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First Generation of Nanoparticles

Final Version

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Abbreviations and Acronyms

ABCP	Amphiphilic block copolymer
AIBN	Azobisisobutyronitrile
AuNPs	Gold nanospheres
AuNRs	Gold nanorods
BTFA	4,4,4-trifluoro-1-phenyl-1,3-butanedione
BW	Biological window
CA	Citric acid
CNRS	Centre National de la Recherche Scientifique
COD	Crystallography Open Database
CSIC	Agencia Estatal Consejo Superior de Investigaciones Cientificas
СТА	Chain Transfer Agent
СТАВ	Cetyl trimethylammonium bromide
DLS	Dynamic light scattering
DNPD	1,3-di(naphthalen-2-yl)propane-1,3-dione
EG	Ethylene glycol
FIBIRYCIS	Fundacion para la Investigacion Biomedica del Hospital Universitario Ramon Y Cajal
FWHMs	Full widths at half maximum
GOF	Goodness of fit
¹ H-NMR	Proton nuclear magnetic resonance
HR-TEM	High-resolution transmission electron microscopy
ICDD	International Centre for Diffraction Data
ICP- AES	Inductively Coupled Plasma - Atomic Emission Spectrometry
ICSD	Inorganic Crystal Structure Database



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Ln ³⁺	Lanthanide ions			
LPO	Lanthanum phosphate (LaPO ₄)			
МА	Methyl acrylate			
MPA	3-mercaptopropionic acid			
MPEGA	Metoxy-polyethylene glycol acid			
MWCO	Molecular weight cut-off			
NIR	Near Infra-Red			
NPO	Neodymium phosphate (NdPO ₄)			
NPs	Nanoparticles			
OA	Oleic acid			
ODE	Octadecene			
PEGA	Polyethylene glycol acid			
PhenA	(1,10-phenanthrolin-4-yl)methyl acrylate			
PL	Photoluminescence			
PTFE	Polytetrafluoroethylene			
QDs	Quantum dots			
RAFT	Reversible addition-fragmentation chain transfer polymerization	ation		
Re	Expected weighted profile factor			
Rp	Profile factor			
Rwp	Weighted profile factor			
SPR	Surface Plasmon Resonance			
TEM	Transmission electron microscopy			
TEM-EDX	Transmission electron microscopy-Energy-dispersive X-ray	spectrosc	сору	
TEOS	Tetraethoxysilan			



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THF	Tetrahydrofuran		
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	а
XRD	X-Ray Diffraction		
YAG	Yttrium aluminium garnet (Y ₃ Al ₅ O ₁₂)		
YIG	Yttrium iron garnet (Y ₃ Fe ₅ O ₁₂)		



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D1.1 FIRST GENERATION OF NANOPARTICLES

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 the first generation of lanthanide (Ln³⁺) and transition metal (TM) - doped nanoparticles (NPs), with their basic structural, morphological and luminescence features. Report consists of synthesis and basic characterization of purposeful materials examined so far. Materials will be divided and presented under Tasks given in the Grant.



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TASK 1.1: SYNTHESIS OF Ln³⁺ 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 (Ln³⁺) 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. Nd³⁺-doped LaPO₄ and NdPO₄ nanopowders and colloids

Nanopowder synthesis: Herein 4 samples of LaPO₄ (LPO) doped with Nd³⁺ (2, 5, 25 mol%) and NdPO₄ (NPO) nanopowders were prepared by conventional hydrothermal synthesis. In the first step, stoichiometric quantities of the La(NO₃)₃*6H₂O and Nd(NO₃)₃*6H₂O were dissolved in the appropriate amount of water. Solution of NaOH (7.4ml, 1M) was added to the well-stirred nitrate mixture. Appropriate amount of the ammonium hydrogen-phosphate was dissolved in water and added to the NaOH/rare-earth nitrates mixture. The resulting solutions (20ml) were transferred into a 50ml Teflon-lined Stainless Steel Autoclave. Autoclave was kept at 140°C for 30h and naturally cooled to room temperature. White precipitates were collected, washed several times with distilled water and ethanol and finally dried at 40°C for 22h. Detailed precursor quantities are given in Table 1.

	La(NO3)3*6H2O (g)	Nd(NO ₃) ₃ *6H ₂ O (g)	(NH4)2HPO4 (g)	NaOH (ml)	H2O (ml)
LaPO₄: 2mol%Nd	0.8486	0.0175	0.2695	7.4	12.6
LaPO₄: 5mol%Nd	0.8227	0.0438	0.2695	7.4	12.6
LaPO4: 25mol%Nd	0.6495	0.2192	0.2695	7.4	12.6
NdPO ₄	/	0.8767	0.2695	7.4	12.6

 $\label{eq:constraint} \textbf{Table 1} Detailed \ precursor \ quantities \ used \ for \ Nd^{3+}-doped \ LaPO_4 \ and \ NdPO_4 \ nanopowders \ synthesis.$



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Colloid synthesis: Herein, 4 samples of LaPO₄ doped with Nd³⁺ (2, 5, 25 mol%) and NdPO₄ colloids were synthesized by colloidal method. In brief, the solution of trisodium-citrate dihydrate was added drop by drop to the mixture of La(NO₃)₃*6H₂O and Nd(NO₃)₃*6H₂O solutions in the stoichiometric ratio (solutions were mixed in corresponding concentration ratio of Nd³⁺ ions with respect to La³⁺ ions up to stoichiometric NdPO₄) at room temperature. The white precipitate consisting of the La³⁺ (Nd³⁺)-Cit³⁻-complex is formed, and then completely dissolved by a vigorous stirring and the addition of (NH₄)₂HPO₄ solution. Further, the resulting transparent solution was stirred for 1 h at room temperature. The dialysis against distilled water for 24 h was utilized for the removal of excess ions. Detailed precursor quantities are given in Table 2.

	La(NO ₃) ₃ *6H ₂ O (ml)	Nd(NO ₃) ₃ *6H ₂ O (ml)	Sodium citrate (ml)	(NH4)2HPO4 (ml)
LaPO4: 2mol% Nd ³⁺	19.6	0.4	25	10
LaPO4: 5mol% Nd ³⁺	19	1	25	10
LaPO4: 25mol% Nd ³⁺	15	5	25	10
NdPO ₄	/	20	25	10

Table 2 Detailed precursor quantities used for Nd³⁺-doped LaPO₄ and NdPO₄ colloid synthesis.

Structural analysis: LaPO₄ and NdPO₄ crystallize in a pure monoclinic monazite phase of a space group $P12_1/n1$ (COD card nos. 9001647 and 9001650, respectively). In these crystal lattices, lanthanide ions are coordinated with nine oxygen atoms forming polyhedrons (LaO₉/ NdO₉), see Figure 1. Figure 2 shows X-ray diffraction patterns of the Nd³⁺-doped LaPO₄ and NdPO₄ nanopowders. The absence of impurity phases indicates that the dopant Nd³⁺ ions were successfully and uniformly incorporated into the LaPO₄ matrix due to the equal valence (+3) and similar ionic radii between the Nd³⁺ (*a* = 0.116 nm) and La³⁺ ions (*a* = 0.122 nm) [1].



Figure 1 Lanthanum phosphate (LaPO₄) and neodymium phosphate (NdPO₄) unit cell.



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Figure 2 Powder X-ray diffraction patterns (Cu K_{α} radiation) of LaPO₄: x% Nd³⁺ (x = 2, 5, 25) and NdPO₄ nanopowders in comparison to the diffraction patterns simulated from single crystal structure data (ICSD). The shifts of selected Bragg reflections towards higher 2 θ values in NdPO₄ are also highlighted.

Relevant results of nanopowders structural analysis (unit cell parameter, crystal coherence size, microstrain values and data fit parameters) obtained by VINCA using built-in software are presented in Table 3. The starting parameters for the structural analysis were taken according to the reference [2]. Crystallite size is in the 6-9 nm range for all samples. Data fit parameters, the profile factor (Rp), the weighted profile factor (Rwp), the expected weighted profile factor (Re) and the goodness of fit (GOF) are small indicating a highly satisfactory reliability. Microstrain values are low suggesting good ion ordering in the nanocrystals.

Table 3 Selected structural parameters obtained from nanopowders XRD measurements using built-in software.

	LaPO ₄ :	LaPO4:	LaPO4:	NdPO ₄
	2mol% Nd	5mol% Nd	25mol% Nd	
Crystallite size (Å)	92.39 (17)	68.52 (18)	90.57 (19)	61.99 (18)
a (Å)	6.8631 (13)	6.8504 (14)	6.8390 (15)	6.8380 (4)
b (Å)	7.1043 (13)	7.0901 (13)	7.0799 (15)	6.9890 (4)
c (Å)	6.5290 (12)	6.5171 (12)	6.5053 (14)	6.4210 (4)
Strain (%)	0.37 (2)	0.39 (5)	0.50 (8)	0.42 (6)
Rwp (%)	5.79	6.22	5.93	7.80
Rp (%)	4.36	4.61	4.47	5.78
Re (%)	3.84	3.94	3.68	3.13
GOF	1.5053	1.5804	1.6130	2.4943



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In order to compare and confirm obtained results the average crystallite size of the sent nanopowders was estimated from the full widths at half maximum (FWHMs) of the resolved reflections in the X-ray powder diffraction patterns by UU partner. A Scherrer constant of K = 0.89 was taken as an average for every reflection (although it was shown that this constant is anisotropic and its value may vary for different (*hkl*) [3]. The results are depicted in Figure 3.



Figure 3 Average crystallite sizes of the solid nanopowders of LaPO₄: x% Nd³⁺ with **(a)** x = 2, **(b)** x = 5, **(c)** x = 25 as well as **(d)** NdPO₄ deduced from the X-ray powder diffraction patterns by the Scherrer approximation. The averaged values, standard errors and 95% confidence intervals based on the data are given in the respective graphs.

The results are summarized in Table 4 and agree very well with the refined structural parameters obtained by the VINCA institute.



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Table 4 Average crystallite sizes of the nanopowders LaPO4: x% N	$Vd^{3+}(x =$	= 2, 5, 2	25) and	NdPO ₄ (derived	from
the X-ray powder diffraction patterns by the Scherrer approximation	on.					

Compound	Average crystallite size / nm
$La_{0.98}Nd_{0.02}PO_4$	10.9 ± 0.5
La _{0.95} Nd _{0.05} PO ₄	10.1 ± 0.4
La _{0.75} Nd _{0.25} PO ₄	11.5 ± 0.5
NdPO ₄	7.0 ± 1.0

UV-VIS characterization: UV-Vis-NIR diffuse reflectance spectra recorded at room temperature for Nd³⁺-doped LaPO₄ and NdPO₄ nanopowders are given in Figure 4. There are several characteristic bands in Nd³⁺-doped LaPO₄ and NdPO₄ nanopowder samples placed around: 355 nm (${}^{4}I_{9/2} \rightarrow {}^{4}D_{3/2}$, ${}^{4}D_{1/2}$), 524 nm (${}^{4}I_{9/2} \rightarrow {}^{4}G_{7/2}$, ${}^{4}G_{9/2}$), 579 nm (${}^{4}I_{9/2} \rightarrow {}^{4}G_{5/2}$, ${}^{2}G_{7/2}$), 744 nm (${}^{4}I_{9/2} \rightarrow {}^{4}F_{7/2}$, ${}^{4}S_{3/2}$), 798 nm (${}^{4}I_{9/2} \rightarrow {}^{4}F_{5/2}$, ${}^{2}H_{9/2}$) and 871 nm (${}^{4}I_{9/2} \rightarrow {}^{4}F_{3/2}$) that correspond to Nd³⁺ transitions [4].



