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LUMINISCENT NANOTHERMOMETERS FOR AGRICULTURE APPLICATIONS

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ROVIRA i VIRGILI

Course: 2018-2019

Universitat Rovira i Virgili

7th June 2019

Contend

1.	Abstract	3
2.	Objective	3
3.	Introduction	4
4.	Theoretical foundations	5
4.1	KYb(WO ₄) ₂ material	5
4.2	Nanothermometry	5
4.2.1	Photoluminescence of Er ³⁺ and Yb ³⁺	5
4.2.2	Photoluminescent thermometers	7
4.3	Pechini method	9
4.4	X-ray diffraction of crystal powder	9
4.4.1	X-ray powder diffraction technique	9
4.4.2	Refinement of the unit cell parameters: Le Bail method	10
4.5	Transmission electron microscopy	11
4.6	Optical properties of the plants	12
5.	Experimental Part	13
5.1	Synthesis of Erbium doped KYb(WO ₄) ₂ nanocrystals by Pechini method	14
5.1.1	Experimental calculations	14
5.1.2	Experimental procedure	16
5.2	Characterization of the synthesis products	17
5.2.1	Crystalline phase identification	17
5.2.2	Unit cell refinement in 10 at. % Er: KYb(WO ₄) ₂ nanocrystals	17
5.2.3	Size distribution of the samples synthesized and coated	17
5.3	Photoluminescence	17
5.4	Study of growth and spectroscopy of the plants	20
5.4.1	Process of plants growth	20
5.4.2	Spectroscopic study of the plants	21
5.4.3	Coating of the nanoparticles and colloidal dispersion of the nanoparticles	21
5.4.4	Laser effect on the root plants	23
6.	Results and discussion	25
6.1	Crystalline phase identification of the synthesized samples	25
6.2	Particle size and size distribution	27
6.3	Photoluminescence	29
6.4	Photoluminescent thermometry in the 10 at.% Er: KYb(WO ₄) ₂	31
6.5	Optical properties of the plants	35
6.5.1	Laser effect on the plants	35
6.5.2	Photoluminescence study of lentil roots	36
7	Conclusions	38
8	Bibliography	39
9	Annex 1	41

1. Abstract

The final objective of this work is to measure the internal temperature of a plant by using the thermometric photoluminescence properties of the Erbium doped $\text{KYb}(\text{WO}_4)_2$ nanocrystals. The synthesis of the nanocrystals is performed by the modified Pechini method. An X-ray powder analysis and a Le Bail refinement have been realized to obtain structural information of the prepared nanocrystals. Also transmission electron microscopy has been performed to obtain the particle size and size distribution of the obtained samples. Furthermore, a spectroscopic characterization of different quantities of Er^{3+} doping has been performed in order to study the sample with major visible intensity in order to be used as a temperature photoluminescence sensor. To end, also an optical spectroscopic study was realized of the roots from the plants that were previously watered with a nanocrystal water dispersion.

Resum:

L'objectiu del treball es l'estudi de la temperatura interna de plantes mitjançant propietats termomètriques de nanopartícules de $\text{KYb}(\text{WO}_4)_2$ dopades amb Erbi. La síntesis d'aquestes nanopartícules, s'ha realitzat seguint el mètode de Pechini, àmpliament estudiat pel grup FiCMA-FiCNA. S'han realitzat anàlisis de Raig X i un refinament seguint el mètode de Le Bail, per obtenir propietats estructurals de les mostres. Apart es va realitzar un anàlisis de microscòpia electrònica de transició per a veure la mida de partícula i la seva distribució. Posteriorment un estudi espectroscòpic de diferents dopatges d'Erbí, va ser realitzat amb l'objectiu de decidir-ne el millor per a ser utilitzat com a termòmetre intern. Finalment, un altre estudi espectroscòpic, però en aquest cas amb arrels de plantes, prèviament regades amb nanopartícules dissoltes en solució, va ésser realitzat amb l'objectiu de veure si les partícules presenten emissió a l'interior de l'arrel.

2. Objective

The objective of this project is to study if the incorporation of Erbium doped $\text{KYb}(\text{WO}_4)_2$ nanocrystals inside a root of plant, allows us to measure the internal temperature of the plant by using the thermometric photoluminescence properties of the nanoparticles. For this purpose, an intermediate milestone of the project will be the optimization of the Erbium doping percentage in order to obtain a maximum green emission from the nanoparticles, synthesized by Pechini method and characterize their performance as fluorescent thermometer.

3. Introduction

The study of nanoparticles is an upcoming field of work given that they have a larger quantity of atoms in their surface when compared with the actual volume of the nanoparticles. This point makes that nanoparticles have unique chemical and physical properties that depends on their composition and size. Recent studies had started to propose the nanoparticles as a temperature sensor, and the study of this will be the project focal point ^[21,22].

In this project the method that will be applied for the synthesis of the nanoparticles of Erbium doped $\text{KYb}(\text{WO}_4)_2$ is the Pechini method, which is based on Sol-gel method for actual synthesis Inorganic powders, and also was broadly studied in the FiCMA-FiCNA research group ^[1]. The method is based on the production of a polymeric resin where metallic ions are distributed homogeneously, followed by calcinations of this polymeric resin at high temperatures, which provokes the break of the network and then, as a result the nanoparticles are produced ^[13]. The samples synthesized will be doped with Erbium,

For the samples produced a study of their crystalline phase and their size will be performed, in order to see if the variation on dopant concentration has any effect on the nanoparticle itself.

Further spectroscopic studies will be realized in order to see which sample has the better emission intensity in the green part of the spectra. And for the sample chosen in the previous process, a study of the optical photoluminescence of the sample at the biological temperature range will be performed. This has the objective to calculate the fluorescence intensity ratio, which will be used as indicator of the temperature of the sample ^[4].

From the variation of the visible photoluminescence with different excitation densities and different temperatures, and applying the fluorescence intensity ratio approach, the temperature calibration will be performed.

This temperature sensing approach will be applied for the measurement of the internal temperature of the plants, more specifically in the roots of the plants. The interest on the root of the plants, is related with the future possibility of this approach to be used in hydroponic crops, which could be temperature monitored with the help of nanoparticles. Lentils plants will be watered with the nanoparticles and a study of their spectroscopic emission will be performed in order to see if this could be a real application.

4. Theoretical foundations

4.1 KYb(WO₄)₂ material

The material synthesized and used in this project is KYb(WO₄)₂, which was previously studied on the FiCMA-FiCNA ^[3], their crystallographic information can be seen in the table 4.1.

KYb(WO₄)₂ belongs to the family of compounds of double potassium rare earth tungstates, with the chemical formula KRE(WO₄)₂ (hereafter KREW, RE= Rare earth: Y and lanthanides elements). The room temperature crystalline phases of these compounds are isostructural, belonging to the monoclinic system, so these crystals show a large anisotropy in all their physical properties. Traditionally, from the early 70's, these compounds have been grown and studied for laser applications, due to their facility of incorporating the lanthanide ions in the structure (substituting the RE till 100% without any important crystalline phase distortion) and also, due to their interesting optical properties ^[3]. In the last decades, the traditional laser crystals have been also synthesised as nanocrystals, this was also the case of the KREW, which was done by first time in 2004 by Galcerán *et al.* ^[1]. As it is known, all spectroscopic parameters in the lanthanides are not affected by the reduction of the size of the host crystal due to the 4f electron shielding, so the main spectroscopic features of the lanthanide doped bulk single crystals are still valid in the Lanthanides doped nanocrystals. In the case of the project the host has been chosen as KYb(WO₄)₂, in which the lanthanide active ion Ytterbium forms part of the hosts, and will have various concentrations, given that the ion Ytterbium will be substituted in different percentages of atomic substitution for ion Erbium, which is commonly referred as doping.

Table 4.1 Crystallographic parameters for the KYbW material

Crystal Data		
Molecular mass		707, 84 g/mol
Crystallographic system		Monoclinic
Spatial group		C2/c
Cell parameters	a	10,590 Å
	b	10,290 Å
	c	7,478 Å
	β	130,70°

4.2 Nanothermometry

4.2.1 Photoluminescence of Er³⁺ and Yb³⁺

Photoluminescence is a physic phenomenon that is based on the emission of electromagnetic radiation, activated by a source of electromagnetic energy. The photoluminescence studied in this work is produced as a result from an up-conversion process. The absorption and emission processes studied are electronic transitions (dipole induced by the electromagnetic field of the light) of the electrons in the partially filled 4f of the lanthanide ions, Ln³⁺. These 4f internal electrons are shielded by the external filled electronic shells, 5s and 5p, so for this reason, these electronic levels are described as Russell Saunders levels belonging to a multielectron ion.

The up conversion process is based in the sequential absorption of two photons and its conversion to an emission of a one higher energy photon. In this case, The Yb^{3+} ion, acting as sensitizer absorbs the photons, and by an energy transfer process, it transfers the energy to the Er^{3+} ion, acting as emitter. The energy transfer process is from the $2\text{F}_{7/2}$ excited state of Yb^{3+} to the $4\text{I}_{11/2}$ excited state of Er^{3+} . The second energy transfer process allows the electrons to populate the excited states $2\text{H}_{11/2} + 4\text{S}_{3/2}$. The electronic transition from these two electronic states to the Erbium ground state, $4\text{I}_{15/2}$, gives place to the green visible emission.

