Synthesis of highly luminescent β-NaYF4: Ho3 + / Yb3 + @ SiO2 nanoparticles

Wilfredo Rondan[1, *], Rubén Puga[1], Carmen R. Eyzaguirre[1]
[1]Universidad Nacional de Ingeniería, Lima, Perú
[*]wilfredo.rondan.h@uni.pe

SUMMARY

In recent years, upconversion photoluminescent nanoparticles (UCNP) have been synthesized with a matrix of $\mathrm{NaYF_4}$ doped with trivalent rare earths ($Yb^{3+}, Er^{3+}, Tm^{3+}$ and Ho^{3+}, since they have promising luminescent properties for biological applications (high sensitivity and low background noise) when 980 nm radiation is incident, this happens due to the property of doping ions. In this investigation, UCNP of $\mathrm{NaYF_4}$ doped with Yb^{3+} and Ho^{3+} (with atomic percentages of 20% and 2%, respectively) were synthesized with a variation in the amounts of yttrium and fluorine in different proportions (Y: F = 1:4, 1:12 and 1:20 respectively) in order to obtain a high luminescence. Also, the synthesized nanoparticles were coated with a layer of 10nm of silicon oxide (SiO_2).
The coated samples were characterized with an X-ray Diffractometer, a Transmission Electron Microscope (TEM) and a spectrometer. Nanoparticles with a Y: F = 1:20 ratio are reported to have a hexagonal crystal structure. In the transmission electron microscope it is evident that 80 nm nanoparticles were obtained with a 10 nm layer of silicon oxide. The emission spectrum is also presented before and after coating the nanoparticles with silicon oxide to see the influence of the silicon oxide layer on the intensity of the emission peaks.

METHODOLOGY

- Synthesis of $\beta - NaYF_4{:}Yb^{3+}/Ho^{3+}$ nanoparticles (Solvotermal)

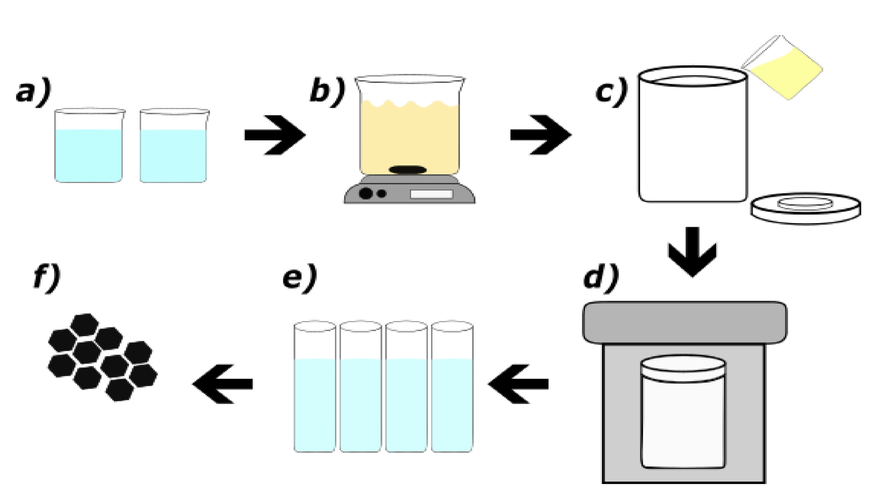

Figure 1. Solvothermal method to synthesize $NaYF_4{:}Yb/Ho$ nanoparticles, with a reaction time of 8h at 200 ° C inside a muffle furnace. a) Rare earth precursors dissolved in ethylene glycol and polyethyliminine dissolved in ethylene glycol. b) Stir until a homogeneous solution is obtained. c) It is poured into a Teflon and c) put in an autoclave to be placed in an oven. e) and f) The nanoparticles are centrifuged, washed and dried.