Figure 4 (a) Diffuse reflectance spectra of the nanopowders LaPO₄: x% Nd³⁺ (x = 2, 5, 25) and NdPO₄ with assigned electronic transitions of Nd³⁺. (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 Nd³⁺ in LaPO₄ (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 \boldsymbol{R}_{∞} as the diffuse reflectance of the powder.

The Kubelka-Munk function is supposed to be linearly dependent on the concentration given that the interactions between the Nd³⁺ 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⁻¹, a



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plot of these signals against the Nd³⁺ content can be well fitted with a linear function ($R^2 = 0.9979$). The intercept is not different from zero within statistical significance ($\alpha = 0.05$, *t* hypothesis test), as should be expected (see Figure 5).



Figure 5 Calibration curve of the integrated Kubelka-Munk signals (see Figure 3(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.

Transmission electron microscopy: The preliminary TEM images (Tecnai 12, U = 100 kV) of $LaPO_4:2\%Nd^{3+}$ and $LaPO_4:5\%Nd^{3+}$ nanopowders show a very good agreement between the estimated crystallite sizes derived from the XRD patterns and the actual sizes of the nanocrystals (see Figure 6). Optimized TEM images of all samples will follow.



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Figure 6 TEM images of (a), (b) LaPO₄: 2% Nd³⁺ (20 nm scale given) and (c) LaPO₄: 5% Nd³⁺ (10 nm scale given) nanopowders taken at 100 kV. Selected single nanocrystals are marked and scales are given at the bottom.

Photoluminescence characterization: In order to elucidate the optimum wavelengths to be considered for investigation of their potential thermometric application in the biological windows (*BW* I: 750 nm – 950 nm; *BW* II: 1000 nm – 1350 nm), photoluminescence emission and excitation spectra of the nanopowders LaPO₄: x% Nd³⁺ (x = 2, 5, 25) and NdPO₄ were investigated. The results are presented in Figures 7 and 8.





Figure 7 NIR luminescence of Nd^{3+} in LaPO₄ doped with (a) 2% Nd^{3+} , (b) 5% Nd^{3+} , (c) 25% Nd^{3+} and (d) in NdPO₄ recorded at room temperature. Biological windows (BW) and the relevant transitions interesting for thermometry in that range are indicated.

In fact, the emission transitions from different Stark states in these nanocrystals can be excited quite selectively. This is not only demonstrated by the excitation spectra (see Figure 8), but also by the corresponding emission spectra upon tuning the respective excitation wavelengths (see Figure 9). This basically allows controlling the intensity of the desired emission transition precisely, but in turn also makes it challenging to find an appropriate excitation wavelength for the investigation of the thermometry processes with a very good resolution and signal-to-noise ratio at the same time.







Figure 8 Photoluminescence excitation spectra of (a) LaPO₄: 2% Nd³⁺, (b) LaPO₄: 5% Nd³⁺, (c) LaPO₄: 25% Nd³⁺ and (d) NdPO₄ recorded at room temperature. The monitored emission wavelengths are indicated in the respective graphs.







Figure 9 Strongest emission peaks dependent upon different excitation wavelengths for (a) $LaPO_4$: 2% Nd^{3+} , (b) $LaPO_4$: 5% Nd^{3+} , (c) $LaPO_4$: 25% Nd^{3+} and (d) $NdPO_4$. The excitation wavelengths are given in the respective graphs.

Further investigations:

- All four Nd³⁺-doped LaPO₄ and NdPO₄ colloids were sent on October 31st, 2018 for dynamic light scattering (DLS) and transmission electron microscopy (TEM) (both to be finished by the middle to end of March 2019) and further luminescence thermometry measurements (emission and decay time; to be finished by the middle of April 2019). However, preliminary DLS measurements performed by UU indicated a destabilization of the colloids during transportation and fresh samples were sent again on January 23rd, 2019 to both UNIVERSITEIT UTRECHT (UU) and UNIVERSITY OF AVEIRO (UAVR).

- On November 9, 2018 one sample, 25mol% Nd-doped LaPO₄ colloid in TRIS, was sent to FIBIRYCIS partner for first, brief assessment of its potential as nanoheater/nanothermometer.



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

2. Eu³⁺-doped LaPO₄ nanopowders

Synthesis: Herein LaPO₄ doped with Eu³⁺ (5 mol%) nanopowder was prepared by conventional hydrothermal synthesis. In the first step, stoichiometric quantities of the La(NO₃)₃*6H₂O (Alfa Aesar, 99.9%) and Eu(NO₃)₃*6H₂O (Alfa Aesar, 99.9%) were dissolved in the appropriate amount of water. Solution of NaOH (7.4ml, 1M) was added to the well-stirred nitrate solutions. Appropriate amount of ammonium hydrogen-phosphate (Alfa Aesar, 98.0%) was dissolved in water and added to the NaOH/rare-earth nitrates mixture. The resulting solution (20 ml) was transferred into a 50ml Teflon-lined Stainless Steel Autoclave. The lid was carefully closed; autoclave was kept at 140°C for 30h and naturally cooled to room temperature. White precipitates formed at the bottom of the autoclave were collected, washed several times with distilled water and ethanol to remove excess ions, and finally dried at 40°C for 22h. Detailed precursor quantities are given in Table 5.

 $\label{eq:constraint} \textbf{Table 5} \ Detailed \ precursor \ quantities \ used \ for \ 5 \ mol\% \ Eu^{3+}-doped \ LaPO_4 \ nanopowder \ synthesis.$

	La(NO3)3*6H2O	Eu(NO3)3*6H2O	(NH4)2HPO4	NaOH	H2O
	(g)	(g)	(g)	(ml)	(ml)
LaPO₄: 5mol%Eu³+	0.8227	0.0446	0.2695	7.4	12.6

Structural analysis: LaPO₄ crystallize in a pure monoclinic monazite phase of a space group $P12_1/n1$ (COD card no. 9001647). Figure 10 shows X-ray diffraction patterns of the 5 mol% Eu³⁺⁻ doped LaPO₄. The absence of impurity phases indicates that the dopant Eu³⁺ ions were successfully and uniformly incorporated into the LaPO₄ matrix due to the equal valence (+3) and similar ionic radii between the Eu³⁺ (a = 0.112 nm) and La³⁺ 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 6. The starting parameters for the structural analysis were taken according to the reference [2]. 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 10 X-ray diffraction pattern of the 5mol% Eu³⁺-doped LaPO₄ nanopowder.

Table 6 Selected structural parameters obtained from XRD measurements.

	LaPO ₄ : 5mol% Eu ³⁺
Crystallite size (Å)	55.3 (4)
a (Å)	6.719 (14)
b (Å)	7.385 (14)
с (Å)	6.002 (9)
Strain (%)	1.71 (5)
<i>Rwp(%)</i>	11.95
<i>Rp(%)</i>	8.84
Re(%)	3.67
GOF	3.2546

Further investigations:

- VINCA prepared hybrid Eu^{3+} -doped $LaPO_4$ / Ag nanopowder (please look at the paragraph 6 for further results).



3. Gold nanospheres (AuNPs) and AuNPs@SiO2 core-shell nanostructures

Prepared by VINCA

*Synthesis of gold nanospheres and AuNPs@SiO*² *core-shell nanostructures:* Colloidal dispersion of spherical AuNPs was prepared using sodium citrate as a reducing and stabilizing agent [5]. The colloid consisting of AuNPs with an average diameter of 17 nm was prepared as follows: 200 ml of 1 mM HAuCl₄ was stirred and heated in a round-bottom flask fitted with a reflux condenser; after reaching the boiling point, 20 ml of 38.8 mM sodium citrate was rapidly added. The formation of AuNPs was indicated by almost instant solution's colour change, from yellow to burgundy. The colloidal dispersion was boiled and stirred for additional 15 minutes, and then cooled down to the room temperature with continuous stirring.

For the AuNPs@SiO₂ core-shell nanostructures synthesis, 5 ml of previously prepared AuNPs (sample AuNPs_04_0001) was centrifuged (30 min at 12000 rpm). The precipitate was redispersed in 300 µl of Milli-Q deionized water and vigorously stirred with 210 µl of Tetraethoxysilane (TEOS) for minimum 2 min. This mixture was rapidly added to the 5 ml of ethanol with pH already adjusted to highly alkaline by ammonium hydroxide (NH₄OH, 417 µl), and stirred at room temperature. Since the thickness of SiO₂ shell is a function of the reaction duration, the reaction between components was interrupted by adding ethanol excess at different time intervals, after 10, 15, and 20 min, for AuNPs@SiO₂_04_0002, AuNPs@SiO₂_04_0003, and AuNPs@SiO₂_04_0004, respectively. At the end, all the samples were centrifuged, and cleansed (two times by ethanol and one time by water), at 10000 rpm for 30 min. Finally, gained precipitates were redispersed in 5 ml of water.

UV-VIS characterization: The citrate-stabilized gold nanoparticles (AuNPs) with spherical shape and 17 nm in size are directly silica coated using a modified Stöber process. By simply varying the synthesis reaction time (10, 15 and 20 min), the silica shell thickness is increased (from *Sample 2 to* 4), respectively. Figure 11 shows UV-VIS absorption spectra of bare and SiO₂ covered gold nanospheres (AuNPs). Since the position of surface plasmon resonance (SPR) band (520 nm) of AuNPs is sensitive to NPs size, shape and inter-particle distance, as well as to the properties of their surrounding medium, when SiO₂ is condensed onto the NPs surface, the SPR absorption is shifted to higher wavelengths. In the *Sample 2*, the AuNPs are partialy SiO₂ coated, the SPR band is shifted to 521 nm, whereas the weak second one (803 nm) appeared due to aggregation of some unstable AuNPs, regarding the sample cleaning process (the excess of citrate ions is removed during the Au colloid re-concentration). After 15 and 20 min, when a thin silica shell was deposited around the AuNPs, the SPR band is red-shifted to 523 nm due to a local increase in refractive index of SiO₂ (1.456; [6]) compared to water (1.33). In these cases, scattering effect becomes significant.



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Figure 11 UV-VIS absorption spectra of bare and SiO₂ covered gold nanospheres (AuNPs).

Further investigations:

- All four AuNPs samples (bare and covered with SiO₂) were sent on October 31, 2018 to WPAS for transmission electron microscopy (TEM) mesurements.

- According to TEM results WPAS partner will choose sample/s for fabrication of AuNPs-hybride structures.

