample with 20 nm scale given at the bottom.

**Photoluminescence characterization:** Figure 4a shows photoluminescent excitation spectra ( $\lambda_{em} = 1057 \text{ nm}$ ) of the selected 2mol% Nd<sup>3+</sup>-doped LPO nanopowder in the 550-900nm range, while Figure 4b shows NIR emission under OPO excitation ( $\lambda_{ex} = 580 \text{ nm}$ ). Excitation in the NIR range (e.g.  $\lambda_{ex} = 750 \text{ nm}$  or 808 nm) did not afford similarly well resolved emission spectra.



**Figure 4** Photoluminescence of the 2mol% Nd<sup>3+</sup>-doped LPO nanopowder: a) excitation spectrum ( $\lambda_{em}$  = 1057 nm) and b) emission spectra ( $\lambda_{ex}$  = 580 nm).



This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No **801305.** 

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Room temperature luminescence is very weak, but specifically detectable. Attached H<sub>2</sub>O or other high vibrational energy ligands may strongly quench the NIR-related Nd<sup>3+</sup> emission. Similar observations have already been addressed for other NIR-emitting lanthanides in core-only nanocrystals such as  $\beta$ -NaYF<sub>4</sub>:Er<sup>3+</sup>. Also, high doping concentrations quench the Nd<sup>3+</sup> emission by means of the cross relaxation process [Nd1, Nd2]: [<sup>4</sup>F<sub>3/2</sub>, <sup>4</sup>I<sub>9/2</sub>]  $\rightarrow$  [<sup>4</sup>I<sub>11/2</sub>, <sup>4</sup>I<sub>15/2</sub>] and final non-radiative return to the ground level <sup>4</sup>I<sub>9/2</sub>.

**Photoluminescent thermometry:** In order to avoid concentration quenching photoluminescent temperature measurements were performed on selected 2mol%Nd<sup>3+</sup>-doped nanopowder and presented in Figure 5.



**Figure 5** a) Temperature-dependent emission spectra and b) photoluminescence intensity ratio vs. temperature of the selected 2mol%Nd<sup>3+</sup>-doped LPO nanopowder.

#### Further investigations:

- in order to overcome Nd<sup>3+</sup> photoluminescence quenching small LPO:Nd<sup>3+</sup> nanocrystals will be shelled with un-doped LPO or SiO<sub>2</sub> shell
 - manuscript discussing and summarizing all presented (in both D1.1\_Del1\_First Generation of

Nanoparticles and this Report) is Under preparation



### 1.2. Nd<sup>3+</sup>-doped LaPO<sub>4</sub> and NdPO<sub>4</sub> colloids

**Introduction:** In the previous deliverable (D1.1\_Del1\_First Generation of Nanoparticles) colloidal synthesis of LaPO<sub>4</sub> (LPO) doped with Nd<sup>3+</sup> (2, 5, 25 mol%) and NdPO<sub>4</sub> (NPO) is presented.

*Additional colloid synthesis:* Additional colloid sample, LPO doped with 10mol% Nd<sup>3+</sup>, is synthesized according to the procedure given in D1.1\_Del1\_First Generation of Nanoparticles. Detailed precursor quantities for additional 10mol% Nd<sup>3+</sup> sample are given in the Table 2.

 Table 2 Detailed precursor quantities used for 10mol%Nd<sup>3+</sup>-doped LaPO<sub>4</sub> colloid synthesis.

	La(NO3)3*6H2O	Nd(NO3)3*6H2O	Sodium	(NH4)2HPO4
	(ml)	(ml)	citrate (ml)	(ml)
LaPO4: 10mol% Nd <sup>3+</sup>	2	18	25	10

**Dynamic light scattering:** Table 3 shows dynamic light scattering measurement for the set of Nd<sup>3+-</sup> doped (2,5,10,25 and 50mol%) LaPO<sub>4</sub> and NdPO<sub>4</sub> colloids. All samples were ultrasonically treated for 30 minutes prior the measurements. Samples show a slight tendency to form aggregates despite of the cool storage.

Table 3 Dynamic light scattering measurement for the set of  $Nd^{3+}$ -doped (2,5,10,25 and 50mol%) LaPO<sub>4</sub> and NdPO<sub>4</sub> colloids

Backward scattering measurements ( $\theta = 173^{\circ}$ )				
$La_{1-x}Nd_xPO_4$	$\langle d \rangle / \text{ nm}$	${\rm Number}\%$	Polydispersity index	
x = 0.02	$240.7 \pm 12.96$ $60.84 \pm 8.34$	$0.3 \\ 99.7$	$0.88 \pm 0.06$	
x = 0.05	$123.5 \pm 3.60$ $20.81 \pm 3.61$	$0.7 \\ 99.3$	$0.42 \pm 0.05$	
x = 0.25	$86.16 \pm 20.75$ $26.42 \pm 2.93$	0.3 99.7	$0.49 \pm 0.04$	
x = 1.00	$64.70 \pm 12.92$ $16.54 \pm 1.90$	$0.6 \\ 99.4$	$0.51 \pm 0.17$	

*UV-VIS characterization:* UV-Vis-NIR absorption spectra recorded at room temperature for the set of Nd<sup>3+</sup>-doped (2,5,10,25 and 50mol%) LaPO<sub>4</sub> and NdPO<sub>4</sub> colloids are given in the Figure 6. There are several characteristic bands in Nd<sup>3+</sup>-doped nanopowder samples placed around: 351 nm ( $^{4}I_{9/2} \rightarrow ^{4}D_{3/2}$ ,  $^{4}D_{1/2}$ ), 525 nm ( $^{4}I_{9/2} \rightarrow ^{4}G_{7/2}$ ,  $^{4}G_{9/2}$ ), 581 nm ( $^{4}I_{9/2} \rightarrow ^{4}G_{5/2}$ ,  $^{2}G_{7/2}$ ), 745 nm ( $^{4}I_{9/2} \rightarrow ^{4}F_{7/2}$ ,  $^{4}S_{3/2}$ ),



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799 nm ( ${}^{4}I_{9/2} \rightarrow {}^{4}F_{5/2}$ ,  ${}^{2}H_{9/2}$ ) and 862 nm ( ${}^{4}I_{9/2} \rightarrow {}^{4}F_{3/2}$ ) that correspond to Nd<sup>3+</sup> transitions [5]. The bands are visible above 10mol% Nd-doped colloids.



**Figure 6** UV-Vis-NIR absorption spectra recorded at room temperature for the set of Nd<sup>3+</sup>-doped LaPO<sub>4</sub> colloids

**Photoluminescent characterization:** Figure 7 shows photoluminescence emission spectra ( $\lambda_{ex} = 808 \text{ nm}$ ) of the *x* mol% Nd<sup>3+</sup>-doped LPO (*x* = 2, 5, 25) and NPO colloids set in the 850-1500nm range, while Table 4 shows absolute quantum yield values for the *x* mol% Nd<sup>3+</sup>-doped LPO (*x* = 2, 5, 25) and NPO colloids. Photoluminescence spectra show that there is no concentration quenching even with high doping concentrations and complete replacement of La<sup>3+</sup> with Nd<sup>3+</sup> ion.



**Figure 7** Photoluminescence emission spectra of the *x* mol% Nd<sup>3+</sup>-doped LPO (x = 2, 5, 25) and NPO colloids under  $\lambda_{ex} = 580$  nm.



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Sample	Exc (nm)	Abs QY
LPO_Nd_2mol%_04_008	808	(9.0±0.9)x10 <sup>-6</sup>
LPO_Nd_5mol%_04_008	576.77 W/cm <sup>2</sup>	(2.7±0.3)x10 <sup>-5</sup>
LPO_Nd_25mol%_04_0010	LPD	(3.2±0.3)x10 <sup>-5</sup>
NPO_04_0003		(5.3±0.5)x10 <sup>-5</sup>

**Table 4** Absolute quantum yield values of the  $x \mod Md^{3+}$ -doped LPO (x = 2, 5, 25) and NPO colloids

### **1.3.** Tm<sup>3+</sup> -doped LaPO4 nanopowders

A set of  $Tm^{3+}$ -doped LaPO<sub>4</sub> nanopowders is obtained according to the Nd<sup>3+</sup>-doped LaPO<sub>4</sub> synthesis given in detail in the D1.1\_Del1\_First Generation of Nanoparticles. Detailed precursor quantities for synthesized samples are given in Table 5.