The mechanism, seen in the following figure, of the process is that one ion works as a *sensitizer* (Yb^{3+}), receptor of the energy, and the other one as *emitter* (Er^{3+}) of the electromagnetic radiation ^[4].

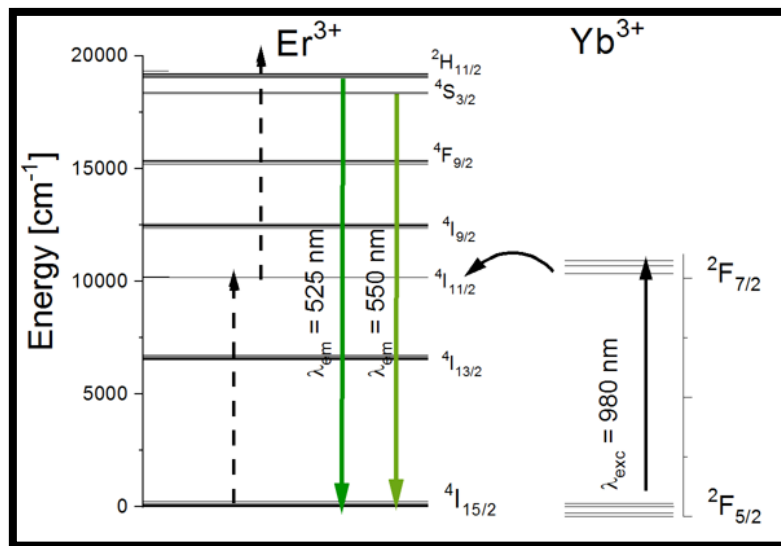


Figure 4.1 Scheme for up-conversion emission process of the Yb^{3+} to Er^{3+}

The Erbium electronic transitions that will be used in this work are the following:

Table 4.2 Electronic transitions for Er^{3+} ion

Erbium (Er^{3+})	Energy (cm^{-1})	Wavelength (nm)
$4\text{S}_{3/2} \rightarrow 4\text{I}_{15/2}$	18200	550
$2\text{H}_{11/2} \rightarrow 4\text{I}_{15/2}$	19300	525

4.2.2 Photoluminescent thermometers

The objective is to do an experimental measurement of the temperature from the luminescence. This measurement is done by recording the emissions from two different energy levels, which thermally coupled, ^[4].

First of all, we need to take into consideration the parameters that will allow us to obtain the temperature, using the expression:

$$\Delta = \frac{I_1}{I_2} \quad (4.1)$$

Where Δ , is the principal thermal parameter related to the two integrated intensities of both emissions (I_1 and I_2).

4.2.2.1 Thermal sensitivity

Thermal sensitivity shows the variations from Δ in regard to the variations of temperature, the common parameter for this is S_r , which is the relative sensitivity;

$$S_r = \frac{1}{\Delta} \left| \frac{\partial \Delta}{\partial T} \right| \quad (4.2)$$

This parameter is expressed in percentage of change and Kelvin (%/K). Also, this parameter is independent from the thermometer nature, this means we can do other measurements in different environments, without the need of recalculating the previous equation.

4.2.2.2 Rationalization of the thermal answer

The calculations are done based on the two different electronic transitions that will produce light and using the Boltzmann model for thermal equilibrium between the electronic population of the two emitting states.

4.2.2.3 Single-center emission. Boltzmann Law

At this point the focus is to talk about two levels on a thermal equilibrium, basically thermally coupled levels (TCL), the relation that we found between them, if the electronic populations, N_i , are used, is;

$$N_2 = N_1 \left(\frac{g_2}{g_1} \right) \exp \left(\frac{-\Delta E}{k_B T} \right) \quad (4.3)$$

In the equation (4.3), the “g” are the degenerations of the TCL, the ΔE is the energy gap between the two TCL. If we express the thermal parameter as the ratio of intensities between the emissions of these two TCL, as the transitions $2 \rightarrow 0$ and $1 \rightarrow 0$, being 2 and 1, the two excited thermally coupled levels and the 0 the ground state. Knowing that the intensity of any emission can be directly related to the electronic population of that level, multiplied by the $\hbar \omega_i A_i$, where A_i is the radiative transition rate. If we combine equation 4.3 with this expression of the intensity, this is used to obtain the equation of the thermometric parameter;

$$\Delta = \frac{I_2}{I_1} = \frac{\hbar \omega_2 A_2 N_2}{\hbar \omega_1 A_1 N_1} = B \exp\left(\frac{-\Delta E}{k_B T}\right) \quad (4.4)$$

$$\text{where } B = \frac{\omega_2 A_2 g_2}{\omega_1 A_1 g_1}$$

That expression will be correct when the two TCL have a $\Delta E > 2000 \text{ cm}^{-1}$.

The answers from the detector are related to the intensities of the levels and the extrapolation of the temperature will be given by;

$$T = \frac{\Delta E}{k_B \ln\left(\frac{B}{\Delta}\right)} \quad (4.5)$$

At an experimental level the B constant can be determined, this is by representing the Δ vs the pump power of the laser. The value of the Δ obtained at no-laser excitation, is Δ_0 . After that the B was computed by using the equation 4.5, with the condition of $T = 300 \text{ K}$ and $\Delta = \Delta_0$.

4.2.2.4 Relative sensitivity in UNCP

The thermal behavior can be predicted before the synthesis of nanoparticles that are single emitting center, the quantification is done from the relative sensitivity that is obtained from the emission intensities (combining eq. 4.2 and 4.4), knowing previously the ΔE ;

$$S_r = \frac{\Delta E}{k_B T^2} \quad (4.6)$$

We find the uncertainty of the temperature as;

$$\delta T = \frac{k_B T^2}{\Delta E} \frac{\delta \Delta}{\Delta} \quad (4.7)$$

In our work, the interest is focused in the TCL in a single center. The ion responsible as single center is the Er^{3+} . The thermally coupled levels are its pair of excited levels, $^2\text{H}_{11/2}$ & $^4\text{S}_{3/2}$, that they usually have an electronic gap around 800 cm^{-1} , which it allows to populate the energy levels $^2\text{H}_{11/2}$ from the $^4\text{S}_{3/2}$ as a result from the energetic proximity.

4.3 Pechini method

The method for synthesizing the nanocrystals that is going to be used in this project is based on sol-gel methods, those are routes for synthesize inorganic powders at low temperatures^[14]. The method is called Pechini, developed and patented by M. Pechini in the year 1967^[13]. A variation of the original method, developed by Montserrat Galcerán in the FiCMA & FiCNA group^[1], will be the route chosen for the obtaining of nanoparticles.

The synthesis of nanoparticles by the Pechini method, starts by producing the sol, which is done by dissolving metal ion complexes in organic solvent, after that an hidrolization is required in order to obtain a colloidal metal oxide/hydroxide precipitate. Experimentally this is done by complexing the dissolved reactants (in water) with Ethylenediamine (EDTA) and after that adding Polyethileneglycol (PEG). By heating the solution, it will get denser, as result of the formation of a polymeric gel that is obtained from the reaction of Fischer esterification, between the EDTA and the PEG. Resulting in a gel, in which the metal ions are complexed by the carboxylic groups of the EDTA, as well as the solvent that remains retained in the polymer. A second and higher heating will allow the polymer to break and the solvent to evaporate, also allowing the inorganic powder to crystalize.

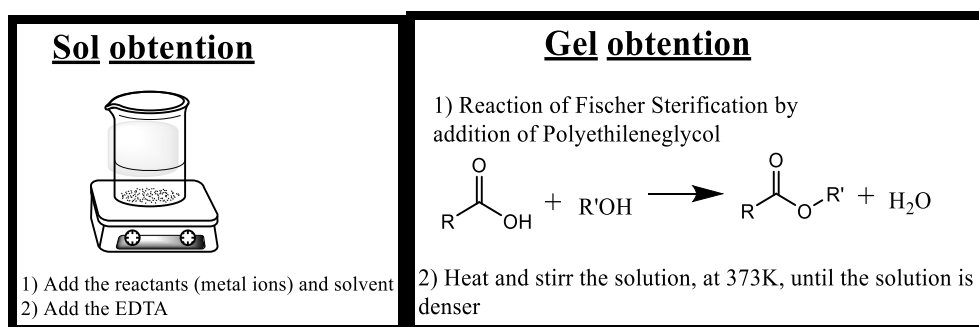


Figure 4.2 Scheme of both process in the Pechini method

4.4 X-ray diffraction of crystal powder

4.4.1 X-ray powder diffraction technique

By definition, the X-ray are an electromagnetic radiation but his principal characteristic is that their direction and course of propagation is based on a wave vector, commonly known as $\vec{K}$. The characteristic wavelength is in the range between $0.1 < \lambda < 10 \text{ \AA}$. W. L. Bragg demonstrated that even the X-ray where diffracted by the crystals, their behavior was as if they were reflected by plans of the crystal. Bragg based his theory on the information that can be obtained of the direction of the rays diffracted by the family of crystallographic planes (hkl), from the reciprocal network^[6]. This can only be obtained in the systems that meet the conditions of Bragg Law, named after his developer.

$$n\lambda = 2d_{hkl} \cdot \sin\theta \quad (4.8)$$

In the equation, n is a natural number, λ is the wavelength of the incident X-ray, d is the distance between parallel planes and θ is the angle of incidence.