Prepared by WPAS

Synthesis: Gold nanoparticles (AuNPs) were prepared by reduction of the HAuCl₄ with sodium citrate [7,8]. Freshly prepared water solution of sodium citrate was added to 9.95 ml of HAuCl₄ water solution under constant temperature (80°C) and vigorous stirring. The color of the mixture turned wine red after few minutes indicating the production of Au nanoparticles. Detailed precursor quantities are given in Table 7.



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Sample	Composition	Sodium citrate solution		Maximum at	Estimated size
		Concentration	Amount		
FET_7	AuNP's	0.34M	47µl	543	50
FET_8	AuNP's	0.34M	23µl	534	50
FET_9	AuNP's	0.34M	94µl	523	20
FET_10	AuNP's	0.34M	188µl	520	15
FET_24	AuNP's	0.34M	47µl	524	20
FET_25	AuNP's	0.17M	47µl	528	30
FET_26	AuNP's	0.34M	30µl	520	15
FET_27	AuNP's	0.17M	30µl	529	40
FET_28	AuNP's	0.085M	47µl	534	50
FET_29	AuNP's	0.17M	47µl	528	40
FET_29a	AuNP's	0.17M	47µl	519	15
FET_29b	AuNP's	0.17M	47µl	518	15
FET_30	AuNP's	0.34M	47µl	520	15
FET_31	AuNP's	0.425M	47µl	523	15/20
FET_32	AuNP's	0.51M	47µl	521	15
FET_33	AuNP's	0.68M	47µl	524	20

Table 7 Detailed precursor quantities for AuNPs synthesis.

UV-VIS characterization: Based on the literature [8] the average particle size of obtained materials was estimated based on the maximum intensity of the surface plasmon resonance of Au nanoparticles (Figure 12). With increasing the amount of sodium citrate decreasing in the Au nanoparticles size is observed.



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Figure 12 The absorption spectra of different AuNPs.

Light-to-heat conversion: First attempt to measure light-to-heat conversion using AuNPs is presented in Figure 13.



Figure 13 Heating and cooling of colloidal AuNPs under 532 nm photoexcitation.

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Future investigations:

- Further studies on AuNPs will be performed to adjust their absorption spectra to emission of Ln³⁺ ions and to laser lines at 808 and possibly 980 nm. Due to plasmonic effect, such materials are strong absorbers and shell effectively converts light to heat.

- These materials will further be combined with UCNPs (within polystyrene nanobeads) to combine nanothermometry of lanthanide and transition metal thermometers as well as heating from AuNPs.

4. Gold nanorods (AuNR) and AuNRs@SiO₂ core-shell nanostructures

Synthesis of gold nanorods and AuNRs@SiO₂ core-shell nanostructures: Gold nanorods (AuNRs) were synthesized according to the seed-mediated growth method [9]. Firstly, Au seed solution was prepared as follows: in the mixture of cetyl trimethylammonium bromide (CTAB, 5 ml, 0.2 M) and HAuCl₄ (5 ml, 0.5 mM) freshly prepared with vigorous stirring, ice-cooled aqueous solution of sodium borohydride (NaBH₄, 0.6 ml, 0.01 M) was added. The formation of Au seed was indicated by the light brownish-yellow colour of the solution, which was kept at the room temperature (at least 2 h) prior to use. For the preparation of AuNRs, CTAB solution (5 ml, 0.2 M) was gently mixed with silver nitrate (AgNO₃, 0.15 ml, 4 mM) and HAuCl₄ (5 ml, 1 mM) solutions. Immediately after adding ascorbic acid (70 µl, 0.778 mM) drop by drop, the solution was discoloured, and 10 µl of Au seed was added. Within 10 to 20 min, the colour of the reaction mixture gradually changes, from light to dark violet/blue. Since CTAB crystalizes at the temperatures below 25 °C, the experiment was performed in the warm bath, at ≈ 30 °C, with occasional gentle mixing. The as-prepared AuNRs were centrifuged (15 min at 12000 rpm) in order to eliminate CTAB excess. Precipitate was redispersed in 500 µl of Milli-Q deionized water, and refrigerated prior to use.

For AuNRs@SiO₂ core-shell nanostructures synthesis, 500 μ l of AuNRs was heated to the room temperature (since the CTAB crystalized in the refrigerator) and dissolved in 4.5 ml of water. As prepared AuNRs, with pH adjusted to 10-11 with 0.1 M NaOH, were placed into the oil-bath (temperature was tuned to 90°C) and stirred. Then, 15, and 50 μ l of TEOS were added for AuNRs@SiO₂_04_0006, and AuNRs@SiO₂_04_0007, respectively, and the reaction was continued for 7 h. Finally, the solution was centrifuged for 15 min at 12000 rpm, and redispersed in 5 ml of water.

UV-VIS characterization: Figure 14 shows UV-VIS absorption spectra of bare and SiO₂ covered gold nanorods (AuNRs). The spectrum of AuNRs solution shows two absorption bands, a weak transverse SPR wavelength around 512 nm and a strong longitudinal SPR wavelength around 761 nm. These AuNRs were further coated with silica by adding different volumes of TEOS into the final nanorods solutions, 15 and 50 μ l for sample 6 and 7, respectively. After being coated with silica, the AuNPs exhibit a 1-2 nm red-shift in the longitudinal SPR peak, due to the slight increase in the refractive index of the surrounding thin SiO₂ shells. The increased absorption of AuNR's longitudinal axis might indicate that dense and uniform silica coatings diminish NRs excitons quenching through an efficient isolation.



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Figure 14 UV-VIS absorption spectra of bare and SiO₂ covered gold nanorods (AuNRs).

Further investigations:

- All three AuNRs samples (bare and covered with SiO_2) were sent on October 31st, 2018 to WPAS for transmission electron microscopy (TEM) mesurements.

- According to TEM results WPAS partner will choose sample/s for fabrication of AuNRs-hybride structures.

- VINCA prepared hybrid Nd³⁺-doped LaPO₄ / AuNRs@SiO₂ core-shell nanopowder starting from two AuNRs@SiO₂ colloid samples. Please look at the following paragraph.

5. Hybrid Nd³⁺-doped LaPO₄ / AuNRs@SiO₂ core-shell nanopowders

Synthesis: Herein, 2 hybrid Nd³⁺-doped LaPO₄ / AuNRs@SiO₂ core-shell nanopowders were prepared according to the microwave-hydrothermal procedure reported for Nd³⁺-doped LaPO₄ nanopowders with AuNRs@SiO₂ core-shell colloids (with longitudinal SPR wavelengths 714 nm and 735 nm) used instead of water. Detailed precursor quantities are given in Table 8.

 Table 8
 Detailed precursor quantities used for Nd³⁺-doped LaPO₄/AuNRs@SiO₂ core-shell nanpowder.

Sample	La(NO ₃) ₃ *6H ₂ O	Nd(NO3)3*6H2O	(NH4)2HPO4	NaOH	H2O	AuNRs
	(g)	(g)	(g)	(ml)	(ml)	(ml)
LaPO4: 25mol%Nd³+ AuNRs	0.6495	0.2192	0.2695	7.4	/	12.6

Structural characterization: LaPO₄ crystallize in a pure monoclinic monazite phase of a space group $P12_1/n1$ (COD card no. 9001647). Figure 15 show X-ray diffraction patterns of hybrid



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25mol% Nd³⁺-doped LaPO₄ / AuNRs@SiO₂ core-shell nanopowders. The absence of impurity phases indicates that the dopant Nd³⁺ ions were successfully and uniformly incorporated into the LaPO₄ matrix due to the equal valence (+3) and similar ionic radii between Nd³⁺ (a = 0.116 nm) and La³⁺ ion (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 9. The starting parameters for the structural analysis were taken according to the reference [2]. 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.



Figure 15 X-ray diffraction patterns of hybrid 25mol% $Nd^{3+}-doped\ LaPO_4$ / AuNRs@SiO_2 core-shell nanopowders.

	LaPO4: 25mol% Nd ³⁺ AuNRs_714nm	LaPO4: 25mol% Nd ³⁺ AuNRs_735nm
Crystallite size (Å)	67.0 (3)	67.2 (6)
a (Å)	6.8347 (19)	6.8478 (19)
b (Å)	7.0701 (19)	7.0748 (19)
c (Å)	6.4920 (17)	6.4996 (18)
Strain (%)	0.40 (9)	0.48 (6)
Rwp(%)	6.16	6.46
<i>Rp(%)</i>	4.65	4.86
Re(%)	3.56	3.60
GOF	1.7327	1.7959

 Table 9 Selected structural parameters obtained from XRD measurements.



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UV-VIS characterization: UV-Vis-NIR diffuse reflectance spectra recorded at room temperature for 25mol% Nd³⁺-doped LaPO₄ / AuNRs@SiO₂ core-shell nanopowders are given in Figure 16. There are several characteristic bands placed around: 357 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 (${}^{4}I_{9/2} \rightarrow {}^{4}F_{7/2}$, ${}^{4}S_{3/2}$), 799 nm (${}^{4}I_{9/2} \rightarrow {}^{4}F_{5/2}$, ${}^{2}H_{9/2}$) and 872 nm (${}^{4}I_{9/2} \rightarrow {}^{4}F_{3/2}$) that corresponds to Nd³⁺ transitions [4].



Figure 16 UV-Vis-NIR diffuse reflection spectra of Nd³⁺-doped LaPO₄ / AuNRs@SiO₂ core-shell nanopowders.

Further investigations:

- Hybrid 25 mol% Nd³⁺-doped LaPO₄ and AuNRs@SiO₂ core-shell nanostructure will be sent to one of the partners for further photoluminescent measurements in NIR range and transmission electron microscopy (TEM).

6. Hybrid Eu³⁺-doped LaPO₄ / Ag nanopowders

Synthesis: Herein, 2 hybrids Eu³⁺-doped LaPO₄ / Ag nanopowder samples were synthesized. Silver (Ag) colloid was synthesized as follows. A large excess of NaBH₄ was required to reduce the ionic silver and to stabilize the silver nanoparticles that were formed. 4.25 mg of silver nitrate (AgNO₃) was dissolved in 250 ml of water purged by argon for 30 min. Under vigorous stirring, reducing agent NaBH₄ (25 mg) was added to the solution, which immediately changed colour to yellow indicating the formation of silver nanoparticles and left for 30 min in argon atmosphere. The concentration of silver colloid was 0.0001 M. In the same way the silver colloids of higher concentrations (2x10⁻⁴ M and 1x10⁻³ M) were prepared and further used for hybrid 5 mol% Eu³⁺-doped LaPO₄ and Ag colloid nanostructure. Hybrid Eu³⁺-doped LaPO₄ /Ag nanopowders were prepared according to the microwave-hydrothermal procedure reported for Eu³⁺-doped LaPO₄ nanopowder using Ag colloids (2x10⁻⁴ M and 1x10⁻³ M) concentration) instead of water. Detailed precursor quantities are given in Table 10.