Table 5 Detailed precursor quantities used for *x* mol% Tm<sup>3+</sup>-doped LaPO<sub>4</sub> nanopowder synthesis

	La(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	Tm(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	NaOH	$H_2O$
	(g)	(g)	(g)	(ml)	(ml)
LaPO <sub>4</sub> : 2mol%Tm	0.8486	0.0178	0.2695	7.4	12.6
LaPO4: 5mol%Tm	0.8227	0.0445	0.2695	7.4	12.6
LaPO <sub>4</sub> : 10mol%Tm	0.7794	0.0890	0.2695	7.4	12.6
LaPO4: 15mol%Tm	0.7361	0.1335	0.2695	7.4	12.6
LaPO4: 20mol%Tm	0.6928	0.1780	0.2695	7.4	12.6
LaPO <sub>4</sub> : 25mol%Tm	0.6495	0.2225	0.2695	7.4	12.6

*Structural analysis:* In the case of Tm<sup>3+</sup> ion heavy doping of LaPO<sub>4</sub> to TmPO<sub>4</sub> was not possible above 15 mol% of dopant TmPO<sub>4</sub> crystallizes in a tetragonal xenotime structure type differently to the monoclinic monazite type LaPO<sub>4</sub>. Figure 8 shows X-ray diffraction patterns of the set of Tm<sup>3+</sup>-doped (2, 5, 10, 15, 20 and 25mol%) LaPO<sub>4</sub> nanopowders. Impurity phases are clearly visible in the 20 mol% and 25 mol% Tm<sup>3+</sup>-doped samples.

Relevant results of structural analysis (unit cell parameter, crystal coherence size, microstrain values and data fit parameters) are presented in Table 6. The starting parameters for the structural analysis were taken according to the reference [2]. Crystallite size is in the 6-10 nm range for all samples. Data fit parameters and the goodness of fit are small indicating a highly satisfactory reliability. Microstrain values are low suggesting good ion ordering in the nanocrystals.



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**Figure 8** Powder X-ray diffraction patterns (Cu  $K_{\alpha}$  radiation) of LaPO<sub>4</sub>: x% Tm<sup>3+</sup> (x = 2, 5, 10, 15, 20 and 25) nanopowders in comparison to the diffraction patterns simulated from single crystal structure data.

Table 6 Selected structural parameters obtained from nanopowders XRD measurements using built-in
software

	LPO_Tm_ 2mol%	LPO_Tm_ 5mol%	LPO_Tm_ 10mol%	LPO_Tm_ 15mol%
Crystallite size (Å)	71.46 (2)	100.3 (3)	80.3 (5)	57.92 (5)
Strain (%)	0.35 (7)	0.46 (3)	0.53 (6)	0.32 (3)
Rwp (%)	6.22	5.69	5.17	5.63
Rp (%)	4.60	4.37	3.96	4.21
Re (%)	3.88	3.64	3.59	3.49
GOF	1.6035	1.5631	1.4399	1.6129
a (Å)	6.8591 (18)	6.8539 (13)	6.8449 (16)	6.843 (2)
b (Å)	7.0974 (18)	7.0965 (13)	7.0855 (16)	7.063 (2)
с (Å)	6.5192 (17)	6.5256 (12)	6.5160 (15)	6.510 (2)



This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No **801305**.

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*UV-VIS characterization:* UV-Vis-NIR diffuse reflectance spectra recorded at room temperature for the set of Tm<sup>3+</sup>-doped LaPO<sub>4</sub> nanopowders are given in Figure 9. There are several characteristic bands in Tm<sup>3+</sup>-doped LaPO<sub>4</sub> nanopowder samples placed around: 460 nm ( ${}^{3}H_{6} \rightarrow {}^{1}G_{4}$ ), 680 nm ( ${}^{3}H_{6} \rightarrow {}^{2}F_{2,3}$ ), 790 nm ( ${}^{3}H_{6} \rightarrow {}^{3}H_{4}$ ) and 1210 nm ( ${}^{3}H_{6} \rightarrow {}^{3}H_{5}$ ) that correspond to Tm<sup>3+</sup>-based transitions [3].



Figure 9 UV-Vis-NIR diffuse reflectance spectra recorded at room temperature for the set of  $Tm^{3+}$ -doped LaPO<sub>4</sub> nanopowders

#### Further investigations:

- Transmission electron microscopy and photoluminescence characterization of the set of  $\rm Tm^{3+}$  doped LPO samples will be performed.

#### 1.4. Nd<sup>3+</sup> -doped LiLa P<sub>4</sub>O<sub>12</sub> nanocrystalline powders

In order to compare the two phosphate matrices (LaPO<sub>4</sub> and LiLaP<sub>4</sub>O<sub>12</sub>), a set of Nd<sup>3+</sup>-doped (2,5,10,25 and 50mol%) LiLaP<sub>4</sub>O<sub>12</sub> and LiNdP<sub>4</sub>O<sub>12</sub> nanocrystalline powders were synthesized by the co-precipitation method.

**Synthesis:** In the first step, stoichiometric quantities of  $Li_2CO_3$  (Alfa Aesar, 99%) and  $La(NO_3)_3 \times 6H_2O$  (Alfa Aesar, 99.9%) were dissolved in appropriate amount of HNO<sub>3</sub> (Baker, 65%). In the next step, stoichiometric quantities of  $(NH_4)_2HPO_4$  (Alfa Aesar, 98%) and Nd(NO<sub>3</sub>)<sub>3</sub> x 6H<sub>2</sub>O (Alfa Aesar, 99.9%) were added in the solution, heated and continuously stirred at 80°C until a clear solution is formed. Then, the solution was dried at 95°C in a hot air oven for about a week. The dried



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and powdered samples were additionally annealed at 450°C for 8 h. Detailed precursor quantities are given in Table 7.

**Table 7** Detailed precursor quantities used for x mol%  $Nd^{3+}$ -doped LiLaP<sub>4</sub>O<sub>12</sub> and LiNdP<sub>4</sub>O<sub>12</sub> nanocrystallinepowder synthesis

	Li <sub>2</sub> CO <sub>3</sub> (99%) [g]	La(NO <sub>3</sub> ) <sub>3</sub> x6H <sub>2</sub> O[g]	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> x6H <sub>2</sub> O (98%) [g]	Nd(NO <sub>3</sub> )x6H <sub>2</sub> O [g]
$LiLa_{0.98}Nd_{0.02}P_4O_{12}$	0.3732	4.2435	5.3902	0.0877
$LiLa_{0.95}Nd_{0.05}P_4O_{12}$	0.3732	4.1136	5.3902	0.2192
$LiLa_{0.90}Nd_{0.10}P_4O_{12}$	0.3732	3.8971	5.3902	0.4383
$LiLa_{0.75}Nd_{0.25}P_4O_{12}$	0.3732	3.2476	5.3902	1.096
$LiLa_{0.50}Nd_{0.50}P_4O_{12}$	0.3732	2.1650	5.3902	2.1900
LiNdP <sub>4</sub> O <sub>12</sub>	0.3732	-	5.3902	4.3834

*Structural analysis:* LiLaP<sub>4</sub>O<sub>12</sub> and LiNdP<sub>4</sub>O<sub>12</sub> crystallize in a pure monoclinic monazite phase of a space group  $P12_1/n1$  (ICSD 416877). In this crystal lattice, lanthanide ions are coordinated with eight oxygen atoms forming polyhedrons (LaO<sub>8</sub>/NdO<sub>8</sub>), see Figure 10.



