

## Report on the outcomes of a Short-Term Scientific Mission<sup>1</sup>

Action number: CA20126 (ref. E-COST-GRANT-CA20126-91f22a93)

Grantee name: Paul GANIGAL

### Details of the STSM

Title: Porous PERsistent Luminescence (PERL) nanoparticles for photodynamic therapy (PDT)

Start and end date: 18/10/2023 to 31/10/2023

### Description of the work carried out during the STSM

Description of the activities carried out during the STSM. Any deviations from the initial working plan shall also be described in this section.

The aim of the mission was to perform luminescence characterizations on lanthanide ion-doped  $\text{YPO}_4$  nanoparticles. First, syntheses were performed using mesoporous silica nanoparticles (MSN) impregnated with the cationic precursors and used as templates for the nanoparticles formation. But the difficulty for the  $\text{PO}_4^{3-}$  anions to access the silica mesopores led us to use a different protocol. New materials were obtained following a microwave-assisted hydrothermal method. The nitrate precursors and phosphoric acid were solubilized into water and heated up in a sealed-vessel placed in a microwave at 120 °C for 30 min. The obtained microporous nanoparticles (Fig.1) presented a mean diameter around 67 nm and their XRD patterns showed the expected xenotime phase.

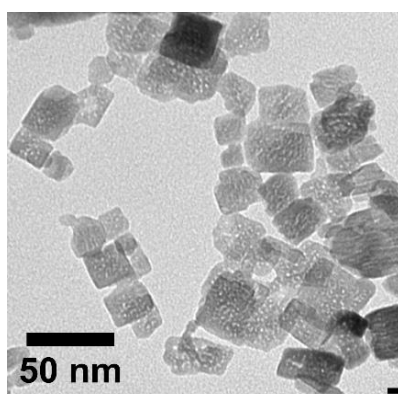


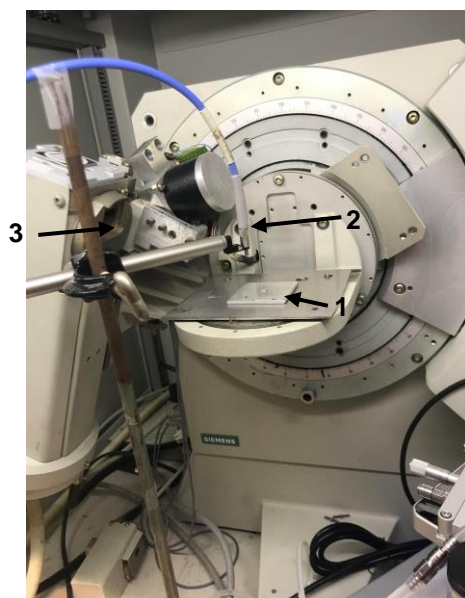
Fig. 1: TEM image of a  $\text{YPO}_4:0.5\% \text{Ce}^{3+}, 0.5\% \text{Ho}^{3+}$  sample

<sup>1</sup> This report is submitted by the grantee to the Action MC for approval and for claiming payment of the awarded grant. The Grant Awarding Coordinator coordinates the evaluation of this report on behalf of the Action MC and instructs the GH for payment of the Grant.

Based on the Dorenbos energy level diagram [1], we prepared  $\text{YPO}_4$  samples with  $\text{Ce}^{3+}$  as the main dopant and  $\text{Ho}^{3+}$  or  $\text{Sm}^{3+}$  as the co-dopant. In  $\text{YPO}_4:\text{Ce}^{3+}$ ,  $\text{Ce}^{3+}$  presents luminescence in the UV-A due to 5d-4f transitions and plays the role of a hole trap after X-ray excitation.  $\text{Ho}^{3+}$  and  $\text{Sm}^{3+}$  play the role of electron traps after X-ray excitation. The influence of various parameters (amount of dopants, amount of phosphoric acid, presence or absence of ethylene glycol that can avoid  $\text{Ce}^{3+}$  oxidation) was investigated.  $\text{YPO}_4:\text{Ce}^{3+},\text{Ho}^{3+}$  nanoparticles obtained by the hydrothermal method were compared to bulk  $\text{YPO}_4:\text{Ce}^{3+}$ ,  $\text{Ho}^{3+}$  powders synthesized by a solid-state reaction.  $\text{YPO}_4:\text{Tb}^{3+},\text{Ho}^{3+}$  sample was also synthesized to produce a green luminescence due to f-f transitions of  $\text{Tb}^{3+}$ . Finally, a  $\text{YPO}_4:\text{Bi}^{3+}$  sample was synthesized with an identical protocol, considering its good UV-A persistent luminescence (PERL) performances as bulk [2].