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	La(NO ₃) ₃ *6H ₂ O (g)	Eu(NO3)3*6H2O (g)	(NH4)2HPO4 (g)	NaOH (ml)	H₂O (ml)	Ag- colloid (ml)
Hybrid Ag/ 5mol%Eu ³⁺ :LaPO ₄	0.8227	0.0446	0.2695	7.4	/	12.6

 $\label{eq:table_to_alpha} \textbf{Table 10} \ \text{Detailed precursor quantities used for hybrid } Eu^{3+} \text{-doped } LaPO_4/Ag \ nanopowders \ \text{synthesis.}$

Structural analysis: LaPO₄ crystallize in a pure monoclinic monazite phase of a space group $P12_1/n1$ (COD card no. 9001647). Figure 17 show X-ray diffraction patterns of the hybrid 5mol% Eu³⁺-doped LaPO₄ / Ag (2x10⁻⁴ M and 1x10⁻³ M) nanopowders. The absence of impurity phases indicates that the dopant Eu³⁺ ions were successfully and uniformly incorporated into the LaPO₄ matrix due to the equal valence (+3) and similar ionic radii between the Eu³⁺ (*a* = 0.112 nm) and La³⁺ ions (*a* = 0.122 nm) [1].



Figure 17 X-ray diffraction patterns of the hybrid 5mol% Eu^{3+} -doped LaPO₄ / Ag (2x10⁻⁴ M and 1x10⁻³ M) nanopowders.

Relevant results of structural analysis (unit cell parameter, crystal coherence size, microstrain values and data fit parameters) are presented in Table 11. The starting parameters for the structural analysis were taken according to the reference [2]. 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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	LaPO ₄ : 5mol% Eu ³⁺ 2·10 ⁻⁴ Ag	LaPO₄: 5mol% Eu³+ 1·10 ⁻³ Ag
Crystallite size (Å)	73.0 (2)	62.9 (2)
Strain (%)	0.38 (7)	0.51 (7)
Rwp(%)	6.61	6.98
<i>Rp(%)</i>	4.96	5.06
<i>Re(%)</i>	3.67	3.72
GOF	1.8004	1.8761
a (Å)	6.8561 (17)	6.853 (2)
b (Å)	7.0875 (17)	7.072 (2)
с (Å)	6.5122 (15)	6.496 (2)

Table 11 Selected structural parameters obtained from XRD measurements.

UV-VIS characterization: UV-Vis-NIR diffuse reflectance spectra recorded at room temperature for the 5mol% Eu³⁺-doped LaPO₄ and hybrid 5mol% Eu³⁺-doped LaPO₄ / Ag (2x10⁻⁴ M) nanopowders are given in Figure 18. A characteristic band is located around 394 nm, visible in both samples and corresponds to the $^{7}F_{0} \rightarrow ^{5}L_{6}$ transition [4].



Figure 18 UV-Vis-NIR diffuse reflectance spectra recorded at room temperature for the 5mol% Eu³⁺-doped LaPO₄ and hybrid 5mol% Eu³⁺-doped LaPO₄ / Ag (2x10⁻⁴ M) nanopowders.

Photoluminescent characterization: The photoluminescent intensity varies in the Eu^{3+} -doped LaPO₄ and the hybrid Eu^{3+} -doped LaPO₄ / Ag nanopowders. Figure 19 shows that PL is enhanced with the Ag nanoparticles incorporation. It is well known that the Ag nanoparticles cause the excitation field enhancement and incensement of the radiative rate of luminescent active centres due to the located surface plasmon effect.







Figure 19 Photoluminescence a) excitation (of representative hybrid 5mol% Eu³⁺-doped LaPO₄ / Ag (1x10⁻³ M) sample) and b) emission spectra (λ_{ex} = 394 nm) of 5mol% Eu³⁺-doped LaPO₄ and hybrid 5mol% Eu³⁺-doped LaPO₄ / Ag (2x10⁻⁴ M and 1x10⁻³ M) nanopowders.

Further investigations:

- Hybrid 5 mol% Eu^{3+} -doped LaPO₄ / Ag nanopowder will be sent to one of the partners for transmission electron microscopy (TEM).

7. Nd³⁺ and Sm³⁺-doped LaF₃ colloids

Synthesis: Herein, 3 samples of the Nd³⁺ and Sm³⁺-doped LaF₃ colloids were synthesized. In brief, the 0.05 M aqueous solutions of all precursors $(La(NO_3)_3*6H_2O, Sm(NO_3)_3*6H_2O/Nd(NO_3)_3*6H_2O, Sm(NO_3)_3*6H_2O/Nd(NO_3)_3*6H_2O, Sm(NO_3)_3*6H_2O/Nd(NO_3)_3*6H_2O, Sm(NO_3)_3*6H_2O/Nd(NO_3)_3*6H_2O, Sm(NO_3)_3*6H_2O/Nd(NO_3)_3*6H_2O, Sm(NO_3)_3*6H_2O/Nd(NO_3)_3*6H_2O, Sm(NO_3)_3*6H_2O/Nd(NO_3)_3*6H_2O, Sm(NO_3)_3*6H_2O/Nd(NO_3)_3*6H_2O, Sm(NO_3)_3*6H_2O/Nd(NO_3)_3*0(H_2O/Nd(NO_3)_3*0(H_2O/Nd(NO_3))_3*0(H_2O/Nd(NO_3)_3*0(H_2O/Nd(NO_3)$ NH_4F , $Na_3C_6H_5O_7$) were prepared in the first step. Then, a sodium citrate solution (20 ml) was added mixture drop-wise temperature the of $La(NO_3)_3*6H_2O$ at room to and $Sm(NO_3)_3*6H_2O/Nd(NO_3)_3*6H_2O$ solutions (total volume 20 ml) in the proportion of 6/12 mol% Sm³⁺/Nd³⁺ with respect to La³⁺. Citrate ions formed complexes with La³⁺(Sm³⁺/Nd³⁺)-ions which resulted in formation of white precipitate. After 30 minutes of vigorous stirring, the white precipitate was completely dissolved by addition of NH₄F (60 ml). The as prepared clear and transparent solution (pH of about 8) was subsequently stirred and heated at 70°C for 1 hour and then cooled down to room temperature. The slow growth of particles and the removal of excess ions (pH value of solution set at 7.0) were accomplished by dialysis against distilled water for 24h. After dialysis, the colloidal aqueous suspensions were clear and stable for months not showing any precipitation. Concentration of nanoparticles in the colloid solutions was around 3 mg/mL. Structural characterization was performed on powder samples obtained by evaporation of aqueous colloidal solutions.



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In the second step, the obtained colloidal LaF₃:12mol% Nd³⁺ nanoparticles were treated in microwave-hydrothermal reactor for 15 min at $T = 160^{\circ}$ C. Detailed precursor quantities are given in Table 12.

Sample	La(NO3)3*6H2O (g)	NH₄F (g)	Na ₃ C ₆ H ₅ O ₇ (g)	Nd(NO ₃) ₃ *6H ₂ O (g)	Sm(NO ₃) ₃ *6H ₂ O (g)
LaF ₃ :12mol% Nd ³⁺	0.3810	0.1111	0.3571	0.0526	/
LaF3:6mol% Sm ³⁺	0.4070	0.1111	0.3571	/	0.0267

Structural analysis: LaF₃ crystallizes in a pure hexagonal phase of a space group $P\bar{3}c1$ (165) (COD Card No. 9008114) (see Figure 20). X-ray diffraction patterns of the LaF₃:6mol% Sm³⁺ and LaF₃:12mol% Nd³⁺ colloidal nanoparticles are shown in Figure 21. X-ray patterns characterized by broad diffraction peaks indicate small crystallite size. The absence of impurity phases indicate that the dopant Nd³⁺ / Sm³⁺ ions were successfully and uniformly incorporated into the LaF₃ matrix due to the equal valence (+3) and similar ionic radii (*a*) between Sm³⁺ (*a* = 1.132 nm) or Nd³⁺ (*a* = 1.163 nm) and La³⁺ ion (*a* = 1.216 nm) [1].



Figure 20 Lanthanum fluoride (LaF₃) unit cell.



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Figure 21 Powder X-ray diffraction patterns (Cu K_{α} radiation) of LaF₃: 12% Nd³⁺ (*top panel*) and LaF₃: 6% Sm³⁺ (*middle panel*) nanopowders in comparison to the diffraction pattern of LaF₃ (trigonal structure, SG $P\bar{3}c1$) simulated from single crystal structure data (ICSD).

The average crystallite size of the nanopowders was estimated from the full widths at half maximum (FWHMs) of the resolved reflections in the X-ray powder diffraction patterns (see Figure 22). A Scherrer constant of K = 0.89 was taken as an average for every reflection. The results are depicted in Figure 22 and compiled in Table 13.







Figure 22 Average crystallite sizes of the solid nanopowders of (a) LaF_3 : 12% Nd^{3+} and (b) LaF_3 : 6% Sm^{3+} deduced from the X-ray powder diffraction patterns by the Scherrer approximation. The averaged values, standard errors and 95% confidence intervals based on the data are given in the respective graphs.

Table 13 Average crystallite sizes of the nanopowders LaF₃: 12% Nd³⁺ and LaF₃: 6% Sm³⁺ derived from the X-ray powder diffraction patterns by the Scherrer approximation. See also Figure 22.

Compound	Average crystallite size / nm
LaF3: 12% Nd ³⁺	3.0 ± 0.3
LaF3: 6% Sm ³⁺	3.3 ± 0.2

UV-VIS characterization: UV-Vis-NIR absorption spectra recorded at room temperature for all three prepared colloidal samples are given in Figure 23. There are several characteristic absorption bands for LaF₃:12mol% Nd³⁺ samples: 521 nm (${}^{4}I_{9/2} \rightarrow {}^{4}G_{7/2}, {}^{4}G_{9/2}$), 576 nm (${}^{4}I_{9/2} \rightarrow {}^{4}G_{5/2}, {}^{4}G_{7/2}$), 737 nm (${}^{4}I_{9/2} \rightarrow {}^{4}F_{7/2}, {}^{4}S_{3/2}$), 796 nm (${}^{4}I_{9/2} \rightarrow {}^{4}F_{5/2}, {}^{2}H_{9/2}$) and 867 nm (${}^{4}I_{9/2} \rightarrow {}^{4}F_{3/2}$) [10]. On the other hand, LaF₃:6mol% Sm³⁺ sample shows only one absorption band around 1155 nm (${}^{6}H_{5/2} \rightarrow {}^{6}F_{9/2}$) [4].



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Figure 23 Absorption spectra of the colloidal LaF_3 :12mol% Nd³⁺ and LaF₃:6mol% Sm³⁺ nanoparticles.

Further investigations:

- Three colloids, two Nd³⁺-doped and one Sm³⁺-doped LaF₃ were sent on January 23rd, 2019 for dynamic light scattering (DLS) and transmission electron microscopy (TEM) (both to be finished by the middle to end of March 2019) and further luminescence thermometry measurements (emission and decay time; to be finished by the middle of April 2019) to Universiteit Utrecht (UU) and University of Aveiro (UAVR).

8. Mn⁴⁺-doped Li_{1.8}Na_{0.2}TiO₃ powders

Synthesis: Herein, 0.5 mol% Mn⁴⁺-doped Li_{1.8}Na_{0.2}TiO₃ powder was synthesized by a solid state reaction in air. The stoichiometric precursor mixture of Li₂CO₃, Na₂CO₃, MnO₂ and anatase TiO₂ (prepared by hydrolysis of titanium isopropoxide) was homogenized in ethyl alcohol for 2 h. The obtained mixture was gradually heated and kept at 670°C for 3 h. Synthesized powder was cold-pressed into compact pellet, additionally treated at 800°C for 72 h and naturally cooled to room temperature.