Figure 10 Lithium, lanthanum phosphate (LiLaP<sub>4</sub>O<sub>12</sub>) structure

Figure 11 shows X-ray diffraction patterns of the Nd<sup>3+</sup>-doped LiLaP<sub>4</sub>O<sub>12</sub> and LiNdP<sub>4</sub>O<sub>12</sub> nanopowders. The absence of impurity phases indicates that the dopant Nd<sup>3+</sup> ions were successfully and uniformly incorporated into the LiLaP<sub>4</sub>O<sub>12</sub> matrix due to the equal valence (+3) and similar ionic radii between the Nd<sup>3+</sup> (a = 0.116 nm) and La<sup>3+</sup> ions (a = 0.122 nm) [1].

Relevant results of structural analysis (unit cell parameter, crystal coherence size, microstrain values and data fit parameters) are presented in Table 8. The starting parameters for the structural analysis were taken according to the reference [4]. Crystallite size is in the micron size range for all samples. Data fit parameters and the goodness of fit are small indicating a highly satisfactory reliability. Microstrain values are low suggesting good ion ordering.



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**Figure 11** Powder X-ray diffraction patterns (Cu  $K_{\alpha}$  radiation) of LiLaP<sub>4</sub>O<sub>12</sub>: x% Nd<sup>3+</sup> (x = 2, 5, 10, 25 and 50) and LiNdP<sub>4</sub>O<sub>12</sub> nanopowders in comparison to the diffraction patterns simulated from single crystal structure data.

**Table 8** Selected structural parameters obtained from nanocrystalline powders XRD measurements using built-in software

ICSD	LiLa <sub>0.98</sub> Nd <sub>0.02</sub> P	LiLa <sub>0.95</sub> Nd <sub>0.05</sub> P	LiLa <sub>0.90</sub> Nd <sub>0.1</sub> P	LiLa <sub>0.75</sub> Nd <sub>0.25</sub> P	LiLa <sub>0.50</sub> Nd <sub>0.50</sub> P	LiNdP <sub>4</sub>
416877	4012	4012	4 <b>0</b> 12	4012	4012	012
Crystall ite size	392 (6)	384 (6)	388 (7)	266 (4)	353 (6)	336 (6)
(Å)						
Strain (%)	0.12 (3)	0.13 (3)	0.10 (6)	0.19 (4)	0.13 (4)	0.15 (4)
Rwp (%)	12.03	12.48	10.38	9.89	9.35	7.17
Rp (%)	8.80	8.95	7.42	7.17	6.55	5.17
Re (%)	3.90	3.82	3.82	4.23	3.94	3.65
GOF	3.0819	3.2644	2.7149	2.3408	2.3711	1.9630
a (Å)	16.5745 (11)	16.5761 (12)	16.5593 (12)	16.5409 (17)	16.500 (2)	16.4342 (12)
b (Å)	7.0997 (4)	7.1017 (4)	7.0957 (4)	7.0919 (6)	7.0804 (8)	7.0632 (4)
c (Å)	9.8711 (6)	9.8692 (7)	9.8596 (6)	9.8436 (9)	9.8096 (12)	9.7472 (7)



This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No **801305**.

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*UV-VIS characterization:* UV-Vis-NIR diffuse reflectance spectra recorded at room temperature for the set of set of Nd<sup>3+</sup>-doped (2,5,10,25 and 50mol%) LiLaP<sub>4</sub>O<sub>12</sub> and LiNdP<sub>4</sub>O<sub>12</sub> nanocrystalline powders are given in Figure 12a. There are several characteristic bands in Nd<sup>3+</sup>-doped nanopowder samples placed around: 354 nm ( ${}^{4}I_{9/2} \rightarrow {}^{4}D_{3/2}$ ), 525 nm ( ${}^{4}I_{9/2} \rightarrow {}^{4}G_{7/2}$ ), 579 nm ( ${}^{4}I_{9/2} \rightarrow {}^{4}G_{5/2}$ ), 746 nm ( ${}^{4}I_{9/2} \rightarrow {}^{4}F_{7/2}$ ), 802 nm ( ${}^{4}I_{9/2} \rightarrow {}^{4}F_{5/2}$ ) and 871 nm ( ${}^{4}I_{9/2} \rightarrow {}^{4}F_{3/2}$ ) that correspond to Nd<sup>3+</sup> transitions [5].



**Figure 12** (a) Diffuse reflectance spectra of the nanopowders LiLaP<sub>4</sub>O<sub>12</sub>: x% Nd<sup>3+</sup> (x = 2, 5,10 and 25) and LiNdP<sub>4</sub>O<sub>12</sub> with assigned electronic transitions of Nd<sup>3+</sup> and (b) Converted Kubelka-Munk plots of the reflectance data.

For future simulations of the energy migration and heat propagation processes and comparison thereof with experimental data, it is necessary to know the doping concentrations of the activator of interest accurately. Thus, the nominal content  $x \mod 6$  of Nd<sup>3+</sup> in LiLaP<sub>4</sub>O<sub>12</sub> (x = 2, 5, 25) was verified by means of diffuse reflectance spectra. The reflectance data was transformed to the Kubelka-Munk function *K/S* that is proportional to the absorption coefficient,

$$\frac{K}{S} = \frac{(1 - R_{\infty})^2}{2R_{\infty}} \sim \alpha \tag{1}$$

with  $R_{\infty}$  as the diffuse reflectance of the powder (Figure 12b).

The Kubelka-Munk function is supposed to be linearly dependent on the concentration given that the interactions between the Nd<sup>3+</sup> ions are not too strong in order to have significant effects upon the absorption coefficient. Upon cumulated integration of the absorption peaks up to 32000 cm<sup>-1</sup>, a plot of these signals against the Nd<sup>3+</sup> content can be well fitted with a linear function ( $R^2 = 0.9826$ ). The intercept is not different from zero within statistical significance ( $\alpha = 0.05$ , *t* hypothesis test), as should be expected (see Figure 13).



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**Figure 13** Calibration curve of the integrated Kubelka-Munk signals (see Figure 10(b)). The dotted line represents a least-square fit to the data. Within statistical significance ( $\alpha = 0.05$ ), the intercept is not different from 0.

**Photoluminescence characterization:** Figure 14a shows photoluminescent excitation spectra ( $\lambda_{em}$  = 1047 nm) of the selected 2mol% Nd<sup>3+</sup>-doped LiLaP<sub>4</sub>O<sub>12</sub> sample in the 550-900 nm range, while Figure 14b shows NIR emission ( $\lambda_{ex}$  = 750 nm) of the selected 2 mol% Nd<sup>3+</sup>-doped LiLaP<sub>4</sub>O<sub>12</sub> sample. Characteristic luminescence of Nd<sup>3+</sup> in LiLaP<sub>4</sub>O<sub>12</sub> microcrystals is detectable and very intense.



**Figure 14** Photoluminescence of the 2mol% Nd<sup>3+</sup>-doped LiLaP<sub>4</sub>O<sub>12</sub> sample: a) excitation spectrum ( $\lambda_{em}$  = 1047 nm) and b) emission spectra ( $\lambda_{ex}$  = 750 nm)

**Photoluminescent thermometry:** Temperature-dependent photoluminescence measurements were performed on a selected 2 mol% Nd<sup>3+</sup>-doped LiLaP<sub>4</sub>O<sub>12</sub> sample and presented in Figure 15. Temperature-dependent luminescence of Nd<sup>3+</sup> is observable, but Boltzmann equilibrium fails at physiological temperatures when probing the levels  ${}^{4}F_{5/2}$  and  ${}^{4}F_{3/2}$ . Cross relaxation (higher Nd<sup>3+</sup> concentrations) could partially help here.



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Figure 15 a) Temperature-dependent emission spectra and b) photoluminescence intensity ratio vs. temperature of the selected 2 mol%  $Nd^{3+}$ -doped LiLaP<sub>4</sub>O<sub>12</sub> sample.