The intensity of the diffracted rays, will be the source of information for the atom positions and also for the structure of the material, as can be seen in the following equation:

$$I(hkl) = k|F_{hkl}|^2 \quad (4.9)$$

In the last equation, the important factor is the F_{hkl} , named structure factor, because it depends on the atomic positions. If we take into consideration that the atom is not in a stable position, meaning that has a thermal agitation in the environment position $\vec{r}_j$ with a probability of vibration u equal to $P(u)$, the structural factor can be expressed as:

$$F_{hkl} = \sum_{j=1} f_j \cdot \exp[2\pi i(hx_j + ky_j + lz_j)] \quad (4.10)$$

In the previous equation:

- f_j : is the diffusion atomic factor.
- x_j, y_j, z_j : are the coordinates for the atomic positions.

The experimental data from the X-ray diffraction of the crystalline powder is represented in the diffractograms, in which the diffraction peaks are characterized for its position (2θ) and its intensity ($I_{(hkl)}$). The experimental results will be compared to JCPDS files, which are obtained from the ICDD (International Centre for Diffraction Data) data base [9], as result identifying the crystalline structure for the experimental synthesized sample.

4.4.2 Refinement of the unit cell parameters: Le Bail method

The Le Bail method is a mathematical adjustment technique for characterization of crystalline material structure, these refers to both cell parameters and atomic position. In our work, we have used the Le bail method only for refining the unit cell parameters of the selected nanocrystals. The method uses the observed intensities (I_{hkl}) from powder diffraction data [12]. These I_{hkl} , observed are extracted from the powder pattern by a profile fitting procedure which does not need any previous structural model but constrains the angular position of the diffraction peaks to be consistent with the cell parameters. Le Bail analysis fits parameters such as the unit-cell parameters, the instrumental zero error, peak width parameters, and peak shape parameters.

Le Bail method calculation starts with given parameters and then with an iteration process finds the experimental unit cell parameters. As any fitting process, there are several parameters to quantify the goodness of the fitting. In this case, the parameters used is the R_p , which should be as small as possible. The R_p factor refers to profile of the crystal, expressed as.

$$R_p = \frac{\sum_i |y_i(2\theta_i) - y_{ci}(2\theta_i)|}{\sum_i y_i(2\theta_i)} \quad (4.11)$$

In the previous equation:

- y_i : numerical values for intensity observed in the sample
- y_{ci} : numerical values for calculated intensity

Crystallite size calculation

Using the X ray powder patterns, it is possible to give an estimation of the crystallite size based on the Scherrer equation ^[23]. This Scherrer equation related the broadening of the X ray diffraction peaks with the reduction of the size of the crystallites. The expression is: $\tau = \frac{\lambda}{\beta \cos \theta}$, where λ is wavelength, θ is half angle, β is Full width at half maximum (FWHM) of the peak.

The Le Bail method for the cell refinement is used by the software DIFRACC^{plus} TOPAS property of Bruker, ^[12].

4.5 Transmission electron microscopy

The transmission electron microscopy is characterization technique used for the determination of some properties of nanoparticles, the recurrent ones are the size and the distribution and homogeneity of the sample.

The microscope, figure, is analog of the conventional light microscope instead of using the photons of the light, it is used a beam of electrons. The electron beam, is characterized by a voltage, which the values can go from 100KeV to 1MeV (using an electron beam light). In the microscope, high energy electrons are generated in a vacuum environment by using a bigger potential difference. The electron beam is condensed by a lens system and oriented to the sample, which interacts with it resulting in diffractions or absorbed, producing a bigger version of the sample to appear on a fluorescent screen ^[8].



Figure 4.3 JEOL-JEM-1011

The resolution of the imaging is enhanced by the high voltage. The vacuum environment is to make sure that none other molecules (such as air) can interfere with the sample. And the only requirement of the technique is that the sample needs to be very thin, this is the reason why is mostly used on nanoparticles.

For the result interpretations a free software, Image J, ^[25] will be used in order to determine both size and size distribution of the nanoparticles.

4.6 Optical properties of the plants

It has been said that the objective of study will be plants, and the roots as the part of it that is chosen. To select it, it has to be considered the way the plant will absorb the nanoparticles, and taken into account that they are dissolved in water, the roots will be the focus point of study given that are the part of the plant, that absorb the nutrients. Furthermore, applications from this should be able to be incorporated in hydroponic crops given that the roots won't be underground, and the lecture of the emission could be possible.

Opposite to per example the leaves, where multiple reflectance techniques have been developed in order to study physical parameters for leaves ^[7,17], few studies have been reported for the roots.

Following the studies carried out in the papers previously mentioned. The infrared reflectivity of the leaves appears to be caused by the internal cellular structure. The IR radiation is diffused and scattered in the internal parts of leaf where undergoes multiple reflections and refractions, in which some parts such as cellulose wall parts will give more reflectivity.

Pigments like chlorophylls ^[7], are invisible in the NIR part of the spectrum ^[17], and have a high level of absorption in the visible part of the spectra. As can be seen in the following figures, these can interfere with the purpose of the project, given that absorption peaks are seen in the zone of the green (550 nm);

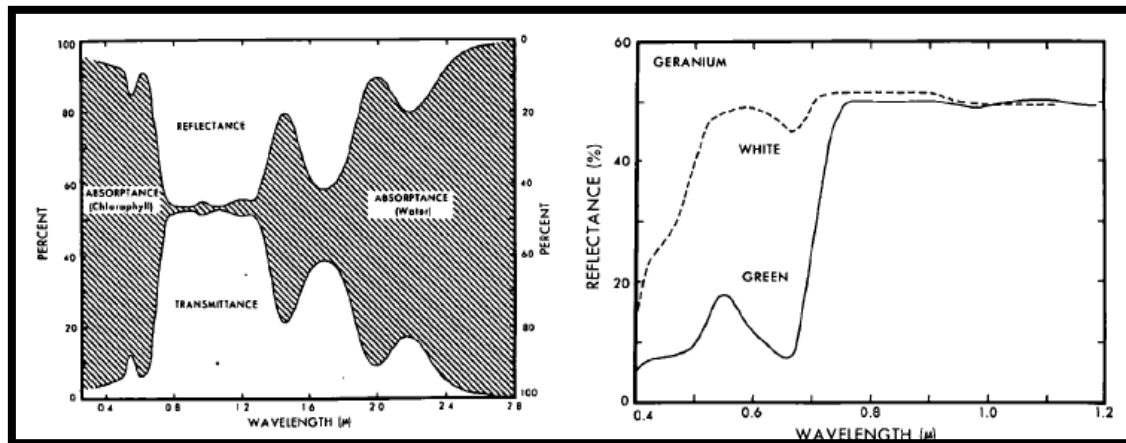


Figure 4.4 Representation of T Vs R from Gates et al., 1965

5. Experimental Part

The method used for the synthesis of nanoparticles is the Pechini as previously mentioned. The material used was proportioned by FiCMA & FiCNA research group. The materials and equipment used were: quartz crucibles, furnace muffle type, and heating plates. More detailed explanation is given in the synthesis section. The used reactants are listed in the following table 5.1.

The characterization of the samples obtained, was mostly done by using an X-ray Siemens EM-10110BU D-5000 diffractometer, with Bragg-Brentano configuration, as well as transmission electron microscope (TEM), JEOL-JEM-1011 model. Both equipment's are situated in the "Servei de Recursos científics i Tècnics" of the URV.

For physic parameters of the plants, such as transmittance, spectrophotometer CARY 5000 was used.

For the optical spectroscopic characterization, two different set-up were used, for studying the nanoparticles and the roots watered with nanoparticles. For the nanoparticles, the set-up used was the photoluminescence (PL) microscope, as well as a diode laser Lumics D560 400W and $\lambda=980$ nm as excitation source, and heating stage with his respective controller Linkam THMS 600. The detectors used were Spectrum Analyser AQ6373 specific for visible range of the spectra and an Ocean view detector^[2].

For the plant roots, the parts of the set-up were similar, but the photoluminescence microscope was not used, given that the fact that the highly focused laser beam present in the PL microscope could easily burn the roots, so these measurements were done by direct excitation of the laser without focusing, as can be seen in figure 5.7.