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Structural analysis: $Li_{1.8}Na_{0.2}TiO_3$ crystallizes in a monoclinic structure with C2/c space group. XRD pattern of 0.5 mol% Mn⁴⁺-doped $Li_{1.8}Na_{0.2}TiO_3$ sample together with corresponding ICDD card No. 01-077-8280 is presented in Figure 24. Neither other phase peaks nor traces of impurities were detected indicating that dopant Mn⁴⁺ ions have been effectively incorporated into the $Li_{1.8}Na_{0.2}TiO_3$ host lattice.



Figure 24 a) X-ray diffraction pattern 0.5 mol% Mn^{4+} -doped $Li_{1.8}Na_{0.2}TiO_3$ nanopowder and b) unit cell of the structure.

UV-VIS characterization: UV-Vis diffuse reflectance spectrum recorded at room temperature for the 0.5 mol% Mn⁴⁺-doped Li_{1.8}Na_{0.2}TiO₃ sample is given in Figure 25. The band located around 280 nm can be assigned to the ${}^{4}A_{2} \rightarrow {}^{4}T_{1}$ transition while strong band located around 490 nm corresponds to the ${}^{4}A_{2} \rightarrow {}^{4}T_{2}$ transition of Mn⁴⁺ ions.



Figure 25 UV-Vis diffuse reflectance spectra recorded at room temperature for the 0.5 mol% Mn^{4+} -doped $Li_{1.8}Na_{0.2}TiO_3$.



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Photoluminescent characterization: Emission spectra ($\lambda_{ex} = 490 \text{ nm}$) measured over 10-350K temperature range (see Figure 26a) show changes of spectral shape and intensity of the emission from Mn⁴⁺ ${}^{2}E_{g} \rightarrow {}^{4}A_{2g}$ transition. At low temperatures, the increase in intensity of the anti-Stokes side-bands upon increasing temperature can be observed because of the thermally driven excitation of phonon modes. At higher temperatures the emission starts to quench (to decrease in intensity) and almost completely vanishes above room temperature. The temperature dependence of the emission lifetime presented in Figure 26b shows similar trends, with a temperature increase the lifetime clearly decreases.



Figure 26 Mn⁴⁺-doped Li_{1.8}Na_{0.2}TiO₃: a) emission spectra and b) lifetime recorded over 10-350K temperature range (λ_{ex} = 490 nm).

9. Lanthanide and transition metal ions co-doped colloidal NaYF₄

Recently, new approach to the energy transfer between lanthanides and transition metals have been investigated with Mn^{2+} ions potentially attractive for temperature dependent sensitization of Ln^{3+} ions [11-14]. In order to understand how the temperature affect energy transfer and spectral properties of Mn^{2+} ions herein, two samples of Mn^{2+} and Mn^{2+}/Eu^{3+} doped NaYF₄ NPs were synthesized and preliminary studied.



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Figure 27 Excitation spectrum of NaYF₄:Mn²⁺ and NaYF₄: Mn²⁺/Eu³⁺ samples monitored at ${}^{5}D_{0}\rightarrow {}^{7}F_{2}$ Eu³⁺ transition at 614 nm.



Figure 28 Emission spectra of NaYF4:Mn²⁺ and NaYF4: Mn²⁺/Eu³⁺ samples excited at 396 nm.



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Figure 29 Emission of Eu³⁺ ions in NaYF₄: Mn^{2+}/Eu^{3+} samples monitored under excitation of 320 nm into Mn^{2+} absorption band. It is important to note $Mn^{2+} \rightarrow Eu^{3+}$ energy transfer.

First observations (Figs. 27-29) suggest there is an energy transfer between Mn²⁺ and Eu³⁺ ions in the NaYF₄. Results are promising since transition metal absorption/emission should be much more susceptible to temperature variation (towards nanothermometers) as compared to conventional f-f transitions in Ln³⁺ ions.

Further investigations:

- To determine susceptibility of energy transfer between Mn²⁺ and Eu³⁺ ions.

- Synthesis of NPs which combine luminescent thermometry in NIR (Yb³⁺Mn²⁺ \rightarrow Tb³⁺ energy transfer) and light-to-heat generation (Nd³⁺ \rightarrow Yb³⁺ \rightarrow Sm³⁺/Dy³⁺) to understand is it possible to sensitize the up-conversion (Yb³⁺Er³⁺ and Yb³⁺Tb³⁺) with temperature sensitive Mn²⁺ absorber.



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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. Ag₂S 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 Ag₂S QDs is set and will be improved (size distribution and q) to make them operational for bio-applications in the NIR spectral region.

Ag₂S colloidal dispersions

Synthesis: Herein, 6 colloid samples were synthesized. All chemicals used in the experiments were of analytical grade and used without any purification. In a typical procedure, silver nitrate (AgNO₃), 3-mercaptopropionic acid (MPA) and ethylene glycol (EG) as the solvent were placed in reaction vessel, sealed and stirred for 10 minutes prior to microwave hydrothermal treatment. Microwave hydrothermal reactor used in this set of experiments is purchased under NanoTBTech project (see Figure 30). Detailed precursor quantities and reaction parameters are given in Table 14 for all 6 samples while Figure 31 shows initial stages of nucleation of Ag₂S colloidal dispersions. In order to remove EG synthesized samples were dispersed in methanol and centrifuged (4000 rpm, 10 min). Finally, obtained precipitates were dispersed in methanol using ultrasonic bath (30 min).



Figure 30 Microwave-hydrothermal reactor used in this set of experiments and purchased under NanoTBTech project.



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Sample	AgNO3 (g)	MPA (ml)	EG (ml)	Temperature (°C)	Time (min.)
1	0.0255	0.305	4.5	160	30
2	0.0255	0.305	4.5	145	60
2*	0.0255	0.305	4.5	145	50
3	0.0255			120	70
4 **				145	10
	0.0255	0.305	4.5	145	15
				145	35
5	0.051	0.71	4.5	145	60
6	0.051	0.71	4.5	160	60

* Sample was cooled to 70 ℃ between two heating steps ** Sample was cooled to 50 ℃ between heating steps



Figure 31 Initial stages of nucleation of Ag₂S colloidal dispersions.









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UV-VIS characterization: Absorption spectra of synthesized samples are presented in Figure 32. Absorption spectra of samples 2, 3 and 5 are characterized with the maximum at about 1.55 eV (800 nm). This band gap value is significantly blue-shifted compared to bulk value of Ag_2S (0.9 – 1.1 eV), which clearly indicates that synthesized particles are prone to quantum confinement effects. Existence of multiple peaks in sample 3 spectrum point to presence of particles with different sizes. Absorption spectra of samples 1, 4 and 6, however, have distinct shoulder at about 1.2 eV (1030 nm) meaning that the particles are still in quantum confinement regime, but with higher radius. These preliminary results show that emission of samples 1, 4 and 6 can be expected between 1000 and 1250 nm, which is ideal for bio-applications in the NIR spectral region.

Further investigations:

- All six samples were sent on January 23rd, 2019 for dynamic light scattering (DLS) and transmission electron microscopy (TEM) and further luminescence thermometry measurements (emission and decay time) (all to be finished by the middle/end of May 2019) to UNIVERSITEIT UTRECHT (UU) and UNIVERSITY OF AVEIRO (UAVR).

- According to the obtained results VINCA will continue efforts toward developing improved QDs synthesis methodology (size distribution and *q*) to make them operational for bio-applications in the NIR spectral region.



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TASK 1.3: NANOHEATERS AND HEATER-THERMOMETER NANOPLATFORMS

Under TASK 1.3: NANOHEATERS AND HEATER-THERMOMETER NANOPLATFORMS nanoheaters from i) magnetic NPs (Fe₂O₃, Fe₃O₄, Y₃Fe₅O₁₂, Ln³⁺-doped Fe₂O₃) and ii) highly absorbing luminescent NPs $(NaNdF_4)$ are prepared. In i) efficient heating can be achieved by the magnetic field whereas in ii) heating is produced through strong non-radiative relaxation processes, following optical absorption.

1. Fe³⁺-doped Y₃Al₅O₁₂ (YAG) and Y₃Fe₅O₁₂ (YIG) powders

Synthesis: Herein, 3 samples with following formula: Y₃Al_{4.995}Fe_{0.005}O₁₂, Y₃Al_{4.95}Fe_{0.05}O₁₂ and $Y_3Fe_5O_{12}$ were synthesized. Chemicals used in the experiments were: metal nitrates (yttrium(III)) nitrate hexahydrate, Y(NO₃)₃*6H₂O; aluminium(III) nitrate nonahydrate, Al(NO₃)₃*9H₂O; iron(III)nitrate nonanhydrate, Fe(NO₃)₃*9H₂O; all Alfa Aesar, 99.9%, 98%, 98+%, respectively); citric acid -CA (HOC(COOH)(CH₂COOH)₂, Sigma Aldrich, ACS reagent, \geq 99.5%) and ethylene glycol - EG (HOCH₂CH₂OH, Sigma Aldrich, anhydrous, 99.8%). In a typical procedure, calculated amounts of metal nitrate precursors were added to the solution of CA in EG (M: CA: EG = 1: 5: 25) and stirred at 80°C. Stirring was continued for 30 minutes and after that heating temperature was set to 120°C. The reaction mixture was stirred at 120°C until the brownish gel was obtained (the time needed for this step is approximately 5 hours). Fe-doped $Y_3Al_5O_{12}$ gels were transferred into the alumina crucible and placed into the furnace at 350°C for 30 minutes, followed by calcination at 1100°C for 2 hours. For Y₃Fe₅O₁₂ (YIG) gel temperature treatment was 800°C for 2 hours, followed by calcination at 1100°C for 2 hours. After the calcination samples were cooled down to room temperature and grinded in a mortal. Obtained Fe-doped $Y_3Al_5O_{12}$ powders were pale-yellow while $Y_3Fe_5O_{12}$ was green in colour. Detailed precursor quantities are given in Table 15.

Samples	Y3(NO3)3*6H2O (g)	Al(NO3)3*9H2O (g)	Fe(NO3)3*9H2O (g)	CA (g)	EG (ml)
Y3Al4.995Fe0.005O12	1.93	3.28	0.034	12.9	18.9
Y ₃ Al _{4.95} Fe _{0.05} O ₁₂	1.88	2.91	0.331	12.9	18.9
<i>Y</i> ₃ <i>Fe</i> ₅ <i>O</i> ₁₂	1.55	/	2.73	10.4	15.1

Structural analysis: Yttrium aluminum garnet (Y₃Al₅O₁₂) crystallizes in a body-centered cubic structure (see Figure 33) with $Ia\overline{3}d$ (230) space group. In the corresponding symmetry, Al/Fe sites are alternating between tetrahedral and octahedral coordination. XRD patterns of Fe⁺³-doped $Y_3Al_5O_{12}$ and $Y_3Fe_5O_{12}$ powders together with corresponding COD cards No. 2003066 and 2101364, respectively, are presented in Figure 34. Neither other phase peaks nor traces of impurities were detected indicating that dopant Fe³⁺ ions have been effectively incorporated into the Y₃Al₅O₁₂ host lattice.