#### Further investigations:

- manuscript discussing and summarizing all presented results is Under preparation

#### **1.5. Gold nanospheres (AuNPs) and AuNPs@SiO<sub>2</sub> core-shell nanostructures**

*Introduction:* In the previous deliverable (D1.1\_Del1\_First Generation of Nanoparticles) it was stated that these samples will be furthered characterized by transmission electron microscopy (TEM).

**Transmission electron microscopy:** Transmission electron microscopy images are given as Figures 16 and 17. Images show that for the sample with presumably thinner  $SiO_2$  layer (Figure 16) Au NPs are somewhat better dispersed compared with the sample with the presumably thicker  $SiO_2$  layer (Figure 17) where NPs agglomeration is clearly visible. Further optimization of the synthesis protocol is needed.



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Figure 16 TEM images of the core-shell AuNPs@SiO<sub>2</sub> (AuNPs@SiO<sub>2</sub>\_04\_0002) under: a) high (20nm bar) and b) low (200nm bar) magnification



Figure 17 TEM images of the core-shell AuNPs@SiO<sub>2</sub> (AuNPs@SiO<sub>2</sub>\_04\_0004) under: a) high (20nm bar) and b) low (200nm bar) magnification

#### Further investigations:

- further optimization of the synthesis will be done.

## 1.6. Hybrid Eu<sup>3+</sup>-doped LaPO<sub>4</sub> / Ag nanopowders

*Introduction:* In the previous deliverable (D1.1\_Del1\_First Generation of Nanoparticles) synthesis, structural and optical (UV-VIS and photoluminescence) characterization of hybrid Eu<sup>3+</sup>-doped LaPO<sub>4</sub> nanopowders is reported. Now, additional samples with higher Ag nanopowders concentrations were synthesized and characterized. The set now consists of six samples: 5 mol% Eu<sup>3+</sup>-doped LPO with a concentration of 0.1x10<sup>-4</sup> M, 2x10<sup>-4</sup> M, 1x10<sup>-3</sup> M, 2x10<sup>-3</sup> M, 3x10<sup>-3</sup> M Ag nanoparticles.



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*Structural analysis*: Figure 18 show X-ray diffraction patterns of the hybrid 5 mol% Eu<sup>3+</sup>-doped LaPO<sub>4</sub> / Ag nanopowders. The absence of any impurity phases, even up to the highest Ag concentration, indicates that the dopant Eu<sup>3+</sup> ions were successfully and uniformly incorporated into the LaPO<sub>4</sub> matrix.



Figure 18 X-ray diffraction patterns of the hybrid 5 mol% Eu<sup>3+</sup>-doped LaPO<sub>4</sub> / Ag nanopowders

*Transmission electron microscopy:* Preliminary TEM images for 5 mol% Eu<sup>3+</sup>-doped LaPO<sub>4</sub> and hybrid 5 mol% Eu<sup>3+</sup>-doped LaPO<sub>4</sub>/3x10<sup>-3</sup> Ag nanopowders are shown as Figure 19. Optimized images will follow.



Figure 19 TEM images of a) 5 mol% Eu $^{3+}$ -doped LaPO $_4$  and b) hybrid 5 mol% Eu $^{3+}$ -doped LaPO $_4/3x10^{-3}$  Ag NPs



This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No **801305.** 

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*UV-VIS characterization:* UV-Vis-NIR diffuse reflectance spectra recorded at room temperature for the 5mol%  $Eu^{3+}$ -doped LaPO<sub>4</sub> and set of hybrid 5mol%  $Eu^{3+}$ -doped LaPO<sub>4</sub> / Ag nanopowders are given in Figure 20. In the sample with the highest Ag concentration line placed around 410 nm that corresponds to the absorption of Ag nanoparticles, is clearly visible.



Figure 20 UV-Vis-NIR diffuse reflectance spectra recorded at room temperature for the 5 mol%  $Eu^{3+}$ -doped LaPO<sub>4</sub> and hybrid 5 mol%  $Eu^{3+}$ -doped LaPO<sub>4</sub> / Ag nanopowders

**Photoluminescent characterization:** The photoluminescent intensity varies in the  $Eu^{3+}$ -doped LaPO<sub>4</sub> and the hybrid  $Eu^{3+}$ -doped LaPO<sub>4</sub> / Ag nanopowders. Figure 21 shows that the PL is enhanced with incorporation of Ag nanoparticles. It is well known that the Ag nanoparticles cause an enhancement of the excitation field and an increase of the radiative rate of active luminescent centres due to a located surface plasmon effect.



**Figure 21** Photoluminescence a) emission spectra ( $\lambda_{ex} = 394 \text{ nm}$ ) of 5 mol% Eu<sup>3+</sup>-doped LaPO<sub>4</sub> and hybrid 5 mol% Eu<sup>3+</sup>-doped LaPO<sub>4</sub> / Ag nanopowders and b) integrated emission intensity vs. Ag nanoparticles concentration



This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No **801305**.

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#### Further investigations:

- manuscript discussing and summarizing all presented results here is Under preparation

#### 1.7. Nd<sup>3+</sup>-doped LaF<sub>3</sub> colloids

*Introduction:* In the previous deliverable (D1.1\_Del1\_First Generation of Nanoparticles) synthesis, structural and UV-VIS characterization of the Nd<sup>3+</sup> and Sm<sup>3+</sup>-doped LaF<sub>3</sub> colloids was given.

*Dynamic light scattering*: Dynamic light scattering results are presented in Table 9.

**Table 9** Dynamic light scattering measurements of the Nd3+-doped LaF3 colloid

Forward	scattering	measurements	$(\theta =$	$12.8^{\circ})$
---------	------------	--------------	-------------	-----------------

$LaF_3:Ln^{3+}$	$\langle d  angle$ / nm	Polydispersity index
$04_{0001} (12\% \text{ Nd}^{3+})$	$635.1 \pm 128.5$	$0.58\pm0.29$
$0401\_0003 (12\% \text{ Nd}^{3+})$	$626.7\pm56.87$	$0.91\pm0.09$
$04_{0002} (6\% \text{ Sm}^{3+})$	$614.0\pm49.1$	$1.00 \pm 0.00$

Backward scattering measurements ( $\theta = 173^{\circ}$ )

$LaF_3:Ln^{3+}$	$\langle d  angle \ / \ { m nm}$	Number%	Polydispersity index
0.4  0.001  (1.9%  N.43+)	$67.26 \pm 16.52$	0.1	1.00 + 0.00
$04_{0001} (12\% \text{ Nd}^{-1})$	$3.526 \pm 0.750$	99.9	$1.00 \pm 0.00$
$0.401  0.002  (1.2\% \text{ NJ}^{3+})$	$134.7\pm38.1$	0.1	0.80 + 0.19
$0401_{0003}(12\% \text{ Nd}^{-1})$	$5.736 \pm 0.654$	99.9	$0.89 \pm 0.12$
04,0000,(6%,S=3+)	$385.9 \pm 32.5$	0.7	$0.78 \pm 0.01$
$04_{0002} (6\% \text{ Sm}^{\circ})$	$62.05 \pm 9.56$	99.3	$0.78 \pm 0.01$

**Photoluminescent characterization:** Figure 22 shows the photoluminescence emission spectra of the 12 mol% Nd<sup>3+</sup>-doped LaF<sub>3</sub> colloids under  $\lambda_{ex}$  = 808 nm. Table 9 shows absolute quantum yield values of the 12 mol% Nd<sup>3+</sup>-doped LaF<sub>3</sub> colloids.