- Nanoparticle coating. (Reverse microemulsion)

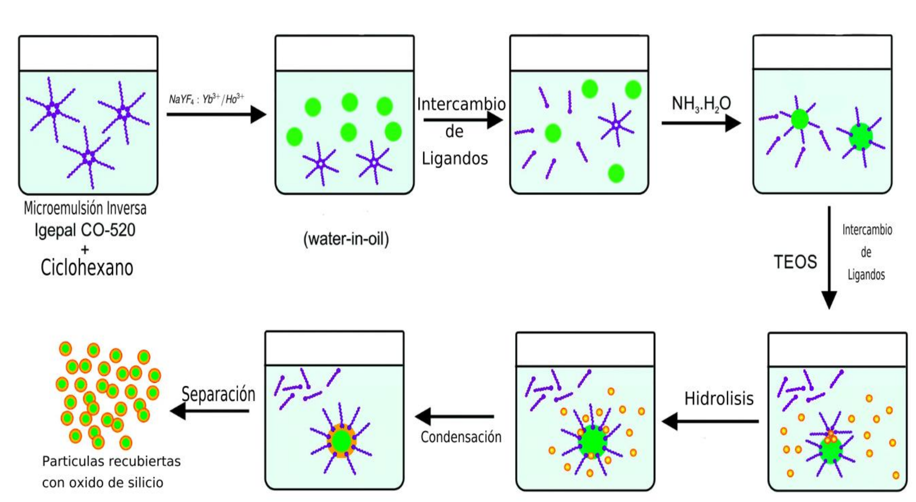

Figure 2. Coating of the $\beta - NaYF_4{:}\ Yb^{3+}, Ho^{3+}$ nanoparticles with 10 nm of silicon oxide (SiO_2) by the inverse microemulsion method. TEOS was used as the silicon precursor.

RESULTS

- Diffractogram of $\beta - NaYF_4{:}Yb^{3+}/Ho^{3+}$ @SiO_2 nanoparticles.