Table 5.1 Toxicological information from reactants used in the project

Reactants for Pechini synthesis		
Reactants	Chemical formula	Toxicological information
Ammonium Para tungstate	$(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41}$	 Irritant
Potassium carbonate	K_2CO_3	 Irritant
Ytterbium Nitrate	$\text{Yb}(\text{NO}_3)_3$	 Irritant

Erbium Nitrate	$\text{Er}(\text{NO}_3)_3$	 Irritant, corrosive and flammable
Ethylenediamine	$\text{C}_2\text{H}_8\text{N}_2$	 Irritant
Polyethyleneglycol	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$	 Irritant
(3-aminopropyl) triethoxysilane	$\text{C}_9\text{H}_{23}\text{NO}_3\text{Si}$	 Irritant

5.1 Synthesis of Erbium doped $\text{KYb}(\text{WO}_4)_2$ nanocrystals by Pechini method

5.1.1 Experimental calculations

The synthesis of Erbium doped $\text{KYb}(\text{WO}_4)_2$ is done starting with the powders of the different reactants, the initial quantities were obtained with following calculations, in this case to obtain 2 g of 3 at % $\text{Er:KYb}(\text{WO}_4)_2$;

$$\begin{aligned}
 2 \text{ g } 3 \text{ at. \% Er: KYb}(\text{WO}_4)_2 &\times \frac{1 \text{ mol } 3 \text{ at \% Er: KYb}(\text{WO}_4)_2}{707,56 \text{ g}} \\
 &\times \frac{1 \text{ mol } \text{K}_2\text{CO}_3}{2 \text{ mol } 3 \text{ at. \% Er: KYb}(\text{WO}_4)_2} \times \frac{138,205 \text{ g}}{1 \text{ mol } \text{K}_2\text{CO}_3} \times \frac{100 \text{ g pure}}{99,9 \text{ g pure}} \\
 &= 0,1956 \text{ g } \text{K}_2\text{CO}_3
 \end{aligned}$$

The molar mass of the product is not always the same, this is due to the doping variations of the different products to be synthesized, so because of that, the calculations of the reactants will be different for each Erbium doping value. The following calculations are for the product doped with 25 at. % of Erbium;

$$\begin{aligned}
 \text{Molar mass } 25 \text{ at. \% Er KYb}(\text{WO}_4)_2 &= \text{MM Yb} * 0,75 + \text{MM Er} * 0,25 + \text{MM K} + \text{MM W}_2\text{O}_8 \\
 &= 173,05 \frac{\text{g}}{\text{mol}} * 0,75 + 162,26 \frac{\text{g}}{\text{mol}} * 0,25 + 39,1 \frac{\text{g}}{\text{mol}} + 495,68 \frac{\text{g}}{\text{mol}} \\
 &= 705,13 \frac{\text{g}}{\text{mol}}
 \end{aligned}$$

All of the other reactant quantities were obtained by doing similar calculations and taking into account all of the stoichiometry relations shown in the bibliography ^[1]. The results for all of the doping are;

Table 5.2 Reactant weight for first step of the synthesis

Reactants	Grams of reactant depend on product					
	1 at. % Er;KYbW	3 at. % Er;KYbW	5 at. % Er;KYbW	10 at. % Er;KYbW	25 at. % Er;KYbW	50 at. % Er;KYbW
K₂CO₃	0,1955	0,1956	0,1956	0,1957	0,1961	0,1969
(NH₄)₁₀W₁₂O₄₁	1,4558	1,4567	1,4567	1,4578	1,4611	1,4667
Yb(NO₃)₃	1,2565	1,2319	1,2065	1,1438	0,9554	0,6394
Er(NO₃)₃	0,0125	0,0376	0,0627	0,1254	0,3144	0,6312

The next step of the procedure is to form a chelate of the metal and the complex. The complex reactant is the EDTA; this is because it has a more acid capacity than for example citric acid that was used previously in that type of synthesis. For the calculations of this reactant, it is needed to take into account the stoichiometry, in this case is CM = [CA]/[Metal] = 1, as described in ^[1]. Example with 3 at % of Erbium;

$$2 \text{ g } KYb(WO_4)_2 \times \frac{1 \text{ mol } KYb(WO_4)_2}{707,56 \text{ g}} \times \frac{1 \text{ mol } EDTA}{1 \text{ mol } KYb(WO_4)_2} \times \frac{292,24 \text{ g } EDTA}{1 \text{ mol } EDTA} = 1,6527 \text{ g } EDTA$$

As seen in the previous step, the quantity of reactant is different for every doping;

Table 5.3 EDTA weights for the complexation

Reactants	Grams of reactant					
	1 at. % Er;KYbW	3 at. % Er;KYbW	5 at. % Er;KYbW	10 at. % Er;KYbW	25 at. % Er;KYbW	50 at. % Er;KYbW
EDTA	1,6517	1,6527	1,6527	1,6539	1,6577	1,6642

The last step before the calcination, is to do an esterification, and with the objective of doing that the reactant used is Polyethileneglycol (PEG), the stoichiometry of this step is CE = [CA]/[PEG] = 2 ^[1], and so the calculations for this reactant are;

$$2 \text{ g } KYb(WO_4)_2 \times \frac{1 \text{ mol } KYb(WO_4)_2}{707,56 \text{ g}} \times \frac{2 \text{ mol } EG}{1 \text{ mol } KYb(WO_4)_2} \times \frac{62,07 \text{ g}}{1 \text{ mol } PEG} \times \frac{1,11 \text{ mL } EG}{1 \text{ g } PEG} = 0,63 \text{ mL}$$

In this case the variations of the quantity to be used of this reactant among the different synthesis for different doping is minimum, and because the addition of PEG is with a 2 mL pipette, in all the cases the quantity added was the same.

5.1.2 Experimental procedure

The following description is for the case in which the product to be obtained was 2 g of $\text{KYb}(\text{WO}_4)_2$ [3] doped with 3 at. % Erbium [5]. The first step was to weight the reactants; 0,1956 g of K_2CO_3 , 1,4567 g of $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41}$, 1,2319 g of $\text{Yb}(\text{NO}_3)_3$ and lastly 0,0376 g of $\text{Er}(\text{NO}_3)_3$.

All of them, and deionized water, will be add in a quartz crucible and then dissolved by magnetic stirring with help of heat supplied by a heating plate and a magnet, as can be seen in the figure 5.1.A.

In a beaker the 1, 6527 g of EDTA were dissolved, the same way as the other reactants, and then added to original crucible. The next step was to add the Polyethileneglycol (PEG), more precisely 1, 6 mL with help of a 2 mL pipette and a rubber bulb. When all of the reactants are in the crucible, a heating process at the temperature around 373 K, as seen in the figure 5.1.B, is done in order to evaporate the water (solvent) and obtaining a denser solution, which is the gel.

For the last steps, the crucible will be introduced in a muffle type furnace in order to do the calcinations. The first one, is a pre-calcination under a temperature of 573 K during 3 h, the objective is to decompose the organic phase of the gel, figure 5.1.D. Then the sample is cooled to ambient temperature and introduced in the muffle type furnace for the last step. A calcination of 5 h and 973 K, will allow us to obtain the nanoparticles, figure 5.1.E, for then end, cool it and put it in a container for conservation.

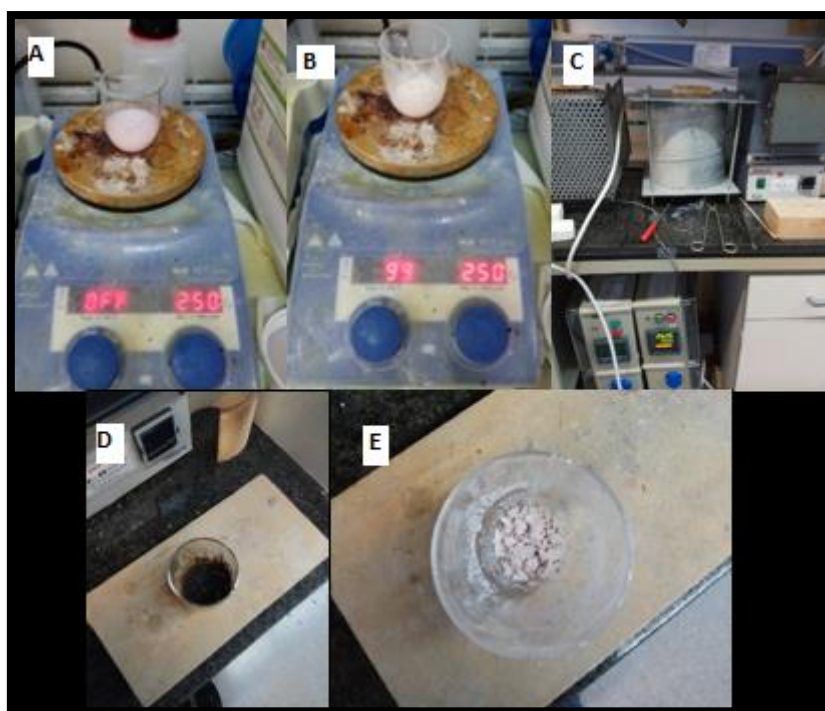


Figure 5.1. Synthesis steps for Pechini Method. A, B, C, D.

5.2 Characterization of the synthesis products

5.2.1 Crystalline phase identification

The samples that were previously synthesized by doing the modified Pechini method were then identified by X-ray powder diffraction. The equipment used was Siemens D-5000 diffractometer. The diffractogram was taken from theta angle 5 until 70, step units 0, 5°, time step 3 s.

The obtained diffractograms were compared with the reference diffractogram patterns that can be found in the International center for Diffraction Data (ICDD) data base. The software DIFRACC.EVA, property of Bruker, allows us to compare the diffractogram of our experimental sample with another one, that matches with the experimental and that can be found in the ICDD data base [9].