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Figure 22 Photoluminescent emission spectra of the 12 mol% Nd<sup>3+</sup> -doped LaF<sub>3</sub> colloids under  $\lambda_{ex}$  = 808 nm Table 10 Absolute quantum yield values of the 12 mol% Nd<sup>3+</sup>-doped LaF<sub>3</sub> colloids

Sample	Exc (nm)	Abs QY
LaF_Nd_12mol%_04_0001	808	(5.2±0.5)x10 <sup>-5</sup>
LaF_Nd_12mol%_04_0003	LPD 576,77 (W/cm <sup>2</sup> )	(4.9±0.5)x10-5

Further investigations:	
- comparison between low-phonon energy LaF $_3$ and LaPO $_4$ / LiLaP $_4O_{12}$ matrix will be done	

## 1.8. Mn<sup>4+</sup>-doped Li<sub>1.8</sub>Na<sub>0.2</sub>TiO<sub>3</sub> powders

Manuscript summarizing the data entitled "Li<sub>1.8</sub>Na<sub>0.2</sub>TiO<sub>3</sub>:Mn<sup>4+</sup>: The highly sensitive probe for the low-temperature lifetime-based luminescence thermometry " is published in *Optics Communications* (https://doi.org/10.1016/j.optcom.2019.07.056).



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## 2. TASK 1.2: SEMICONDUCTOR COLLOIDAL NANOTHERMOMETERS

An alternative strategy on the preparation of Cd- and Pb-free QDs due to their (expected) low toxicity is performed. Ag<sub>2</sub>S is chosen because it requires considerably simpler synthesis conditions, compared to those for III-V QDs (NIR emission 800-1300 nm with q values in water of 0.30). The microwave-hydrothermal synthesis for Ag<sub>2</sub>S QDs is set and will be improved (size distribution and *q*) to make them operational for bio-applications in the NIR spectral region.

### 2.1. Ag2S colloidal dispersions

#### 2.1.1. Ag2S from VINCA partner

*Introduction:* In the previous deliverable (D1.1 Del1 First Generation of Nanoparticles) synthesis, structural and UV-VIS characterization of the Ag<sub>2</sub>S colloids was presented. There is still an issue with the colloids stability even after cold storage and ultrasound treatment prior the measurements, please see Figure 23.



Figure 23 Images of the samples after photoluminescent measurements

**Photoluminescent characterization:** Figure 24 shows photoluminescent emission spectra of the Ag<sub>2</sub>S colloid samples under  $\lambda_{ex}$  = 350 nm, while Table 11 shows absolute quantum yield values. The spectra show broad luminescence in the 1000-1400 nm range with the main peak placed around 1150 nm and the shoulder around 1250 nm. An additional peak at higher wavelengths could be attributed to the defect level emissions. In order to make more crystalline Ag<sub>2</sub>S nanoparticles and minimize defect level emission, an additional sample was synthesized. Detailed precursor quantities are given in Table 12.



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Figure 24 Photoluminescent emission spectra of the Ag<sub>2</sub>S colloid samples under  $\lambda_{ex}$  = 350 nm

**Table 11** Absolute quantum yield values of the Ag2S colloid samples

Sample	<b>Exc (nm)</b> LPD 576,77 (W/cm <sup>2</sup> )	Absolute QY
Ag <sub>2</sub> S_01_0001		(5.0±0.5)x10-4
Ag <sub>2</sub> S_01_0002	(5.0±0.5)x10 <sup>-4</sup>	
Ag <sub>2</sub> S_01_0003	909	(2.3±0.2)x10 <sup>-3</sup>
Ag <sub>2</sub> S_01_0004	808	(2.4±0.2)x10 <sup>-3</sup>
Ag <sub>2</sub> S_01_0005	(3.3±0.3)x10 <sup>-3</sup>	
Ag <sub>2</sub> S_01_0006		(1.5±0.2)x10 <sup>-3</sup>

Table 12 Precursor quantities and reaction parameters used for additional Ag<sub>2</sub>S colloid synthesis.

Sample	AgNO <sub>3</sub> (g)	MPA (ml)	EG (ml)	Temperature (°C)	Time (min.)
7	0.0255	0.305	4.5	160	60



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### 2.1.2. Ag<sub>2</sub>S from CNRS partner

*Synthesis:* For the synthesis of the Ag<sub>2</sub>S colloids in toluene (see Figure 25), the procedure is given in [6] and presented as a scheme in Figure 26.



Figure 25 Synthesized Ag<sub>2</sub>S colloidal sample



Figure 26 Scheme of the  $Ag_2S$  colloid synthesis in toluene



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*Transmission electron microscopy:* Representative transmission electron microscopy image is given as Figure 27 while Figure 28 shows the respective size distribution of the nanoparticles.



Figure 27 TEM image of the synthesized Ag<sub>2</sub>S nanoparticles in toluene



Figure 28 Respective nanoparticles size distribution.

*UV-VIS characterization:* UV-VIS absorption of the  $Ag_2S$  colloid given as Figure 29 shows an appreciable absorption in the BW-I range.



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*Photoluminescent characterization:* Photoluminescence measurements of the Ag<sub>2</sub>S colloids in the NIR range given in Figure 30 shows emission in the BW-II range.



Figure 30 Photoluminescence of the  $Ag_2S$  colloid in toluene



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## 2.1.3. Commercial Ag<sub>2</sub>S colloid

Commercial Ag<sub>2</sub>S colloid in water was purchased from *Zeqiao Technology Hongkong Ltd.* (please see Figure 31) and characterized in detail by the CNRS and UAVR partners.



Figure 31 Commercial Ag<sub>2</sub>S colloid

*Transmission electron microscopy:* Representative transmission electron microscopy images are given as Figure 32 while Figure 33 shows respective size distribution of the nanoparticles.



Figure 32 TEM images of the commercial  $Ag_2S$  nanoparticles



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Figure 33 Respective nanoparticles size distribution.

*UV-VIS characterization:* UV-VIS absorption of the commercial Ag<sub>2</sub>S colloid is given as Figure 34.



Figure 34 UV-VIS absorption spectra of the commercial  $Ag_2S$  colloid

*Photoluminescent characterization:* Quantum yield measurements were performed on commercial Ag<sub>2</sub>S and given in Table 13.



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Table 13 Quantum yield and brightness	s values for the commercial Ag <sub>2</sub> S colloid
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P. Density (W/cm <sup>2</sup> )	Φ	$\epsilon_{808} (M^{-1} cm^{-1})$	B <sub>808</sub> (M <sup>-1</sup> cm <sup>-1</sup> )
20	$(8.0 \pm 0.8) \times 10^{-4}$	178±3	0.14±0.01
64	$(7.8 \pm 0.8) \times 10^{-4}$		0.14±0.01
102	$(7.1 \pm 0.7) \times 10^{-4}$		0.13±0.01
145	$(7.1 \pm 0.7) \times 10^{-4}$		0.13±0.01

#### Further investigations:

- Toward green Ag<sub>2</sub>S synthesis following the procedure given in [7]

- Optimize Ag\_S photoluminescence properties by Ag\_S@ZnS synthesis

- Thermometer validation

- Finding the best PL parameters for  $Ag_2S$ 



## 3. TASK 1.3: NANOHEATERS AND HEATER-THERMOMETER NANOPLATFORMS

Under *TASK 1.3: NANOHEATERS AND HEATER-THERMOMETER NANOPLATFORMS* nanoheaters from i) magnetic NPs ( $Fe_2O_3$ ,  $Fe_3O_4$ ,  $Y_3Fe_5O_{12}$ ,  $Ln^{3+}$ -doped  $Fe_2O_3$ ) and ii) highly absorbing luminescent NPs (NaNdF<sub>4</sub>) are prepared. In i) efficient heating can be achieved by a magnetic field whereas in ii) heating is produced through strong non-radiative relaxation processes, following optical absorption.