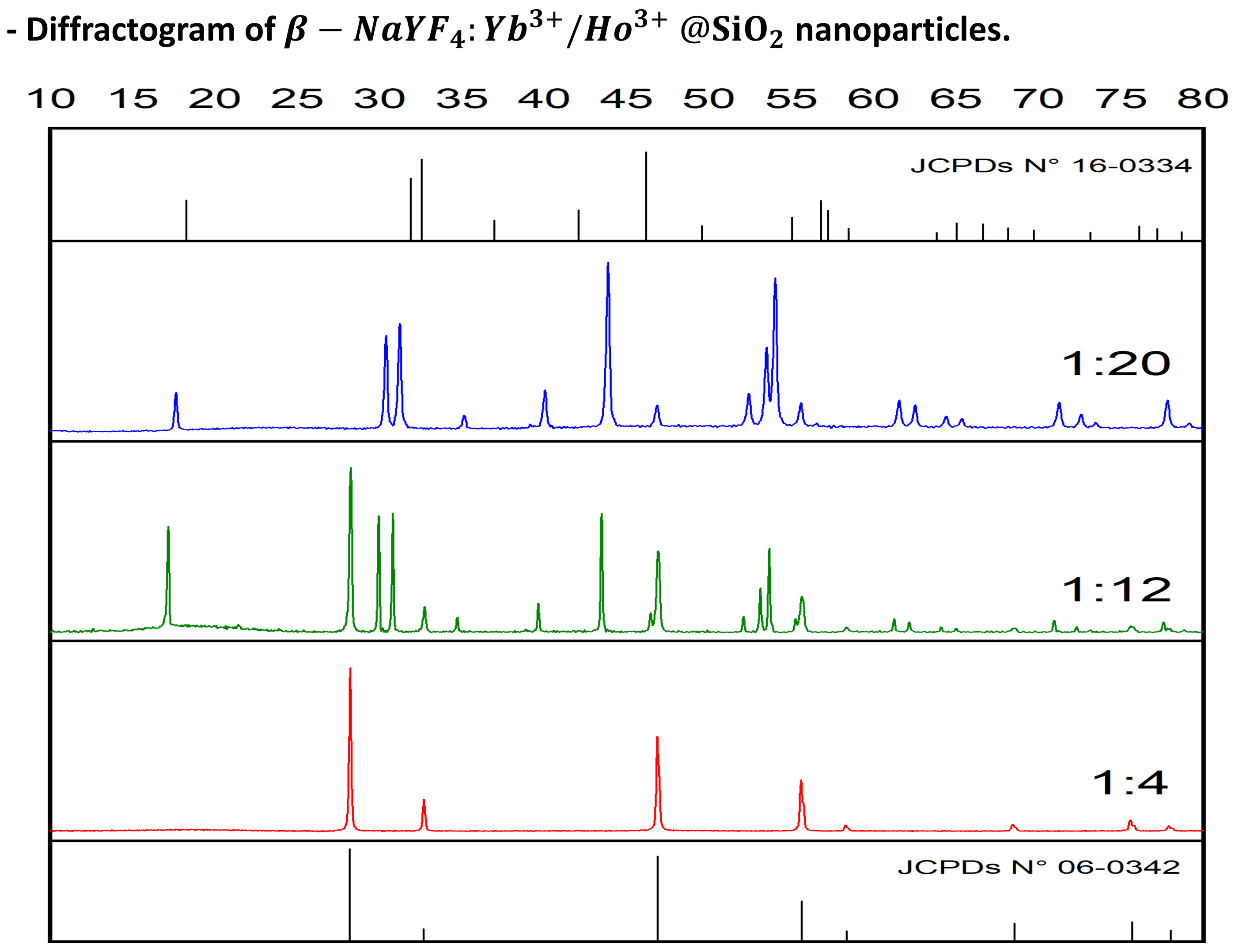

Figure 4. X-ray diagram of the $NaYF_4$ sample doped with Yb and Ho and coated with Silicon Oxide (SiO_2). With a ratio of 1: 4, 1:12 and 1:20 of Yttrium with respect to Fluorine.

- Emission spectra of the nanoparticles.