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Figure 33 Yttrium aluminum garnet ($Y_3Al_5O_{12}$) and yttrium iron garnet ($Y_3Fe_5O_{12}$) unit cell.



Figure 34 XRD patterns of a) Fe-doped YAG and b) YIG.

Relevant results of structural analysis (unit cell parameter, crystal coherence size, microstrain values and data fit parameters) are presented in Table 16. The starting parameters for the structural analysis were taken according to the reference [15,16]. The crystallite size increases with Fe^{3+} doping due to replacement of smaller Al^{3+} ion with bigger in size Fe^{3+} . 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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	Y ₃ Al _{4.995} Fe _{0.005} O ₁₂	Y ₃ Al _{4.95} Fe _{0.05} O ₁₂	<i>Y</i> ₃ <i>Fe</i> ₅ <i>O</i> ₁₂
Crystallite size (Á)	168 (3)	356 (4)	466 (4)
a (Á)	12.0362 (10)	12.0420 (4)	12.3773 (4)
b(Å)	12.0362 (10)	12.0420 (4)	12.3773 (4)
c(Á)	12.0362 (10)	12.0420 (4)	12.3773 (4)
Strain (%)	0.27 (7)	0.12 (3)	0.104 (15)
Rwp (%)	9.60	9.90	2.45
Rp (%)	4.79	7.35	1.91
Re (%)	6.85	6.49	1.66
GOF	1.4024	1.5249	1.4752

UV-VIS characterization: UV-Vis-NIR diffuse reflectance spectra of Fe-doped Y₃Al₅O₁₂ (Fe-doped YAG) and Y₃Fe₅O₁₂ (YIG) powders recorded at room temperature are presented in Figure 35. With Fe³⁺ increase in composition two bands placed around 600 nm (with shoulder around 700 nm) and 900 nm arise. The band located around 600 nm and the shoulder at 700 nm can be assigned to the ${}^{6}A_{1} \rightarrow {}^{4}T_{2}$ transition of Fe³⁺ ions in the octahedral site with a contribution of ${}^{6}A_{1} \rightarrow {}^{4}T_{1}$, ${}^{4}T_{2}$ transitions of Fe³⁺ ions in the tetrahedral site. The band at 900 nm corresponds to the ${}^{6}A_{1} \rightarrow {}^{4}T_{1}$ transition of iron ions in the octahedral site [17].



Figure 35 UV-Vis-NIR diffuse reflectance spectra recorded at room temperature of Fe-doped $Y_3Al_5O_{12}$ (Fe-doped YAG) and $Y_3Fe_5O_{12}$ (YIG) powders.



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Hyperthermia measurements under magnetic field: Hyperthermia measurements under magnetic field were preformed on all three samples and presented in Figure 36 for $Y_3Al_{4.95}Fe_{0.05}O_{12}$ and $Y_3Fe_5O_{12}$ ones. More precisely, temperature of the powder samples was followed by thermal camera under irradiation. Figure 29 clearly shows that YIG sample presents a huge increase of temperature under alternative magnetic field (144.5 kHz and 100 G) with obtained 52°C temperature increase. On the other side $Y_3Al_{4.995}Fe_{0.005}O_{12}$ and $Y_3Al_{4.95}Fe_{0.05}O_{12}$ samples did not show any temperature increase under alternative magnetic field (471 kHz and 180 G).



Figure 36 Hyperthermia measurements under alternative magnetic field for: a) $Y_3Al_{4.95}Fe_{0.05}O_{12}$ (471 kHz and 180 G) and b) $Y_3Fe_5O_{12}$ (144.5 kHz and 100 G) sample.

Transmission electron microscopy:







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Future plans:			
 Dispersion of Comparison suspension. It iron oxide name 	f YIG sample into stabile suspension for further investigation a of YIG suspension with iron-oxide nanoflowers and nanos is already reported that iron-oxide nanoflowers suspension oparticles [18].	nd comp pheres (n outperf	arison. see Figure 37) forms standard

2. Nd³⁺, Sm³⁺ and Dy³⁺ doped colloidal NaYF₄

Synthesis: Preparation of lanthanide 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)₃Ln lanthanide precursors were added to the three-neck flask with 12 ml OA and 30 ml 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 (0.2964 g) and sodium hydroxide (0.2 g) dissolved in 10 ml 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 upconverting nanoparticles (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 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 5 ml chloroform. Detailed precursor quantities are given in Table 17.



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Sample	Composition		Precursors	
		Nd_2O_3	Sm_2O_3	Dy_2O_3
FET_1	NaNdF ₄	0.3364g	х	Х
FET_2	$NaDyF_4$	х	х	0.3729g
FET_3	$NaSmF_4$	х	0.3487	Х
		Y ₂ O ₃	Sm_2O_3	Nd_2O_3
FET_12	NaYF4:1%Nd, 1%Sm	0.2212	0.0034	0.0033
FET_13	NaYF4:1%Nd, 2%Sm	0.219	0.0069	0.0033
FET_14	NaYF4:1%Nd, 5%Sm	0.2122	0.0174	0.0033
FET_15	NaYF4:1%Nd, 10%Sm	0.2009	0.0348	0.0033
		Y ₂ O ₃	Dy_2O_3	Nd_2O_3
FET_16	NaYF4:1%Nd, 1%Dy	0.2212	0.003736	0.033
FET_17	NaYF4:1%Nd, 2%Dy	0.219	0.0074	0.0033
FET_18	NaYF4:1%Nd, 5%Dy	0.2122	0.0186	0.0033
FET_19	NaYF4:1%Nd, 10%Dy	0.2009	0.0373	0.0033

Table 17 Detailed precursor quantities used for Ln³⁺-doped NaYF₄ colloidal nanoparticles synthesis.



Figure 38 Example of morphology of the NaYF₄ core-shell NPs obtained in the lab of WPAS. The representative wide field TEM (a, e), HR-TEM (b, f), SAED (c, g) of \mathbb{Z} -NaYF₄:20%Yb,2%Ho core (top row a-c) and \mathbb{Z} -NaYF₄:20%Yb, 2%Ho@ β -NaYF₄core@shell (bottom-row e-g) NPs. The cores presented and characterized in the pictures (top row a-c), were further used to deposit the shell, and such core@shell NPs are presented and characterized in panels (bottom row e-g).



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Structural analysis: According to Burns [19] the hexagonal NaYF₄ structure belongs to the P6 group, where there is a nine-fold coordinated position occupied by Y^{3+} , another nine-fold occupied position occupied by Y^{3+}/Na^+ (in the ratio 3 : 1) and a six-fold coordinated position occupied by Na⁺ and vacancies (ratio 1 : 1) (Figure 39).



Figure 39 Visualization of hexagonal NaYF₄ structure

The phase purity and high crystallization degree of synthesized nanocrystals were confirmed using X-Ray Diffraction and obtained patterns are presented in Figs. 40 and 41. Performed Rietveld analysis enables to determine the information concerning basic crystallographic parameters of synthesized nanocrystals. Selected structural parameters obtained from Rietveld refinement analysis are enlisted in Table 18 for analyzed samples.

Sample	Grain size [nm]	а	С	strain	Rwp	Rp	Re	GOF
NaNdF ₄	12.4	6.10441	3.71629	0.019	4.31	4.10	3.62	1.62
NaDyF ₄	14.3	5.99209	3.56930	0.160	5.51	4.21	3.54	1.82
NaSmF ₄	15.9	6.07195	3.65111	0.031	5.90	4.62	3.89	1.79





Figure 40 The XRD patterns of β - sodium yttrium fluoride doped with Nd³⁺ and Sm³⁺.



Figure 41 The XRD patterns of β - sodium yttrium fluoride doped with Nd³⁺ and Dy³⁺.

UV-VIS characterization: Absorption spectra of the obtained samples have been measured and presented in Figures 42 and 43. In the samples co-doped with Nd³⁺ and Sm³⁺ (Figure 42), one may note optical transition typical for Nd³⁺ and Sm³⁺ ions. Especially interesting and perspective are the Nd³⁺ absorption bands, which lay in Near Infrared Spectral Region (NIR), i.e. ${}^{4I_{9/2}} \rightarrow {}^{4}F_{5/2}$ at 796 nm. The presence of Sm³⁺ built into the material was evidenced as well, but the role of Sm³⁺ is to non-radiatively convert the photons energy into heat. The energy level scheme of Nd³⁺-Sm³⁺ and Nd³⁺⁻

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 Dy^{3+} presented in Figure 44, shows that $Nd^{3+} \rightarrow Sm^{3+} / Dy^{3+}$ energy transfer (ET) is highly probable, and due to numerous close by energy levels of Sm^{3+} / Dy^{3+} , non-radiative depopulation should occur under ~800 nm radiation.



Figure 42 Absorption spectra of synthesized samples co-doped with Nd³⁺ and Sm³⁺.

Absorption spectra of the samples co-doped with Nd³⁺ and Dy³ and presented in Figure 43. It is important to add, that beside Nd³⁺ ions absorbing at 793.5 and 805 nm (${}^{4}I_{9/2} \rightarrow {}^{4}F_{5/2}$,), Dy³⁺ ions display similar absorption coefficient at 908 nm (~0.6).



Figure 43 Absorption spectra of synthesized samples co-doped with Nd³⁺ and Dy³⁺. This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No **801305**.





Figure 44 Schematic energy levels and transitions in Nd³⁺-Sm³⁺ and Nd³⁺-Dy³⁺ systems. After absorption by Nd³⁺ ions energy transfer occurs to Sm³⁺ and Dy³⁺ ions followed by non-radiative depopulation of excited states. This non-radiative de-population shall be responsible for heat generation.

Dy³⁺

Nd³⁺

Sm³

Nd³⁺

For more precise description of the absorption peaks, the absorption spectra of fully concentrated NaNdF₄, NaSmF₄ and NaDyF₄ with ascribed peaks are shown below (Figs 45-47).



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Figure 45 Absorption spectra of fully concentrated sodium neodymium fluoride (NaNdF₄).



Figure 46 Absorption spectra of fully concentrated sodium samarium fluoride (NaSmF₄).



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Figure 47 Absorption spectra of fully concentrated sodium dysprosium fluoride (NaDyF₄).

- NaNdF₄ shows most intense and multiple absorption bands (absorbance \sim 1-3.5) in the visible and NIR spectral region, which is important to effectively absorb the photoexcitation.

- Sm^{3+} shows reasonable absorption around 1100, 1250, 1500-1600 nm (absorbance > 0.5).

- Dy^{3+} shows absorption at 800, 900, 1100, 1300 nm (but the absorbance is low < 0.5).

- It may be reasonable to combine 2 or 3 ions to get efficient heating, e.g. Nd^{3+} as absorber at 800 nm and Sm^{3+} with Dy^{3+} as non-radiative heat generators.

- It is clearly visible that the peak intensities ascribed to the Sm $^{3+}$ and Dy $^{3+}$ ions transitions increase with increasing concentration of the ions.