All samples were fully characterized by XRD, TEM, Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS), and photoluminescence spectroscopy at the home institute.

At Lumilab, X-ray excited radioluminescence and persistent luminescence measurements after X-ray irradiation were performed in a home-built setup (Picture 1) inside a Siemens D5005 X-ray diffractometer (Cu anode, not filtered) operated at 40kV, 40 mA yielding an estimated air kerma rate of  $15 \text{ Gy}\cdot\text{min}^{-1}$  at the position of the sample. A 10 min irradiation was chosen for all the samples.

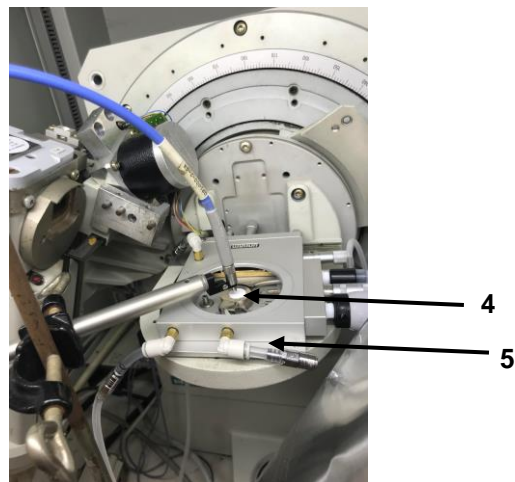


Picture 1: PERL setup with the sample holder (1), optical fiber (2) and X-ray source (3)

Thermally stimulated luminescence (TSL) experiments were performed on samples that presented the most intense PERL to characterize the charge trapping/detrapping phenomena at the origin of the PERL phenomenon. Heating was performed by a resistive heating element in the same instrument. Cooling systems were added with a liquid nitrogen Dewar for low temperature and a water pump for high temperature. The samples were shaped into pellets and placed on the sample holder below the optical fiber (Pictures 2 and 3). By irradiating the sample and then applying a linear temperature ramp of  $30 \text{ }^\circ\text{C}/\text{min}$ , we expected to observe a peak of luminescence at a definite temperature and confirm Dorenbos diagram predictions concerning electron trapping at  $\text{Ho}^{3+}$  and  $\text{Sm}^{3+}$ . From Dorenbos predictions, the main TSL peak of  $\text{YPO}_4:\text{Ce}^{3+},\text{Ho}^{3+}$  and  $\text{YPO}_4:\text{Tb}^{3+},\text{Ho}^{3+}$  samples is at  $55 \text{ }^\circ\text{C}$  ( $\text{Ho}^{3+}$  electron trap), whereas the peak for  $\text{YPO}_4:\text{Ce}^{3+},\text{Sm}^{3+}$  is expected at  $370 \text{ }^\circ\text{C}$  ( $\text{Sm}^{3+}$  electron trap).



Picture 2: TSL setup with the Dewar (1), water pump (2) and temperature controller (3)



Picture 3: Zoom on the pellet (4) and the TSL sample holder (5)

[1] Bos, A. J. J., et al. (2011). "Study of TL glow curves of YPO<sub>4</sub> double doped with lanthanide ions." *Radiation Measurements* 46(12): 1410-1416

[2] Liu, Q., et al. (2021). "Non-Rare-Earth UVC Persistent Phosphors Enabled by Bismuth Doping." *Advanced Optical Materials* 9(8)

## **Description of the STSM main achievements and planned follow-up activities**

Description and assessment of whether the STSM achieved its planned goals and expected outcomes, including specific contribution to Action objective and deliverables, or publications resulting from the STSM. Agreed plans for future follow-up collaborations shall also be described in this section.

*(max. 500 words)*

- PERL measurements:

We could not observe any PERL on the microporous  $\text{YPO}_4:\text{Ce}^{3+},\text{Ho}^{3+}$  samples prepared by the hydrothermal method. Hence, we annealed all the samples at 1100 °C for 5 h under air. The obtained powders presented a mean size around 78 nm and showed a few larger mesopores (Fig. 2). Their photoluminescence was 5 times more intense.