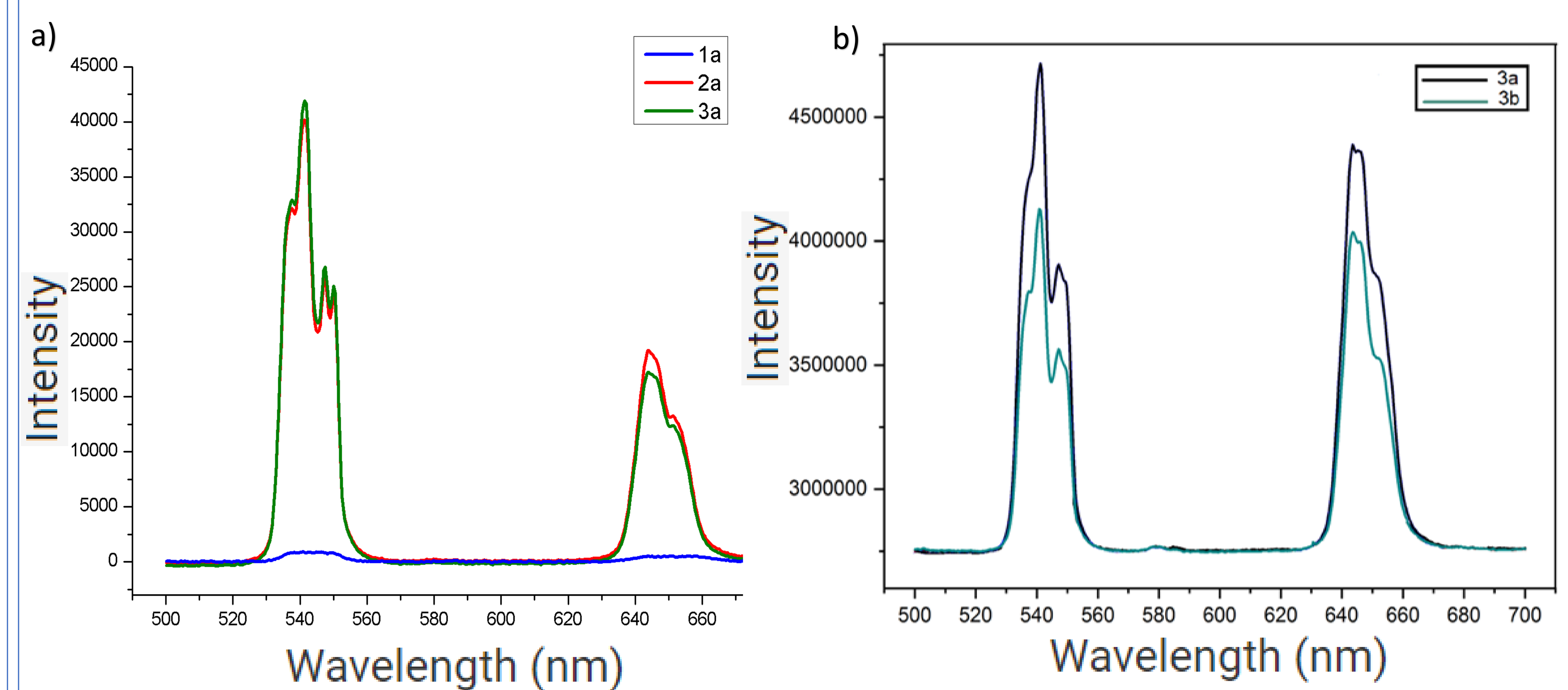

Figure 5. a) Upconversion spectrum; emissions in 541nm and 648nm of the nanoparticles with an increase in the proportions of Yttrium in 1: 4, 1:12 and 1:20 with respect to Fluorine. b) Comparison of the luminescence of the uncoated particles (3a) and nanoparticles coated with SiO_2 (3b).