5.2.2 Unit cell refinement in 10 at. % Er: KYb (WO₄)₂ nanocrystals

For the sample that showed the best emission, X-ray analysis with other experimental parameters was performed. In this case it's the step size was smaller, 0.02° and the time was 16 s, in order to have a more defined peaks and better signal/noise ratio.

The refinement of the cell parameters was performed by the software DIFFRAC^{plus}.TOPAS, the calculations realized were based on the Le Bail method [ref]. The initial structural parameters used to start the iteration calculations were based in crystallographic structural information of the KYb(WO₄)₂ single crystal [9].

5.2.3 Size distribution of the samples synthesized and coated

For all of the samples, an analysis with TEM was performed. The objective was to determine the size of the crystalline grain and also their distribution. The instrumental used is the one mentioned in. The samples were prepared as: a small quantity of sample is taken with a scoopula and then put in a vial, which will be filled up with ethanol. Then introduced in the ultrasounds for 15 minutes. Afterwards, with a micropipette 1 mL of this liquid dispersion of the sample is put in a cooper grid. The prepared copper grids, with the samples evaporated are introduced in the sample holder of the TEM microscope.

5.3 Photoluminescence

The study of the photoluminescence of the samples was done using two different two set-ups. With the first one (shown in figure 5.2.A) the objective was to collect the emission from all the different samples to be measured in equal conditions using an integrating sphere in order to identify which sample shows the highest visible emission. The second set-up, shown from the figure 5.3.B consists in a photoluminescence microscope used to study under different temperatures and different excitation intensity, the variation of the emission spectra, with further purpose of calculating the Δ . (In Annex 1, a conversion table for the intensity used in the laser header to the laser power is given).

Both set-ups, as well as the devices used, were placed in the optics laboratory from the FiCMA-FiCNA group.

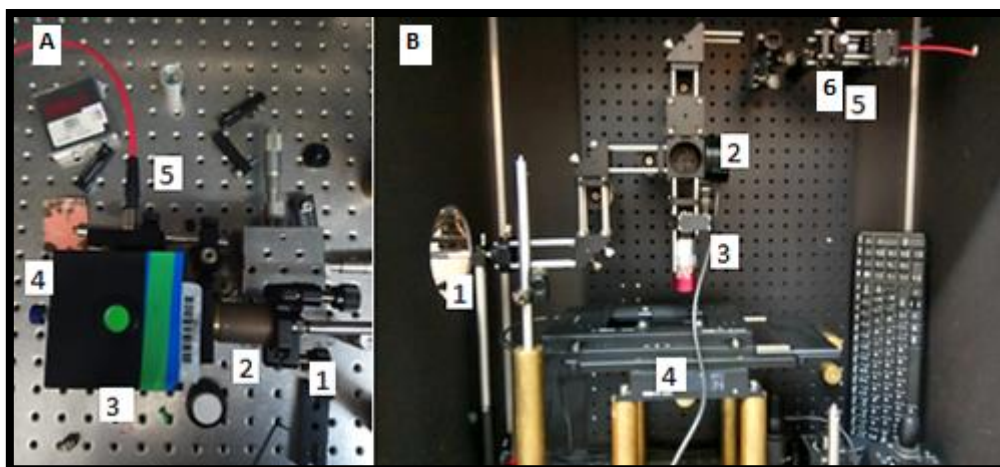


Figure 5.2 a) 1: laser, 2: collimator, 3: integrating sphere, 4: sample holder, 5: Optical fibre Connected to detector.
b) 1: laser optic fibre, 2: dichroic mirror, 3: objective 10x, 4: support, 5: optic fibre Connected to detector, 6: short-pass filter

Table 5.4 Devices specifications for Figure 5.2

Figure 5.2.a 1st set-up		Figure 5.2.b 2on Microlum set-up	
Devices	Specifications	Devices	Specifications
Excitation source	Lumics diode laser D560 400W 975 nm	Excitation source	Lumics diode laser D560 400W 975 nm
Laser optic fiber	HI-1060, corning	Laser optic fiber	HI-1060, corning
Laser display	Lumics diode controller	Laser display	Lumics diode controller
Collimator	TC25APC-980	Dichroic mirror	Edmund Optics Barrington Dichroic short pass 750 nm
Detector	Oceanview Sony LX511B	Objective	10 X
Detector optic fiber	Thorlabs FT038 core 600 nm	Short pass filter	Thorlabs, short pass filter cut-off 750 nm
Chiller	Coherent	Detector	Yokogawa, Optical Spectrum Analyzer AQ6373
		Detector optical fiber	Thorlabs FT038 core 600 nm
		Chiller	Coherent

For the first set-up, all of the samples previously synthetized were introduced in a vial and then placed in the holder, with the objective of obtaining their emission spectrum. In all of the cases the laser was working at 15 A. The detector used in this case was the OceanView. The spectra were obtained with 400 ms of time acquisition for each nanometer.

The photoluminescence dependence with temperature and excitation laser power for the 10 at.% Er:KYb(WO₄)₂ nanocrystals was performed in the set-up figure 5.3. b. Given that the sample was a crystalline powder, as support a platina was used, specifically Linkam THMS 600.

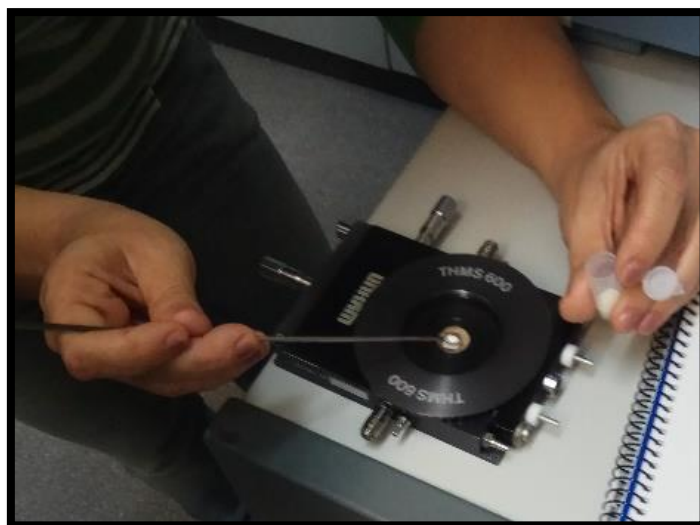


Figure 5.3. Linkam THMS 600 platina and collocation of the sample for the measurement.

For the measurements of the variation of the emission in relation to the excitation laser power, the laser intensity range was 12,5 A to 17,5 A. The spectra were obtained in intervals of 0.5 A. As the up conversion process is a non-linear process, there's an excitation power laser threshold in which it is activated. In our case, none up conversion visible emission could be seen until the excitation laser power is 12 A.

For the photoluminescence dependence with temperature, two temperature ranges were selected. The first one was from 300 K to 340 K and the spectra were obtained every 5 K, this had the purpose to see the behavior of the nanoparticles in a biological temperature range ^[11]. Furthermore, measures were done at a second temperature range from: 340 K until 440 K ^{18]}, with temperature increase steps of 20 K.

The sample was located in the Linkam THMS platina, allowed to do the temperature measurements with the respective temperature controller, Linkam TP92.

The detector in this case was the Optical Spectrum analyzer AQ6373, produced by Yokogawa. The optimized measurement parameters of use for this detector and our samples are shown in the table 5.5.

Also needs to take into account that both detectors and all of the samples their range of work is in the visible range of the spectra, and so for this reason the measurements were all done without any focus of light.

Table 5.5 Parameters of use for the OSA AQ6373

Conditions of measurement	
Sensitivity Mode	HIGH 2
Starting Wavelength	480 nm
Ending Wavelength	575 nm
Middle Wavelength	530 nm
Resolution	2 nm
Integrating time	25 s
Integration points	400
Integration interval	0,238 nm

5.4 Study of growth and spectroscopy of the plants

5.4.1 Process of plants growth

For the final purpose of the project, which is the study of nanoparticles inside a plant. A selection of a type of plant and the growth of itself was needed. Taken that the project had limitations of time and the objective of implantation is, per example hydroponic crops, the option was to grow an angiosperm type given that those types of plants are the most diverse group and can easily grow in any type of crop. Due to the time restriction, a plant that could easily grow their roots (part of study), in a time period between one or two weeks, was the ideal choice. Taken into account all this; the final choice was lentil plants.

The growth of the lentil plants was performed using a plastic glass as a container with cotton. First, lentils were put in between cotton surfaces that were previously humidified with water. For the following week the cotton was watered with 3 mL of water every three days, this was done with a syringe for control purposes, with the objective of only maintaining the humid environment. After this time, a eclosion of the lentils could be seen, as well as the first roots, in that moment the top surface of cotton was extracted, to let the plants easily grow and also the quantity of water was augmented to 5 mL and watered every two days. The last step of the process was repeated until nanoparticle colloidal suspension were used to water the lentil plants.



Figure 5.4. Photographs showing the different sequential steps of the growth process of the lentil plants in various days.

5.4.2 Spectroscopic study of the plants

The focus point of all following experimentations is to determine, physical properties of the plants itself, more specifically the transmittance or reflectance. Specifically, which is the optical behaviour of the plants in the excitation wavelength region and also, in the green visible part of the spectrum.