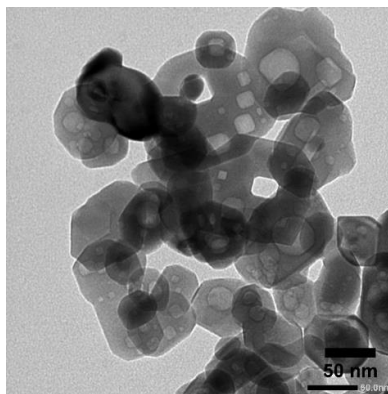


Fig. 2: TEM image of an annealed  $\text{YPO}_4:0.5\% \text{Ce}^{3+},0.5\% \text{Ho}^{3+}$  sample

PERL was measured on the annealed samples. Fig. 3 shows the decays of  $\text{YPO}_4:1\% \text{Ce}^{3+}$  with a varying amount of  $\text{Ho}^{3+}$ . It appeared that the sample with 0.5%  $\text{Ho}^{3+}$  had the highest luminescence intensity and the longest luminescence decay while those with 0%  $\text{Ho}^{3+}$  or 2%  $\text{Ho}^{3+}$  did not present any persistent luminescence. Similar results were found for samples with 0.5%  $\text{Ce}^{3+}$  and varying amount of  $\text{Ho}^{3+}$  (0, 0.5%, 1%, 2%):

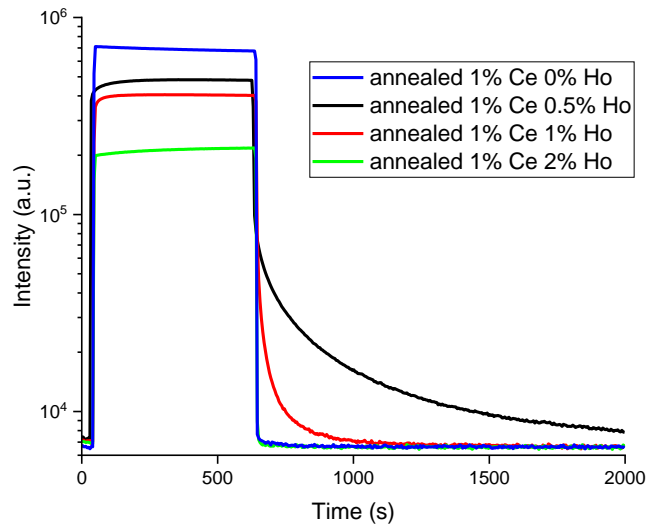


Fig. 3: Comparison of PERL decays for samples with varying amount of  $\text{Ho}^{3+}$

Other measurements (not shown here) showed that:

- The PERL decay was more intense with 1%  $\text{Ce}^{3+}$  than with 0.5%  $\text{Ce}^{3+}$ .
- The presence of ethylene glycol during the synthesis did not have any effect on the intensity or the length of the decay.
- The bulk sample presented a 10% more intense PERL decay than the sample prepared by the hydrothermal way and annealed.
- The best cation/ $\text{PO}_4^{3-}$  ratio for PERL intensity was 1.

$\text{YPO}_4:\text{Tb}^{3+},\text{Ho}^{3+}$  presented PERL decay as shown in Fig. 4. However its decay was much faster than for  $\text{YPO}_4:\text{Ce}^{3+},\text{Ho}^{3+}$

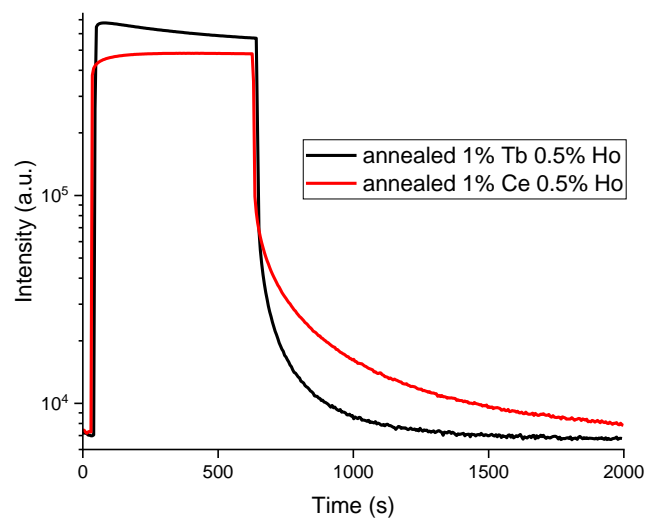


Fig. 4: Comparison of  $\text{YPO}_4:\text{Tb}^{3+},\text{Ho}^{3+}$  and  $\text{Ce}^{3+},\text{Ho}^{3+}$  decays

The  $\text{YPO}_4:\text{Ce}^{3+},\text{Sm}^{3+}$  samples did not show any PERL. This observation is in agreement with Dorenbos diagram and the deeper energy level of  $\text{Sm}^{3+}$  compared to  $\text{Ho}^{3+}$  level.

Unexpectedly,  $\text{YPO}_4:\text{Bi}^{3+}$  nanoparticles did not show any PERL. During the synthesis protocol, we had to solubilize the bismuth nitrate in acid before synthesis. This step could lead to the absence of PERL. This point will be further investigated.