### 3.1. Fe<sup>3+</sup>-doped Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> (YAG), Y<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> (YIG) and Gd<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> (GIG) powders

*Introduction:* In the previous deliverable (D1.1\_Del1\_First Generation of Nanoparticles) synthesis, structural, UV-VIS and magnetic hyperthermia measurements of  $Y_3Al_{4.995}Fe_{0.005}O_{12}$ ,  $Y_3Al_{4.95}Fe_{0.05}O_{12}$  and  $Y_3Fe_5O_{12}$  samples were presented. Samples with low Fe<sup>3+</sup>-doping concentrations did not show any temperature increase while the YIG sample presented huge temperature increase under alternative magnetic field. Here, two additional samples,  $Gd_3Fe_5O_{12}$  and  $Y_3Al_{2.5}Fe_{2.5}O_{12}$  were synthesized and characterized.

*Synthesis:* Two samples with following formula:  $Gd_3Fe_5O_{12}$  (GIG) and  $Y_3Al_{2.5}Fe_{2.5}O_{12}$  were synthesized using the procedure reported in D1.1\_Del1\_First Generation of Nanoparticles. Detailed precursor quantities are given in Table 14.

Samples	$Y(NO_3)_3*6H_2O$ (g)	Gd(NO <sub>3</sub> ) <sub>3</sub> *6H <sub>2</sub> O (g)	Al(NO <sub>3</sub> ) <sub>3</sub> *9H <sub>2</sub> O (g)	Fe(NO <sub>3</sub> ) <sub>3</sub> *9H <sub>2</sub> O (g)	CA (g)	EG (ml)
<i>Y</i> <sub>3</sub> <i>Al</i> <sub>2.5</sub> <i>Fe</i> <sub>2.5</sub> <i>O</i> <sub>12</sub>	1.7	/	1.46	1.49	11.37	16.6
Gd <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub>	/	1.43	/	2.14	8.14	11.85

**Table 14** Precursor quantities used for Gd<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> and Y<sub>3</sub>Al<sub>2.5</sub>Fe<sub>2.5</sub>O<sub>12</sub> powder synthesis

*Structural analysis:* XRD patterns of  $Gd_3Fe_5O_{12}$  and  $Y_3Al_{2.5}Fe_{2.5}O_{12}$  powders together with corresponding COD cards No. 1008147 and 2101364, respectively, are presented in Figure 35. Neither other phase peaks nor traces of impurities were detected indicating that dopant Fe<sup>3+</sup> ions have been effectively incorporated into the  $Y_3Al_5O_{12}$  host lattice.



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Figure 35 X-ray diffraction pattern of  $Gd_3Fe_5O_{12}$  and  $Y_3Al_{2.5}Fe_{2.5}O_{12}$  powders together with corresponding COD cards No. 1008147 and 2101364

Relevant results of structural analysis (unit cell parameter, crystal coherence size, microstrain values and data fit parameters) are presented in Table 15. The starting parameters for the structural analysis were taken according to the reference [8, 9]. The goodness of fit is small indicating a highly satisfactory reliability of the final fitting parameters. Microstrain values are low suggesting good ion ordering in the nanocrystals.

	<b>Gd</b> <sub>3</sub> <b>Fe</b> <sub>5</sub> <b>O</b> <sub>12</sub>	<i>Y</i> <sub>3</sub> <i>Al</i> <sub>2.5</sub> <i>Fe</i> <sub>2.5</sub> <i>O</i> <sub>12</sub>
Crystallite size (Å)	499 (5)	384.3 (6)
a (Á)	12.4719 (5)	12.2087 (13)
b(Å)	12.4719 (5)	12.2087 (13)
c(Á)	12.4719 (5)	12.2087 (13)
Strain (%)	0.098 (15)	0.03 (2)
Rwp (%)	3.18	4.87
Rp (%)	2.34	2.88
Re (%)	1.77	1.97
GOF	1.7938	2.4662

 Table 15 Selected structural parameters obtained from XRD measurements.

*UV-VIS characterization:* UV-Vis-NIR diffuse reflectance spectra of  $Y_3Al_{2.5}Fe_{2.5}O_{12}$  and  $Gd_3Fe_5O_{12}$  powders recorded at room temperature are presented in Figure 36. With  $Gd^{3+}$  replacement in the matrix, two bands placed around 600 nm with a shoulder around 700 nm ( ${}^6A_1 \rightarrow {}^4T_2$  transition of  $Fe^{3+}$  ions in the octahedral site with a contribution of  ${}^6A_1 \rightarrow {}^4T_1$ ,  ${}^4T_2$  transitions of  $Fe^{3+}$  ions in the octahedral site) and 900 nm ( ${}^6A_1 \rightarrow {}^4T_1$  transition of iron ions in the octahedral site) shift toward lower wavelengths [10].





Figure 36 UV-Vis-NIR diffuse reflectance spectra recorded at room temperature of  $Y_3Al_{2.5}Fe_{2.5}O_{12}$  (red) and  $Gd_3Fe_5O_{12}$  (black) powders.

**Particles dispersion and functionalization:** In addition, for the dispersion of the nanoparticles, different functionalization methods were applied. First, suspension in citric acid solutions approach was implemented (reported in Powder-to-colloidal nanoparticles protocol) without success. Next, wet milling and acidic treatmet approach [11] was implemented again with no positive results. Third procedure schematically given as Figure 37 and in [12] is successfully implemented.



Figure 37 Schematic approach for nanoparticles- $NH_2$  functionalization



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Also the approach as given in [13] and depicted in the scheme in Figure 38 was successfully implemented.



Figure 38 Schematic approach for nanoparticles-PEG functionalization

The approaches were applied for YIG, Fe-doped YAG and GIG nanoparticles functionalization and dispersion.

**Dynamic light scattering:** Dynamic light scattering measurement presented in Tables 16-18 show the zeta potential change confirming change in the NPs surface.

Table 1	<b>16</b> Dynamic	light scattering	measurement of YIG,	YIG-NH <sub>2</sub> and YIG	-PEG nanoparticles
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	Hydrodynamic diameter (nm)	Zeta potential (mV)
YIG	aggregates	-7.9
YIG-NH <sub>2</sub>	574 (pdI 0.50)	53.6
YIG-PEG	1256 (pdI 0.77)	-1.3

Table 1	7 Dynamic	light scattering	g measurement of GIG	. GIG-NH <sub>2</sub> and	<b>GIG-PEG</b> nanoparticles
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	Hydrodynamic diameter (nm)	Zeta potential (mV)
GIG	aggregates	-0.9
GIG-NH <sub>2</sub>	369 (pdI 0.70)	-2.7
GIG-PEG	423 (pdI 0.77)	-5.0

Table 18 Dynamic light scattering measurement of Fe-doped YAG, YAG-NH<sub>2</sub> and YAG-PEG nanoparticles

	Hydrodynamic diameter (nm)	Zeta potential (mV)
YAG	aggregates	-1.9
YAG-NH <sub>2</sub>	202 (pdI 0.26)	34.1
YAG-PEG	256 (pdI 0.27)	-1.1



This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No **801305**.

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However, the absorbance properties of the NPs could affect the DLS measurements (for example see Figure 36). The laser used has a wavelength of 633 nm that overlaps with NPs absorption. Therefore, the sensitivity of the measurement could be affected, resulting in the shielding of the small/stable NPs.

#### Further plans:

- Magnetic properties of NPs attract them to the magnetic stirrer so homogeneous suspension can't be completely insured during the functionalization. In order to overcome this issue mechanical stirrer will be used.

- Other functionalization procedures will be implemented.
- Dynamic light scattering measurements will be done with green laser.
- Obtained colloids will be further characterized: colloidal stability, TEM, TGA.

### 3.2. NaNdF<sub>4</sub> doped with Sm<sup>3+</sup>/Dy<sup>3+</sup>

*Introduction:* In the previous deliverables (D1.1 First Generation of Nanoparticles; D1.2 - powder to colloid nanoparticles; D2.1 - Core-shell nanoparticles) synthesis, structural, morphological and optical characterization of  $Nd^{3+}$ ,  $Sm^{3+}$  and  $Dy^{3+}$  doped colloidal  $NaYF_4$  is given. Here, the effect of  $Sm^{3+}$  or  $Dy^{3+}$  ions doping of  $NaNdF_4$  was considered.