The optical measurements were done in the Cary 5000, a spectrophotometer of high performance in the UV-Vis-NIR spectrum, more exactly in the range of 175-3300 nm. Also, mention that is controlled with a computer software, WinUV, which produces graphics for different physical properties, including reflectance and transmittance.

The experimental procedure, was to cut the roots from the plants in half, with help of a knife, in order to have an homogeneous surface, given that if the surface is not flat the possible diffused reflectance's won't be optimal. The plant sample would cover all the central hole aperture of the sample holder of the spectrophotometer, shown in fig 5.5.C. This is because in order to obtain good results all of hole needs to be full, and with a single root alone, this can't be achieved.

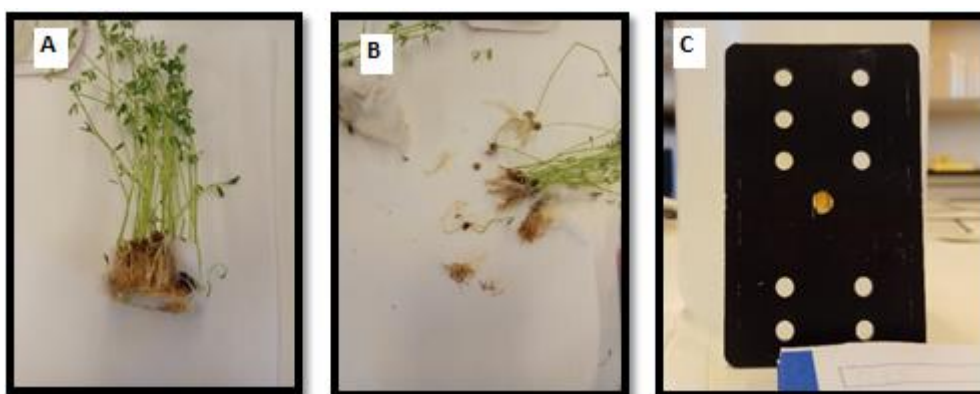


Figure 5.5 Preparation of the roots for spectroscopic analysis. A) The lentil plant to be studied. B) Roots of the lentil plant c) Spectrophotometer holder in which the root plant has been used to cover all the central hole.

5.4.3 Coating of the nanoparticles and colloidal dispersion of the nanoparticles

In order to introduce the Nanoparticles inside the plants, first they should be dispersed in an aqueous colloidal dispersion which will be used for water them. This colloidal dispersion was prepared following two recipes. The first recipe was based on nanoparticle coating route, previously studied in the FiCMA-FiCNA group^[18]. The second recipe was based on the work done by Du, P. *et al.*^[15] about the research of nanoparticles biocompatibility inside rice plants.

The objective of this part is that given the nanoparticles obtained from Pechini, are in majority agglomerates, we want to disaggregate them by the APTES coating, this will also help in the posterior plants absorption.

The method used for the coating was a silanization of the nanoparticles. Experimental procedure consists in dispersing a mass quantity (table 5.6) of the sample, in a 2,5 mL of 3-aminopropylsilane (APTES) and 7,5 mL of water all in an Eppendorf vial. Then the vial is introduced to an ultrasound amplification set-up (figure 5.6), for 5 h with the help of an ice-water bath in order to not let the temperature go higher, to avoid the polymerization of the APTES.

For the ultrasound amplification, a sonicator instrument was used, The sonicator is a VIBRACELL 75115 property of Bio block SC.

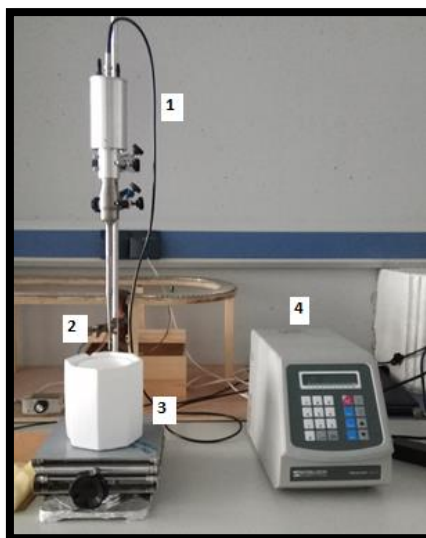


Figure 5.6 1: ultrasound needle, 2: sample holder, 3: ice-water bath, 4: controller

After this process, there is a cleaning of the residual APTES with ethanol, done by simply decanting the Eppendorf vial and then adding 2, 5 mL of ethanol, then centrifuging it, until the ethanol-APTES solution is colorless, and the precipitated coated nanoparticles can be observed at the bottom. Finally, the obtained coated nanoparticles are re-dispersed in 2,5 mL of water. This process has been already demonstrated to be efficient for obtaining a good dispersion of the nanocrystal, without agglomeration ^[18]. In the previous works, the optimized parameters were the ones reported in table 5.6, in the present work small variation of the parameters have been performed to check if it would be possible an improvement of the results.

The ultrasound amplification, in table 5.6, means the percentage of increase from a conventional ultrasound. In addition, the pulse duration, is that every 5s the instruments does a pulse.

Table 5.6 Different experiments for the Sonicator process

Experiment	Ultrasound amplification (%)	Pulse duration	% Vol. Silane-water	NPs weight (mg)	Sonicator time (h)
1	35	3/1	25-75	12	2
2	30	3/1	25-75	10	2
3	30	3/1	25-75	15	2

Besides, as in the work by Du, P *et al.* devoted to the study of the biocompatibility of Fluoride based nanoparticles, various quantities of the sample were dispersed in water, without any coating. In this paper, is shown that the nanoparticles were introduced in the plan itself by osmosis. The only condition is that bigger concentrations of dissolved nanoparticles can affect the growth process of the plans ^[16].

The quantities of mass and water for these dispersions are resumed in the table 5.7. First, the product was weight in an analytical balance and introduced in an Eppendorf vial, with the appropriate quantity of water. Then introduced in the ultrasound for around 20 minutes.

Table 5.7 Weights for dissolutions preparation

	Dissolutions	
	0,01 M	0,001 M
Reactants	Weight of reactant	
KYb(WO ₄) ₂ 10 % at Er ³⁺	0,021 g	0,0021 g
Water	3 mL	3 mL

After both type of solutions were ready, all of the quantities prepared. Were sprayed as close as it could be to the roots, with the help of a Pasteur pipette. Then an overnight wait time in order to let the roots absorb, by osmosis, the nanoparticles.

5.4.4 Laser effect on the root plants

The lentil root under laser excitation performance was studied with set-ups shown in the figure 5.7, both set-ups were mounted in the optic laboratory of the FiCMA-FiCNA group.

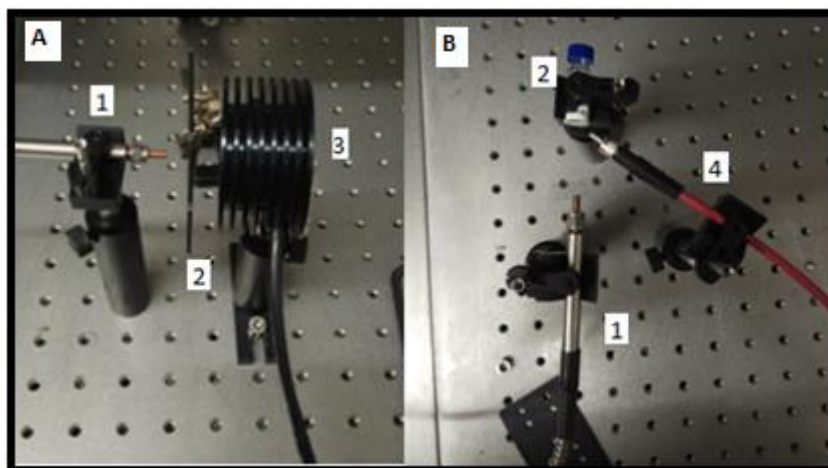


Figure 5.7 A) 1: laser, 2: sample holder, 3: power meter. B) 1: laser, 2: sample holder, 3: optic fibre connected to the detector and at 45° from the laser

Table 5.8 Devices specifications for the figure 5.7

Set-up figure 5.7.a		Set-up Figure 5.7.b	
Devices	Specifications	Devices	Specifications
Laser	Lumics diode laser D560 400W 975 nm	Laser	Lumics diode laser D560 400W 975 nm
Laser optic fiber	HI-1060, corning	Laser optic fiber	HI-1060, corning
Laser display	Lumics diode controller	Laser display	Lumics diode controller
Support	CARY Sample holder 5 mm aperture	Support	CARY Sample holder 5 mm aperture
Detector	Power meter Ophir NOVA II	Detector	Yokogawa, Optical Spectrum Analyzer AQ6373
		Detector optic fiber	Thorlabs FT038 core 600 nm, NA

The objective of the measurements using the first set-up was to study the maximum power of the laser that the plant could resist without burning (or getting dehydrated) and the maximum time of exposure to the laser that the plant could bear.

The second set-up, is for the plant watered with the nanoparticle colloidal suspensions, and the purpose was to see if there was some measurable emission from the particles that were absorbed by the plant ^[16].