To sum-up PERL experiments, we succeeded in the synthesis of  $\text{YPO}_4$  nanoparticles codoped with  $\text{Ce}^{3+},\text{Ho}^{3+}$  and with  $\text{Tb}^{3+},\text{Ho}^{3+}$ . Those nanoparticles were emitting in the UV-A and in the green respectively and presented persistent luminescence properties after annealing and for 0.5%  $\text{Ho}^{3+}$ . Their microporosity was not conserved after annealing but the nanoparticles still presented a few mesopores.

- TSL measurements:

The TSL experiments performed on  $\text{YPO}_4:0.5\% \text{Ce}^{3+},0.5\% \text{Ho}^{3+}$  and  $\text{YPO}_4:1\% \text{Ce}^{3+},0.5\% \text{Ho}^{3+}$  samples annealed at  $1100^\circ\text{C}$  are shown in Fig. 5 and confirmed the Dorenbos predictions concerning electron trapping at  $\text{Ho}^{3+}$ :

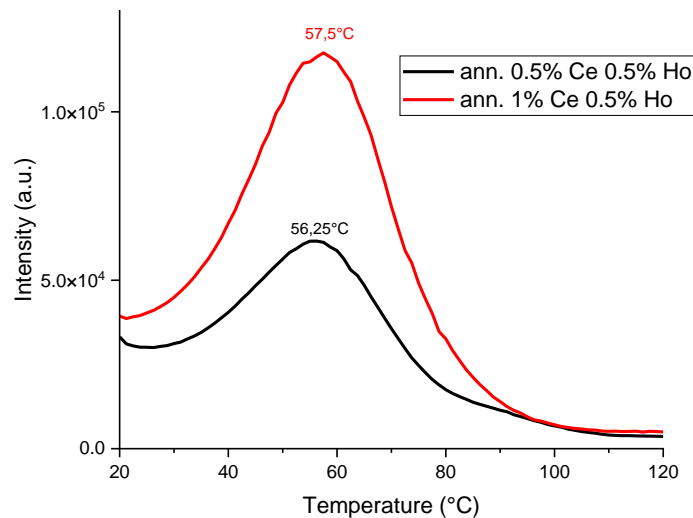


Fig. 5: Peak values during a TSL measurement at  $30^\circ\text{C}/\text{min}$

A focus on the influence of the temperature rate in Fig. 6 showed the expected temperature shift of the peak when the rate is increasing.

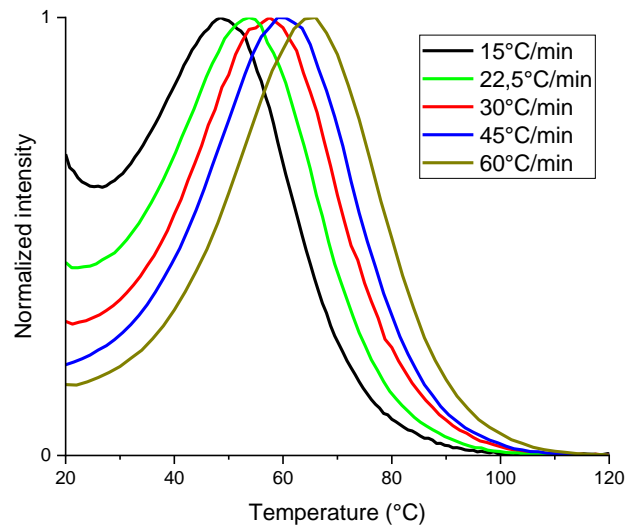


Fig. 6: Influence of the temperature rate for a 1% Ce<sup>3+</sup>, 0.5% Ho<sup>3+</sup> sample

Results and conclusions concerning YPO<sub>4</sub>:Ce<sup>3+</sup>,Ho<sup>3+</sup> are still being discussed in preparation for a future common publication with the host team.

Concerning the other samples, the high peak temperature for Ce<sup>3+</sup>,Sm<sup>3+</sup> complicated the measurements. Samples were also left in Belgium to continue the experiments. Concerning Tb<sup>3+</sup>,Ho<sup>3+</sup>, we should have found a peak at the same temperature as Ce<sup>3+</sup>,Ho<sup>3+</sup> but an error in the temperature rate distorted the results obtained. The sample was also left in Belgium to redo the experiments.

- Optically stimulated luminescence (OSL) measurements:

Due to lack of time, we didn't succeed in obtaining relevant results for those experiments. It will be continued by the team on site.

- Future outlooks:

Discussions will continue between us and the host team to answer some mechanism questions and write an article on nano-sized YPO<sub>4</sub>: Ce<sup>3+</sup>, Ho<sup>3+</sup>. Promising samples with new dopants or new synthesis conditions will be sent to Ghent University to continue the measurements and a new mission for me there next year is possible depending on the progress of my work.