- In case of Nd^{3+} and Dy^{3+} co-doped samples the intensity of peaks ascribed to Nd^{3+} ion transitions is constant.

- In case of Nd³⁺ and Sm³⁺ co-doped samples the intensity of peaks ascribed to Nd³⁺ ion transitions is decreasing with increasing Sm³⁺ concentration. This is very interesting because the amount of Nd³⁺ was the same in every sample.



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Further investigations:

- New set of samples (the samples are either already synthesized or on the short list, Table 19).

- Studying luminescent properties (i.e. emission spectra in Vis/NIR, lifetimes in the Vis) as a function of dopants concentration and temperature to determine the energy transfer processes (i.e. concentration quenching). This will be done of the custom designed and build optical setup, that will be optimized by WPAS and ready to use by March 2019 (see Figure 48).



Figure 48 (Left) Custom built optical setup for automated measurements of temperature dependent emission spectra and luminescence rise- and life-times AND (right) custom made LabVIEW application for automatized measuring of spectroscopic properties.



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<i>NdYb@YbDy</i> To understand ET between Nd ³⁺ and Dy ³⁺ . The samples n
20Nd80Dy act both as thermometers (temperature dependent ET)
80Nd20Dy light-to-heat converters.
50Nd50Dy
NaYF ₄ 100Nd@100Dy
<i>NdYbSm@@NdYb</i> First approach to synthesize NPs which combine luminesc
YbSm@@NdYb thermometry in NIR (Nd \rightarrow Yb ET) and light-to-heat generat
<i>YbDy@@NdYb</i> $(Nd \rightarrow Yb \rightarrow Sm)$. This work will be essential to understand i
NdYbMnEr@@NdYb@@YbSm possible to address a given function, e.g. we plan to deve
NdYbMnEr@@NdYb@@YbSDy spectral "addressing", where 800, 980 and 1064
<i>YbTbMn@@NdYb</i> photoexcitation will activate a given function (either heat
<i>YbTbMn@@NdSm</i> or thermometry).
NaVE, 00Nd - 1 Sm Some VbSm samples have been synthesized already with sn
NaVE, 50Nd - 50 Sm Some Toshi Some for the mechanism of ET H
NaVE, 25Nd - 75 Sm we want to balance the absorption cross section of sensiti
(Nd ³⁺ ions) and light-to-heat converter to achieve high
energy conversion efficiency
NaYE : Yh @ NaGdE: YhEr The sample will be made to understand how precisely we
done the core and the shell in an individual way Using Y or
should provide sufficient contrast in TEM and TEM-EDX wh
Yh and Er, should be doped into core (Yh) and shell (Er). T
will be the first try to understand the formation of core-sh
NPs, in order to address the functions of such complex NPs.

Table 19 Compounds which have been already or will be synthesized shortly.

3. Nanoheaters and hybrid heater/thermometer nanoplatforms

This paragraph addresses the design of hybrid nanoplatforms in which the heating unit is located at the core of the nanostructure while the sensing one will be constituted by a surrounding shell of the sensing material. The design will be specially adapted for their use in intracellular thermometry.

In this type of thermometers, the sensing probe has a molecular nature. It consists of complexes of lanthanide emitting nucleus with light harvesting organic ligands. These molecular probes are encapsulated in the nanoparticle coating near the heater core in order to detect the local temperature of the heater when it is submitted to an external ac magnetic field. The main factors affecting the performance of the probes are: 1) the structure of the complex itself (type of ligands and coordination number) in relation to its optical properties (brilliance, sensitivity); 2) the facility to introduce the probe into the nanoparticle coating; 3) the persistence of the luminescence under the influence of cell chemical environment. In this first stage the efforts have been directed to: i) the



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finding of a molecular probe with an optimal structure; ii) the design and synthesis of polymer coatings with a high capacity to entrap molecular probes (by chemical bonding); iii) the evaluation of the thermometric performance of nanoplatforms containing the probes.

The fabrication of these heater/thermometer nanoplatforms is connected with one of the objectives of WP5, which is to measure the local temperature gradients reached in the nanoplatforms internalized in a cell with respect to the cell bulk temperature. The determination of this gradient involves the measurement of the temperature in the nanoheathers and that of the bulk of the cell. Thus, two types of thermometers are necessary. A first type contains the magnetic nanoheather in the core and the molecular thermometric probes in the polymeric coating. For the second, we are also fabricating a new type of nanoparticles that do not contain magnetic heaters. They consist of copolymer micelles encapsulating molecular thermometric probes in the interior.

Synthesis:

Synthesis of heater/thermometer nanoplatforms. Iron oxide magnetic cores with a high heating power were used. Their synthesis is described in [20]. The coating of the iron oxide cores with a polymer coating embedding the molecular thermometric probes to obtain the heater/thermometer nanoplatforms was carried out as reported previously [21].

Europium and Samarium [$Ln(btfa)_3(H_2O)_2$] complexes were prepared following the synthetic procedure reported by Binnemans et al. [22]. DNPD complexes of Eu and Sm [$Ln(DNPD)_3(H_2O)_2$] were prepared adapting the synthetic method described previously [23,24].

Synthesis of thermometer nanoplatforms. Nanothermometric polymeric micelles have been formed by self-assembly in water of an Amphiphilic block copolymer (ABCP) with Luminescent lanthanides complexes covalent incorporated into the polymer chain. The new Nanothermometer are based in binary mixtures of lanthanide (Eu, Sm) coordination complexes with Ln(L1)₃L2 formula where L1 represents a β-diketonate ligand: 4,4,4-trifluoro-1-phenyl-1,3-butanedione (btfa) or 1,3-di(naphthalen-2-yl)propane-1,3-dione (DNPD) reported to efficiently sensitize the luminescence of the Eu(III) and forming Visible-light sensitized luminescent europium(III)-β-diketonate complex in different systems [23,25]. L2 is an ancillary ligand, (1,10-phenanthrolin-4-yl)methyl acrylate (PhenA) a 1,10 phenanthroline derivative modified with a polymerizable acrylate group and pendant from the polymer chain after polymerization. Europium and Samarium [Ln(btfa)₃(H₂O)₂] complexes were prepared following the synthetic procedure reported by Binnemans et al.[26]. DNPD and Eu and Sm [Ln(DNPD)₃(H₂O)₂] complexes were prepared adapting the synthetic method described previously by McGehee et al. [23] and Reddy et al. [24]. PhenA were prepared according to the according to the synthetic route showed in Figure 49.



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Figure 49 Synthesis of Ancillary Ligand PhenA (L2).

A P(MPEGA-co-PEGA)-b-P(MA-b-PhenA) Amphiphilic block copolymer (ABCP) where the hydrophilic block is a brush-like block of methoxy (MPEGA, Mn: 480) and hydroxyl (PEGA, Mn:460 Da) end capped polyethylene glycol acrylates has been synthetized. The hydrophobic block is a methyl acrylate (MA) polymer containing a discrete number of a second monomer PhenA. The Macro Chain Transfer agent (CTA) P(MPEGA-co-PEGA) and the final diblock copolymer, P(MPEGA-co-PEGA)-b-P(MA-co-PhenA), were prepared using Reversible addition-fragmentation chain transfer polymerization (RAFT) according to the synthetic route showed in Figure 50.





Figure 50 Synthesis of the Macro CTA and final Block Copolymer.

Synthesis of the macroCTA P(MPEGA-co-PEGA). A round bottom schlenk flask (50 mL) was charged with a magnetic stirrer bar, MPEGA (5.04 g, Mn: 480 Da, 10.5 mmol), PEGA (2.10 g Mn: 469 Da, 4.5 mmol), AIBN (16.4 mg, 0.1 mmol), CTA (178.16 mg, 0.5 mmol) and 13.4 mL of Toluene. The mixture was freeze in liquid N₂ and degassed by three freeze-pump-thaw cycles using a schlenk line by purging with N₂ or argon. Finally the mixture was immersed in a thermostatic bath previously heated at 70°C, for 6 hours. The flask was open at the atmosphere and the mixture cool down at room temperature. 25-50 µL of the polymerization reaction mixture was withdrawn, diluted with CDCl₃ and analyzed by ¹H-NMR spectroscopy. Conversion of the polymerization can be calculated from the ¹H-NMR spectrum (90-93%). The reaction mixture was separated by decantation from the mother liquors dried in the rotavapor and purified again by dissolving in CH₂Cl₂ and precipitation in a large excess of diethyl until no signal of the monomer is observed by ¹H-NMR spectroscopy.



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Synthesis of block copolymer P(MPEGA-b-PEGA)-b-P(MA-co-PhenA). The polymerization was conducted adapting the method described for the synthesis of the MacroCTA. A round bottom schlenk flask (25 mL) was charged with a magnetic stirrer bar, Macro-CTA [P(MPEGA-co-PEGA)(0.2mmol), methyl acrylate mmol), PhenA (1 mmol) and AIBN (0.08mmol) and 1,4-Dioxane (6.5 mL). The mixture was freeze in liquid N₂ and degassed by three freeze-pump-thaw cycles using a schlenk line by purging with N₂ or argon. Finally the mixture was immersed in a thermostatic bath previously heated at 70°C, for 6 hours. The flask was open at the atmosphere and the mixture cool down at room temperature. 25-50 μ L of the polymerization reaction mixture was withdrawn, diluted with CDCl₃ and analyzed by ¹H-NMR spectroscopy. A 90% conversion of the polymerization has been calculated from the ¹H-NMR spectrum. The reaction mixture was added dropwise over cold a mixture of cold diethylether and n-hexane. The polymer was separated by decantation from the mother liquors, dried in the rotavapor and purified again by dissolving in THF and reprecipitating in a large excess of diethyl ether/n-hexane. The product was purified by dialysis against MeOH, and finally isolated by vacuum evaporation. Mn_{ABCP (NMR)}: 18793Da, 6.32% in weight of PhenA.

The encapsulation of the complexes in the hydrophobic matrix of the micellar aggregates is expected to improve the stability of the molecular nanothermometer from external effects such as pH, ionic strength among others that can be found in the cell environment. The final complexes were attached to the polymeric chain in a two-step process. In a first stage $Ln(L1)_3(H_2O)_2$ complex were synthetised following the procedure described in the literature in a second step complexed were attached by coordination with the ancillary ligand. This synthetic route was selected as it had several advantages over the synthesis of a polymerizable complex and its direct copolymerization as can be the liability of the complex in the polymerization conditions, the removing the unreacted complex and the difficulty of control the molecular weight. Thus both types of nanothermometers (BTFA and DNPD) were anchored to exactly the same polymer. The process of coordination and micellar formation is shown in Figure 51.







Figure 51 Attachment of the complex to the polymeric chain and micelle formation.