For the roots preparation of the second set-up, the plant were extracted from the cotton and also cleaned with deionized water in order to know, for sure, that if some emission can be seen, came from nanoparticles that were inside the roots.

6. Results and discussion

6.1 Crystalline phase identification of the synthesized samples

All samples obtained after the second calcination were a white powder. The first sample that was synthesized by Pechini method, was the; 3 at % of Er^{3+} $\text{KYb}(\text{WO}_4)_2$. The diffractogram obtained for this sample is shown in the, figure 6.1. The product obtained is highly crystalline, confirmed by the sharpness of the diffraction peaks. The diffractogram of the sample was compared to the JCPDS 054-0249, belonging to the monoclinic crystal $\text{KYb}(\text{WO}_4)_2$. There's no doubt that the experimental sample was correctly synthesized.

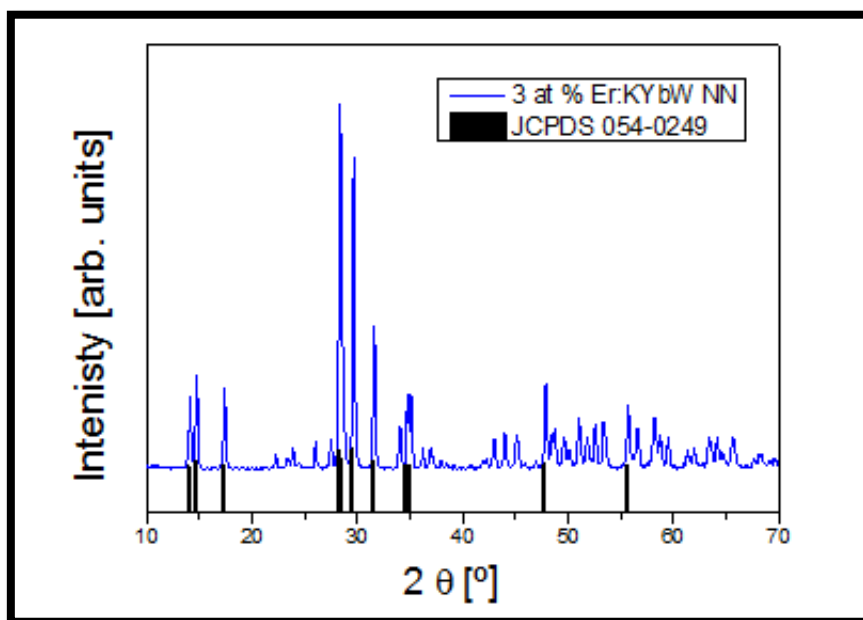


Figure 6.1 X-ray diffractogram for the 3 at % Er: KYbW sample.

All of the other products synthesized were measured and compared to the standard as can be seen in the figure 6.2.

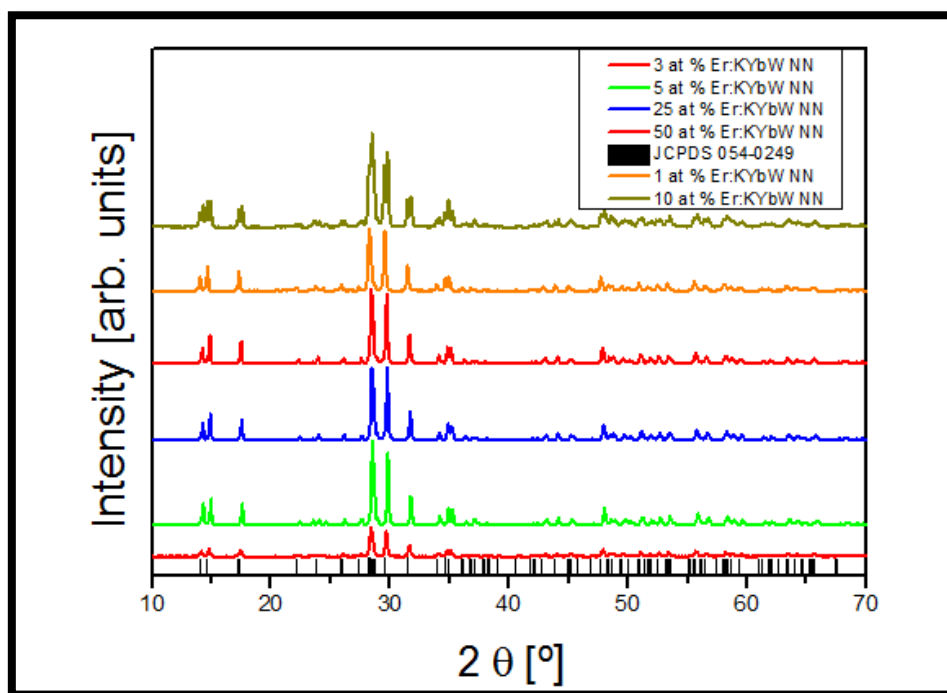


Figure 6.2 X-ray Diffractogram from Er:KYbW nanocrystals with different doping percentage of Erbium.

The unit cell refinement was performed only for the sample 10 at. % Er: KYb(WO₄)₂; which shows the highest emission as shown later. The X-ray diffraction patterns for the refinement are shown in figure 6.3, together with the calculated profile and the difference between them.

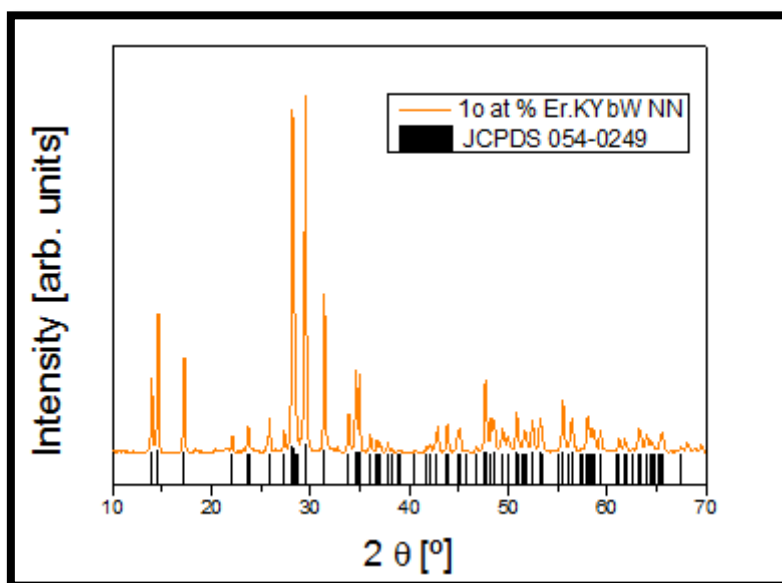


Figure 6.3 X-ray slow diffractogram for 10 at. % Er:KYbW sample

After that procedure an actual cell parameters refinement was done, based on Le Bail method. The unit cell parameters obtained can be seen in the table 6.1.

Table 3 Cell parameters for the sample studied.

Samples	a (Å)	B (Å)	C (Å)	β (deg)	V (Å ³)
KYb(WO ₄) ₂	10,590 (4)	10,290 (6)	7.478 (2)	130,70 (2)	617, 8 (5)
KYb(WO ₄) ₂ nanocrystals	10,6003 (12)	10,2973 (12)	7,5036 (8)	130,753 (3)	618,33 (6)
50 at. %Er: KYb(WO ₄) ₂ nanocrystals	10,6103 (5)	10,2886 (5)	7,5204 (3)	130,75 (2)	621,9 (5)
10 at. % Er: KYb(WO ₄) ₂	10,6131 (5)	10,2756 (4)	7,5174 (3)	130,776 (2)	620,82 (5)

*all parameters, except for the experimental, are from Montse Galcerán *et al.* ^[1]

The parameters of cell comparative from the bibliographic ones, at pure nanocrystals and 50 at. % doping and the experimental ones is that the size of the cell gets bigger as the Erbium concentration also increments. Given that KYbW and KREW are isostructural with group C2/c, we need also to take into account the ion size, which in this case is dependant of the lanthanide contraction, the decrease of ionic radius. This shows in that as the Erbium concentration is bigger the cell is consequently bigger, and as the Ytterbium concentration is bigger, the cell is smaller, in all parameters.

6.2 Particle size and size distribution

The particle size for different samples was studied with TEM, as can be seen in the figure 6.2.1. The samples chosen for the TEM experimental, were the KYb(WO₄)₂ 3, 5 and 25 % at. Doped of Erbium, this had the objective to see if by any means the variation of dopant concentration had any effect on the size of the nanoparticle.

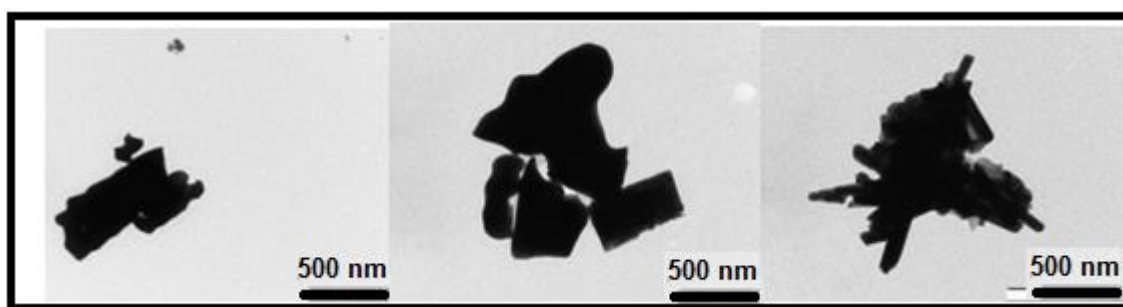


Figure 6.4 TEM images for, left to right, 3, 5 and 25 at. % Er; KYbW.