#### Synthesis:

**Preparation of Precursor**: Stoichiometric amounts of lanthanide oxides  $(Y_2O_3, Nd_2O_3, Sm_2O_3 \text{ or } Dy_2O_3 - 1 \times 10^{-3}M)$  were mixed with 50% aqueous acetic acid. The mixture was transferred to a Teflon vessel and heated to 200°C for 120 min under pressure, with the use of a stainless steel hydrothermal autoclave. The final precursor was obtained by evaporation of residual acid and water in rotary evaporator, and further drying at 165°C for 12 h.

**Preparation of nanoparticles:** In a typical synthesis procedure, the given amounts  $(2 \times 10^{-3} \text{ M Ln}^{3+})$  of  $(CH3COO)_3$ Ln lanthanide precursors were added to the three-neck flask with 12 ml OA and 30ml ODE. The solution was stirred under nitrogen atmosphere and heated slowly to 140 °C, followed by degassing under vacuum for 30 min to remove oxygen and water. After evaporation of residual water, the nitrogen atmosphere was maintained during the synthesis. Then, the reaction temperature was decreased to 50 °C, and during this time, solutions of ammonium fluoride (0.2964g) and sodium hydroxide (0.2g) dissolved in 10ml of methanol were added. Then, the temperature was increased to 75 °C and the mixture was kept at this temperature for 30 min to evaporate methanol. Subsequently, the reaction temperature was increased quickly to 300 °C. The reaction mixture was kept at this temperature for 30 min under nitrogen atmosphere. After the UCNPs formation the mixture was allowed to cool to room temperature. The UCNPs were precipitated by addition of ethanol and isolated by centrifugation at 10000 rpm for 10 min. For



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purification, the resulting pellet was dispersed in a minimal amount of *n*-hexane and again precipitated with excess ethanol. The UCNPs were isolated by centrifugation at 14000 rpm for 10 min. Finally, the purified core UCNPs were dispersed in 5cm<sup>3</sup> chloroform. List of the synthesized samples is given in Table 19.

Table 19 Synthesized samples list

Codoped with Nd <sup>3+</sup> and Sm <sup>3+</sup>	
FET_24	NaSmF <sub>4</sub> :25%Nd
FET_25	NaSmF <sub>4</sub> :50%Nd
FET_26	NaSmF4:99%Nd
Codoped with Nd <sup>3+</sup> and Dy <sup>3+</sup>	
FET_34	NaNdF4:20%Nd
FET_35	NaNdF <sub>4</sub> :50%Nd
FET_36	NaNdF4:80%Nd

*UV-VIS NIR characterization:* The results of the measurement of the absorption spectra in the transmittance mode of the colloidal solution of NaNdF<sub>4</sub>:Sm<sup>3+</sup> nanocrystals (see Figure 39) reveals that co-doped nanocrystals possess several absorption band localized in the NIR spectral range of high absorption cross section which are suitable for the optical excitation localized in 1<sup>st</sup> and 2<sup>nd</sup> optical transparency windows of biological tissues.



Figure 39 Absorption spectra of the colloidal solution of the synthesized NaNdF4:Sm<sup>3+</sup> nanocrystals



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Figure 40 Absorption spectra of the colloidal solution of the synthesized NaNdF4:Dy3+ nanocrystals

In Figure 40 absorption peak near 793 nm originating from  $Nd^{3+}$  ions and not detected in the dysprosium sample is visible. It lowers with  $Nd^{3+}$  concentration decrease. There is a peak near 808 nm from  $Dy^{3+}$  ions that is covered by more intense peak from  $Nd^{3+}$  ions at 803 nm.



 $\label{eq:Figure 41} Figure \ 41 \ Absorbance \ of \ a \ colloidal \ solution \ of \ NaNdF_4: Dy^{3+} \ nanocrystals \ in \ function \ of \ Nd^{3+} \ concentration$ 

Figure 41 show that 793 nm absorbance is increasing as a function of Nd<sup>3+</sup> concentration. However, for 808 nm absorbance the increase is relatively lower.



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*Light-to-heat conversion:* The measurements were performed in air-conditioned room at styrofoam cover to eliminate the influence of surroundings. Main measurement parameters are included in Table 20:

Table 20 Main measurement parameters of the light-into-heat converssion effiviency determination system

Main parameters		Thermovision parameters	
Type of exposure	Continuous wave 793/808 nm	Emissivity (-)	0.96 (black tape)
Laser power (mW)	200	Camera angle (°)	7
Density power $\left(\frac{W}{cm^2}\right)$	~60	Distance (m)	0.3
Laser beam cross-section (mm <sup>2</sup> )	~0.33	Humidity (%)	~50
$Q_0\left(\frac{f}{s}\right)$	0	Air temperature (°C)	~23
$C_{sample}\left(\frac{J}{kg^{*}K}\right)$	4190	Reflected temperature (°C)	~23
$\sum m_i C_{p,I}\left(\frac{J}{K}\right)$	7.7	Surface of averaged measurement (pix <sup>2</sup> / mm <sup>2</sup> )	216 pix <sup>2</sup> ~18mm <sup>2</sup>

Light-to heat conversion efficiency was determinated from equation presented by Roper [14], from experimental data of heating and cooling curve obtained after exposure of the colloidal solution of nanoparticles onto chosen excitation wavelength  $\lambda$ :

$$\eta_T = \frac{hA(T_{max} - T_{amb}) - Q_0}{I(1 - 10^{-A_\lambda})}$$
(1)

$$Q_{0} = \frac{\sum_{i} m_{i} C_{p,i}}{\tau_{s,0}} \cdot \left( T_{max,0} - T_{amb,0} \right)$$
(2)

The hA might be approximated from equation. All variables could be designated from experimental data.

$$\tau_s = \frac{\sum_i m_i C_{p,i}}{hA} \tag{3}$$



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Because of higher absorbance of the  $NaNdF_4$ :Sm<sup>3+</sup> nanocrystals at 793 nm than 808 nm, light-toheat conversion efficiency measurements were performed upon exposure on 793 nm irradiation.



Figure 42 Temperature evolution curves upon turned on and off 793 nm excitation, measured using thermovision camera (tvc) and thermocouple attached to the quartz cuvette, for colloidal solution of NaNdF<sub>4</sub>:Sm<sup>3+</sup> nanocrystals

Table	21 Light-to	heat c	onversion	efficiencie	s for	different	concentration	of Nd <sup>3+</sup>	and Sr	n <sup>3+</sup> ions
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Sample name	Composition	TC/TVC	λ <sub>exc</sub> [nm]	Abs -Λ <sub>exc</sub>	ΔT [°C]	τ <sub>D</sub> [s]	η <sub>hν→Q</sub> [%]
FET 24	NaNdF <sub>4</sub> :	тс			6.5	409.7	74
	75% Sm <sup>3+</sup>	TVC		0.712	7.32	424.0	81
FET 25	NaNdF <sub>4</sub> :	ТС	793		7.9	452.9	68
	50% Sm <sup>3+</sup>	TVC		1.48	8.69	444.7	76
FET 26	NaNdF <sub>4</sub> :	ТС			7.7	451.6	64
	1% Sm <sup>3+</sup>	TVC		2.28	8.49	412.8	78



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 $\label{eq:Figure 43} \mbox{ Light-to-heat conversion efficiency in function of $Nd^{3+}$ concentration for colloidal solution of $NaNdF_4:Sm^{3+}$ nanocrystals}$ 

Absorption peaks from Nd<sup>3+</sup> ions lowers with Nd<sup>3+</sup> concentration decrease. Peaks from Sm<sup>3+</sup> ions increase with Sm<sup>3+</sup> concentration. An unexpected shift was not observed. Generally, light-to-heat conversion efficiency depends strongly on absorbance value. Measurements by thermocouple and thermovision camera differs: thermovision camera (TVC) measurements provides no significant changes in efficiency in function of  $Nd^{3+}$  concentration, but thermocouple (TC) measurements shows strong dispersion in results. Light to heat conversion efficiency does not depend from Nd<sup>3+</sup> concentration.