*Synthesis of P(MPEGA-co-PEGA)-b-P(MA-co-PhenA@Ln(L1)*₃. The Copolymers containing the auxiliary ligand in the polymer chain were reacted with complexes of lanthanides: Sm(L1)₃(H₂O)₂, and (L1)₃(H₂O)₂ . 0.060 mmol of the lanthanide complex Ln(L1)₃(H₂O)₂ were added to a solution of 250 mg of P(MPEGA-co-PEGA)-b-P(MA-co-PhenA) (0.06 mmol of phenanthroline) in Chloroform (10 mL). The mixture was heated at 60 °C (bath temperature) for 12 hours. Solvent was evaporated under vacuum. The polymer was dissolved in THF (10 mL), which is a good solvent for both blocks and is miscible with water. Then the solution was filtered through a 0.2 µm PTFE syringe. Different solutions were prepared for each complex in that way each polymer chain includes a single type of lanthanide ion. This protocol allows the preparation of micelles with different Eu/Sm ratios in an easy way and explore their effect in the performance of the thermometric measurement. Until now just micelles in a ratio 7.5:92.5 (Eu:Sm) has been prepared.

Preparation of P(MPEGA-co-PEGA)-b-P(MA-co-PhenA@Eu_{0.075}**Sm**_{0.925}**(L1)**₃. Self-assembly of the amphiphilic block copolymers in water was performed by a nanoprecipitation procedure. 2.165 mL of a mixture of the freshly prepared Stock solutions of polymer doped with Sm(L1)₃ (2 mL, 92.5% molar) and Eu(L1)₃ (0.165 mL, 7.5% molar) were added to a flask of 25 mL charged with a small magnetic stirrer bar. Then, deionized water was added slowly to the polymer solution with a syringe under slight magnetic stirring to a final water concentration of about 85% (12.8 mL). The mixture was purified by dialysis against distilled water (500-800 mL) for 24 hours in order to remove the THF, using a dialysis tubing cellulose membrane (SpectraPor®) with a Molecular weight



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cut-off (MWCO) of 12500 Da. The dialysis solution was changed at least three times. Sample was left to equilibrate at least one hour before changing the solution.

The morphological analysis was then performed by TEM (Transmission Electron Microscopy), and the hydrodynamic size was measured by DLS (Dynamic Light Scattering). Molar concentration of both lanthanides ions in the micelle solution was analyzed by Inductively Coupled Plasma - Atomic Emission Spectrometry (*ICP- AES*).

Photoluminescent characterization: Iron oxide@P(4-VP)-co-P(PEG)A@Eu_{0.075}Sm_{0.925}(BTFA)₃ heater/thermometer nanoplatforms

The emission spectra of the nanoparticles were recorded with a modular double grating excitation spectrofluorimeter with a TRIAX 320 emission monochromator (Fluorolog-3, Horiba Scientific) coupled to an R928 Hamamatsu photomultiplier. The excitation source was a 450WXe arc lamp. The variation of the spectra of Iron oxide@P(4-VP)-co-P(PEG)A@Eu0.075Sm0.925(BTFA)3 heater/thermometer nanoplatforms with the temperature is plotted in Figure 52.



Figure 52 Variation of the emission spectra of Iron oxide@P(4-VP)-co-P(PEG)A@Eu_{0.075}Sm_{0.925}(BTFA)_3 heater/thermometer nanoplatforms with the temperature.



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P(MPEGA-co-PEGA)-b-P(MA-co[PhenA@EuSm(DNPD)₃)] and *P(MPEGA-co-PEGA)-b-P(MA-co[PhenA@EuSm(BTFA)₃)]* thermometer nanoplatforms

Samples were measured in the same conditions as for Iron oxide@P(4-VP)-co- $P(PEG)A@Eu_{0.075}Sm_{0.925}(BTFA)_3$ heater/thermometer nanoplatforms. The variation of the spectra with the temperature is plotted in Figure 53.



Figure 53 Variation of the emission spectra of P(MPEGA-co-PEGA)-b-P(MA-co[PhenA@EuSm(DNPD)₃)] nanoplatforms with the temperature.



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References:

[1] R.D. Shannon, "Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides", *Acta Crystallographica*, A32, 751-767 (1976).

[2] Y. Ni, J.M. Hughes, A.N. Mariano, "Crystal chemistry of the monazite and xenotime structures", *American Mineralogist*, 80, 21-26 (1995).

[3] J. I. Langford, A. J. C. Wilson, "Scherrer after sixty years: A survey and some new results in the determination of crystallite size" *Journal of Applied Crystallography*, 11, 102-113 (1978).

[4] C. A. Morrison, R. P. Leavitt, "Handb. Phys. Chem. Rare Earths", 5, 461 (1982).

[5] A. Vujačić, V. Vasić, M. Dramićanin, S.P. Sovilj, N. Bibić, S. Milonjić, V. Vodnik, "Fluorescence Quenching of 5,5'-Disulfopropyl-3,3'-dichlorothiacyanine Dye Adsorbed on Gold Nanoparticles", *The Journal of Physical Chemistry C*, 117, 6567–6577 (2013).

[6] A.P. Philipse, A. Vrij, "Preparation and properties of nonaqueous model dispersions of chemically modified, charged silica spheres", *Journal of Colloid and Interface Science*, 128, 121-136 (1989)

[7] Y. Kobayashi , H. Inose, T. Nakagawa, K. Gonda, M. Takeda, N. Ohuchi and A. Kasuya, "Control of shell thickness in silica coating of Au nanoparticles and their X-ray imaging properties", *Journal of Colloid and Interface Science* 358, 329-333 (2011).

[8] W. Haiss, Nguyen T. K. Thanh, J. Aveyard and D.G. Fernig, "Determination of Size and Concentration of Gold Nanoparticles from UV–Vis Spectra", *Analytical Chemistry*, 79 (11), 4215-4221 (2007).

[9] B. Nikoobakht, M.A. El-Sayed, "Preparation and Growth Mechanism of Gold Nanorods (NRs) Using Seed-Mediated Growth Method", *Chemistry of Materials*, 15, 1957–1962 (2003).

[10] D.J. Jovanović, T.V. Gavrilović, S.D. Dolić, M. Marinović-Cincović, M.D. Dramićanin, "Upconversion luminescence of GdVO₄:Nd³⁺/Er³⁺ and GdVO₄:Nd³⁺/Ho³⁺ phosphors under 808 nm excitation", *Optical Materials*, 82, 1-6 (2018).

[11] G. Tian, Z. Gu, L. Zhou, W. Yin, X. Liu, L. Yan, S. Jin, W. Ren, G. Xing, S. Li and Y. Zhao, "Mn²⁺ dopant-controlled synthesis of NaYF₄:Yb/Er upconversion nanoparticles for in vivo imaging and drug delivery"*Advanced Materials*, 24, 1226-1231 (2012).

[12] Z. Bai, H. Lin, K. Imakita, R. Montazami, M. Fujii and N. Hashemi, "Synthesis of Er³⁺/Yb³⁺ codoped NaMnF₃ nanocubes with single-band red upconversion luminescence", *Rsc Advances*, 4, 61891-61897 (2014).

[13] Z. Bai, H. Lin, J. Johnson, S. C. Rong Gui, K. Imakita, R. Montazami, M. Fujii and N. Hashemi, "The single-band red upconversion luminescence from morphology and size controllable Er³⁺/Yb³⁺ doped MnF₂ nanostructures" *J. Mater. Chem. C*, 2, 1736-1741 (2014).

[14] K. L. Reddy, M. Rai, N. Prabhakar, R. Arppe, S. B. Rai, S. K. Singh, J. M. Rosenholm and V. Krishnan, "Controlled synthesis, bioimaging and toxicity assessments in strong red emitting Mn²⁺ doped NaYF₄:Yb³⁺/Ho³⁺ nanophosphors" *Rsc Advances*, 6, 53698-53704 (2016).



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[15] A. Nakatsuka, A.Yoshiasa, T. Yamanaka, "Cation distribution and crystal chemistry of $Y_3Al_{5-x}GaxO_{12}$ ($0 \le x \le 5$) garnet solid solutions", *Acta Crystallographica Section B*, 55, 266-272 (1999).

[16] A. Nakatsuka, A.Yoshiasa, S. Takeno, "Site preference of cations and structural variation in $Y_3Fe_{5-x}GaxO_{12}$ ($0 \le x \le 5$) solid solutions with garnet structure", *Acta Crystallographica Section* B, 51, 737-745 (1995).

[17] H. Serier-Brault, L. Thibault, M. Legrain, P. Deniard, X. Rocquefelte, P. Leone, J.L. Perillon, S. Le Bris, J. Waku, Stéphane Jobic, "Thermochromism in Yttrium Iron Garnet Compounds", *Inorganic Chemistry*, 53, 12378–12383 (2014).

[18] P. Hugounenq, M. Levy, D. Alloyeau, L. Lartigue, E. Dubois, V. Cabuil, C. Ricolleau, S. Roux, C. Wilhelm, F. Gazeau, Rana Bazzi, "Iron Oxide Monocrystalline Nanoflowers for Highly Efficient Magnetic Hyperthermia", *The Journal of Physical Chemistry C*, 116, 15702–157122012 (2012).

[19] J. H. Burns, "Crystal Structure of Hexagonal Sodium Neodymium Fluoride and Related Compounds", *Inorganic Chemistry*, 4, 881–886 (1965).

[20] D. Bonvin, D.T.L. Alexander, A. Millán, R. Piñol, B. Sanz, G.F. Goya, A. Martínez, J.A.M. Bastiaansen, M. Stuber, K.J. Schenk, H.Hofmann and M. Mionić Ebersold, "Tuning Properties of Iron Oxide Nanoparticles in Aqueous Synthesis without Ligands to Improve MRI Relaxivity and SAR", *Nanomaterials* 7, 225 (2017).

[21] R. Piñol, C.D.S. Brites, R. Bustamante, A. Martínez, N.J.O. Silva, J.L. Murillo, R. Cases, J. Carrey, C. Estepa, C. Sosa, F. Palacio, L.D. Carlos, and A. Millán, "Joining Time-Resolved Thermometry and Magnetic-Induced Heating in a Single Nanoparticle Unveils Intriguing Thermal Properties", *ACS Nano*, 9, 3134-3142 (2015).

[22] K. Binnemans, P. Lenaerts, K. Driesena and C. Görller-Walranda, "A luminescent tris(2-thenoyltrifluoroacetonato)europium(III) complex covalently linked to a 1,10-phenanthroline-functionalised sol-gel glass", *Journal of Material Chemistry*, 14, 191-195 (2014).

[23] M.D. McGehee, T. Bergstedt, C. Zhang, A.P. Saab, M.B. O'Regan, G.C. Bazan, V.I. Srdanov, A.J. Heeger, "Narrow Bandwidth Luminescence from Blends with Energy Transfer from Semiconducting Conjugated Polymers to Europium Complexes", *Advanced Materials*, 11, 1349-1354 (1999).

[24] M.L.P. Reddy, V. Divya and R. Pavithran, "Visible-light sensitized luminescent europium(III)-βdiketonate complexes: bioprobes for cellular imaging", *Dalton Transactions*, 42, 15249-15262 (2013).

[25] H. Peng M.I.J. Stich, J. Yu , L. Sun, L.H. Fischer, O.S. Wolfbeis, "Luminescent Europium(III) Nanoparticles for Sensing and Imaging of Temperature in the Physiological Range", *Advanced Materials*, 22, 716–719 (2010).