- Transmission electron microscopy (TEM

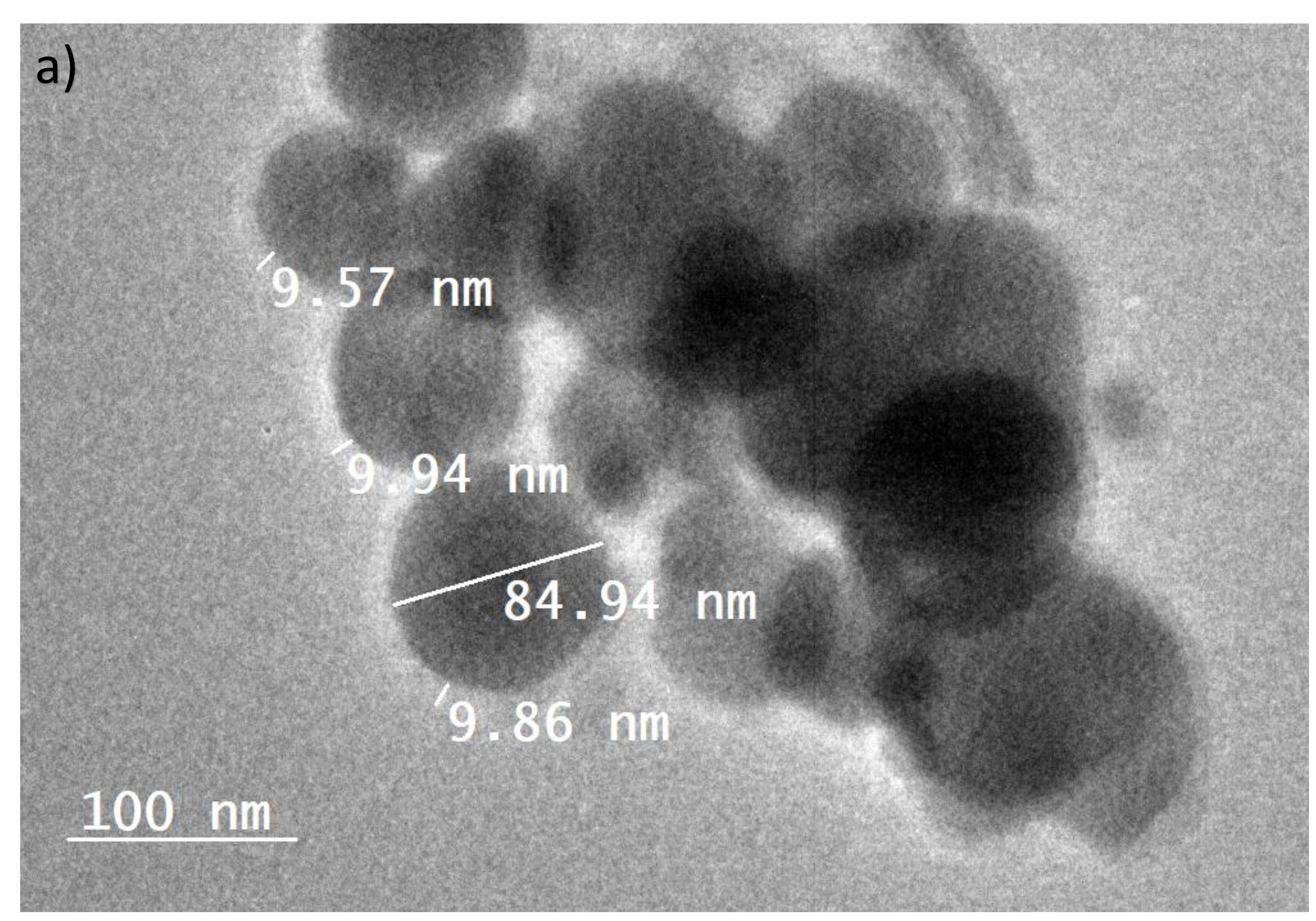

Figure 6. a) Transmission electron microscopy (TEM) of the nanoparticles coated with silicon oxide (SiO_2).

CONCLUSIONES

The results obtained show that it was possible to synthesize nanoparticles of $NaYF_4{:}Yb/Ho@SiO_2$ with a mixture of cubic and hexagonal phases. According to PDF # 01-071-5985 and PDF # 16-0334, there are cubic nanoparticles when the proportion of Yttrium is 4: 1 with respect to Fluorine and when the amount of Fluorine is increased, nanoparticles with hexagonal structure are obtained.
Compared with previous works, the emission at wavelengths 549nm and 648nm increased considerably. The coated nanoparticles show a decrease in luminescence intensity. From the TEM images it can be noted that we obtained nanoparticles with a size of approx. 80 nm. with a coating of 10 nm approx. by SiO_2.

AGRADECIMIENTOS

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BIBLIOGRAPHY

[1] Eliseeva, Svetlana. (2015). Luminescence of Lanthanide Ions in Coordination Compounds and Nanomaterials. DOI: 10.1002/ange.201504040.
[2] J. Dong, Y. Liu, J. (2019) Monodisperse $Na_{0.39}Y_{0.61}F_{2.35}{:}Ln^{3+}$ (Ln=Dy, Tb, Eu) and $NaYF_4$ nano-/micromaterials: Controllable morphology, porous structure, tunable multicolor and energy transfer. Journal of Luminescence.
[4] X. Wang y Y. Li, "Monodisperse nanocrystals: general synthesis, assembly, and their applications," Chem. Commun., pp. 2901–2910, 2007. [En línea]. Disponible: http://dx.doi.org/10.1039/B700183E
[5] J. Shen, L.-D. Sun, y C.-H. Yan, "Luminescent rare earth nanomaterials for bioprobe applications," Dalton Trans., pp. 5687–5697, 2008. [En línea]. Disponible: http://dx.doi.org/10.1039/B805306E