**Figure 44** Temperature evolution curves upon turned on and off 793 nm excitation, measured using thermovision camera (tvc) and thermocouple (tc) attached to the quartz cuvette, for colloidal solution of NaNdF<sub>4</sub>:Dy<sup>3+</sup> nanocrystals



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Figure 45 Temperature evolution curves upon turned on and off 808 nm excitation, measured using thermovision camera (tvc) and thermocouple attached to the quartz cuvette, for colloidal solution of NaNdF4:Dy<sup>3+</sup> nanocrystals

In both experiments maximum temperature increase is greater when the concentration of Nd<sup>3+</sup> is higher.



Figure 46 Temperature increase colloidal solution of NaNdF<sub>4</sub>:Dy<sup>3+</sup> nanocrystals in a function of Nd<sup>3+</sup> concentration

With 808 nm irradiation only slight increase of maximum obtained temperature connected with Nd<sup>3+</sup> concentration increase was observed. It might be caused by fact that both Nd<sup>3+</sup> and Dy<sup>3+</sup> absorb 808 nm irradiation, but Nd<sup>3+</sup> absorption is higher. Increase of Nd<sup>3+</sup> ions concentration affects in rise of temperature increase which is saturating even in only 20% of Nd<sup>3+</sup>.



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 $\label{eq:Figure 47} Figure \ 47 \ Light-to-heat \ conversion \ efficiency \ of \ colloidal \ solution \ of \ NaNdF_4: Dy^{3+} \ nanocrystals in \ function \ of \ Nd^{3+} \ concentration$ 

Sample name	Composition	TC/TVC	$\lambda_{exc}$ (nm)	Abs - $\lambda_{exc}$	ΔT [°C]	τ <sub>D</sub> [s]	$\eta_{h\nu \to Q}$ [%]
		ТС			7.9	459.5	67
FET 34	NaNdF <sub>4</sub> : 20% Dy <sup>3+</sup>	TVC		1.983	8.92	443.1	78
		ТС			8.1	436.8	73
FET 35	NaNdF <sub>4</sub> : 50% Dy <sup>3+</sup>	TVC	793	1.577	9.02	409.6	87
		ТС			7.1	458.5	70
FET 36	NaNdF <sub>4</sub> : 80% Dy <sup>3+</sup>	TVC		0.834	7.84	437.3	81
		ТС			7.4	444.7	72
FET 34	NaNdF <sub>4</sub> : 20% Dy <sup>3+</sup>	TVC		0.948	8.2	423.6	84
		ТС			6.8	493.0	64
FET 35	NaNdF <sub>4</sub> : 50% Dy <sup>3+</sup>	TVC	808	0.767	7.44	412.5	84
		TC			6.0	427.8	73
FET 36	NaNdF <sub>4</sub> : 80% Dy <sup>3+</sup>	TVC		0.579	6.83	427.8	83

Table 3 Light-to-heat conversion efficiencies for different concentration of  $Nd^{3+}$  and  $Sm^{3+}$  ions



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Slightly higher light-to-heat conversion with higher  $Dy^{3+}$  concentration results from the lower absorbance of NaDyF<sub>4</sub>. Although  $Dy^{3+}$  seems to be more effective, Nd<sup>3+</sup> absorb more energy and higher temperature increase is observed. For that reason, the most promising candidate nanoheater is still fully concentrated NaNdF<sub>4</sub>.

#### Further plans:

- Transforming NPs from chloroform into water for more suitable characterisation.

- Improvement of experimental setup for light-to-heat conversion for more accurate results.



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## 4. CONCLUSION AND FURTHER PLANS

After a year of the activity on this project, WP1 gave input in synthesis of various nanoparticlesbased materials as prospect for 2D-thermal bioimaging technologies. Prior to this report, three reports were submitted as deliverables D1, D2 and D10 in which the on-going research of the materials of interest, their syntheses and characterizations were presented. This paragraph includes additional work on developing the materials. Ambitious variety of host materials and dopants proposed in the project and organized in three tasks as materials for: (*i*) Ln<sup>3+</sup> and TM-doped NANOTHERMOMETERS, (*ii*) SEMICONDUCTOR COLLOIDAL NANOTHERMOMETERS, and (*iii*) NANOHEATERS AND HEATER-THERMOMETER NANOPLATFORMS, was almost fully met in the first year.

Consortium 2019 meeting held on 1-2.07.2019 in Wroclaw, Poland joined all the WP1–WP7 partners which enabled for a joined discussion on the progress so far, as well as pans for the next year and the course for what materials should be selected for the up to 5 most promising ones.

General further plan for the WP1 is as follows:

(*i*) Ln<sup>3+</sup> and TM-doped NANOTHERMOMETERS

- Further synthesis of materials with dopant Ln<sup>3+</sup> activators that will include Nd<sup>3+</sup>, Tm<sup>3+</sup>, with or without sensitizer ions (mainly Yb<sup>3+</sup>).
- For *in vitro* materials, Ln<sup>3+</sup> activators will include **Tb**<sup>3+</sup> and **Eu**<sup>3+</sup> dopants.
- Further development and optimisation for syntheses of low-phonon energy hosts as fluorides **Na(Y, Gd, Lu)F**<sub>4</sub>), oxides (**Y**<sub>2</sub>**O**<sub>3</sub>), or phosphates (**LiLaP**<sub>4</sub>**O**<sub>12</sub>, **LaPO**<sub>4</sub>).
- Development of shelling the nanoparticles.

#### (ii) SEMICONDUCTOR COLLOIDAL NANOTHERMOMETERS

- Further development of novel and optimisation of existing syntheses of Ag<sub>2</sub>S semiconductor quantum dots.
- Going towards greener Ag<sub>2</sub>S syntheses

#### (iii) NANOHEATERS AND HEATER-THERMOMETER NANOPLATFORMS

- Optimisation of magnetic Y<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Fe nanoparticles, syntheses and surface modifications.
- Optimisation of fluoride-type highly absorbing nanoparticles.
- Further optimisation of heater-thermometer nanostructures as core-shell nanoplatforms.



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In terms of the materials, further selection was made:

- Low phonon energy host, phosphate materials such as nano-LaPO<sub>4</sub> were selected as adequate host for Ln<sup>3+</sup> dopants for luminescent NPs emitting in BW-II and BW-III. As it was concluded from both, experimental and theoretical conclusions that singly doped Nd<sup>3+</sup> materials may not be the most sensitive candidates for *in vivo* thermometry, a follow-up approach of co-doping Nd<sup>3+</sup> with Yb<sup>3+</sup> and doping with Tm<sup>3+</sup> will be pursued. To lower surface-attached ligands such as H<sub>2</sub>O, the materials will be additionally covered by shell of silica or the un-doped layer of LaPO<sub>4</sub>.
- Low phonon energy host, fluoride materials such as  $Na(Y, Gd, Lu)F_4$  were selected as materials for, in respect to dopant concentration and the selection of core and shell composition, absorber (nanoheater) and/or emitter for both *in vivo* and *in vitro* thermometry.
- Silver-sulfide (Ag<sub>2</sub>S) semiconductor colloidal nanoparticles will be further optimised in terms of different syntheses approaches. It is expected to obtain NIR emission in 800-1300 nm range with high q values.
- For magnetic NPs, further optimisation on the magnetic Y<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> and Fe-doped Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> nanoparticles will be pursued for superior magnetic nanoheaters, as core materials for core-shell heater-thermometer nanostructures.
- Heater/thermometer nanoplatforms will be further optimised two-way, the first as the magnetic nanoheater in the core and the molecular thermometric probes in the polymeric coating, and the second as nonmagnetic but copolymer micelles encapsulating molecular thermometric probes in the interior.



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