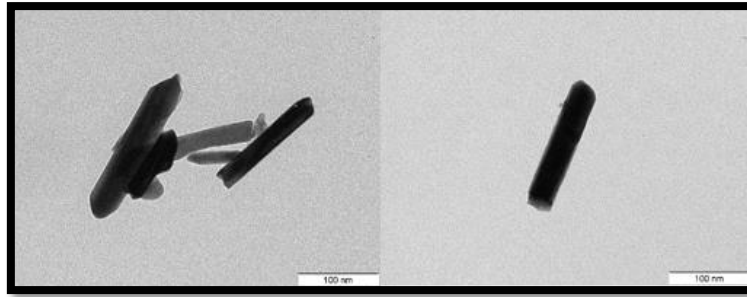


Figure 6.5 TEM images for 10 nm nanoparticles

For the actual study of size distribution, images from TEM as seen in the figure 6.6, were used. Those shown many nanoparticles of each sample and their distribution.

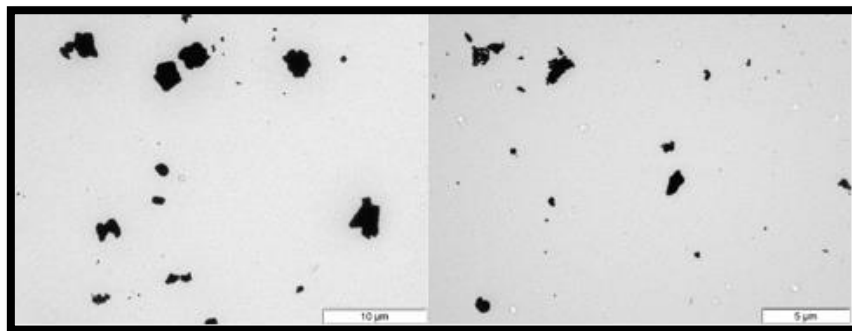


Figure 6.6 Size distribution example for 5 and 25 at % ER; KYBW

The Image J software was used in order to produce the following histograms for each sample, in the figures 6.7.A and 6.7.B. Between the 3 and 25 % of dopant, there are no significant changes, but for the 5 at.% Er doped sample, there were some bigger nanoparticles, as shown in their histogram.

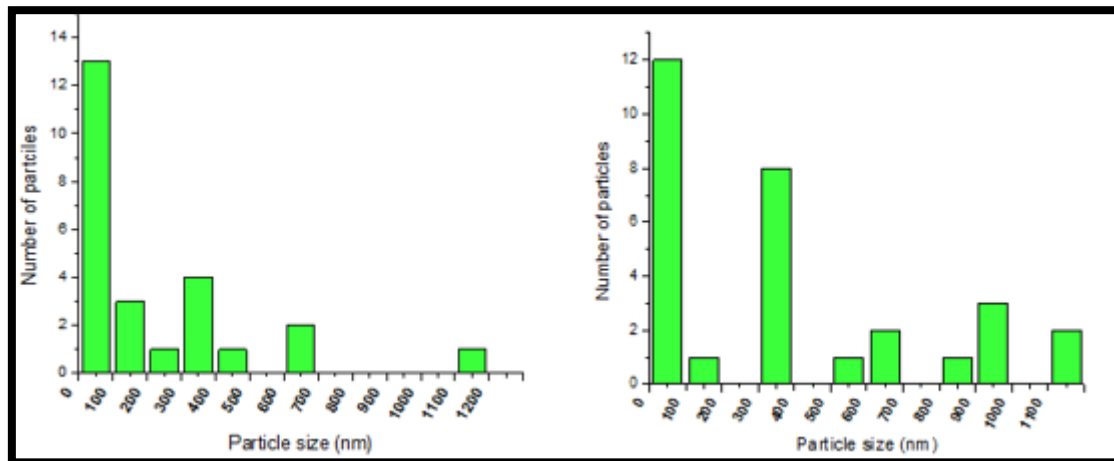


Figure 6.7a) histogram for the 3 at. % Er; KYbW b) histogram for the 25 at. % Er; KYbW

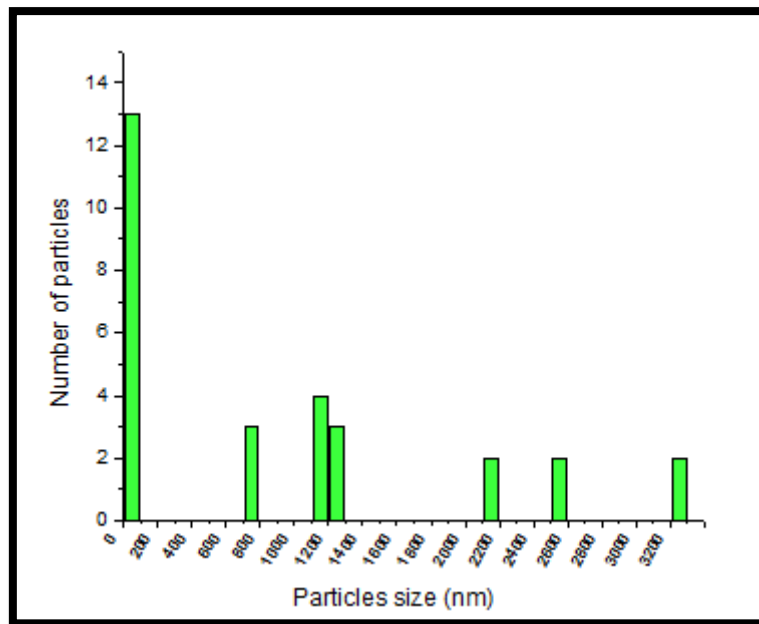


Figure 6.8 Histogram for the 5 at. % Er; KYBW

Even though it looks as if some particles are bigger, this in reality are agglomerations of actual smaller nanoparticles. This can be confirmed with the Scherrer parameter (τ), for the cell refinement, which gave a value of around 130 nm for the crystallite size.

6.3 Photoluminescence

Even though up until this point all of the synthesized products had been presented at the same time, the truth is that a first pack of samples was synthesized. That included the 3, 5, 25 and 50 at. % of Erbium dopant. In order to determine which is the optimum Er concentration, in terms of obtaining the highest erbium green emission, all samples were measured in the same conditions in the 1st described et up. A commercial sample, Er. Yb: NaYF₄, was used in the experiment as a reference. This commercial material is known to be one of the highest efficiency in the up conversion process for the green emission [21].

As it can be seen in the figure 6.9.a, the commercial sample had a much bigger intensity of emission than the samples synthesized.

In figure 6.9 b, it could be seen more clearly the tendency of the efficiency of the up conversion in relation with the Er concentration in the samples, which was not linear.

So for that reason, it was decided to synthesize two new samples of 1 and 10 % at. Erbium dopant, to clarify the results.

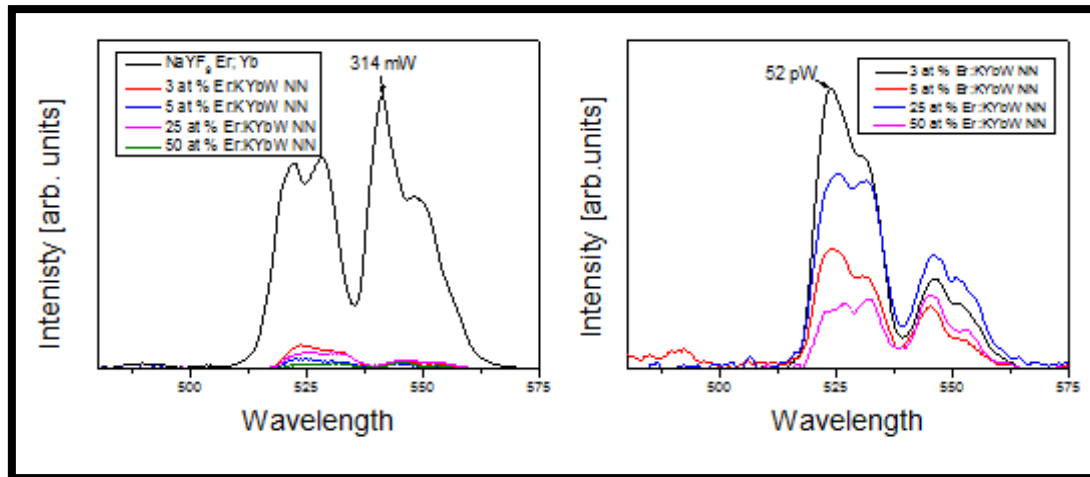


Figure 6.9 figure a) Intensities of experimental samples vs commercial b) Intensities of experimental samples only

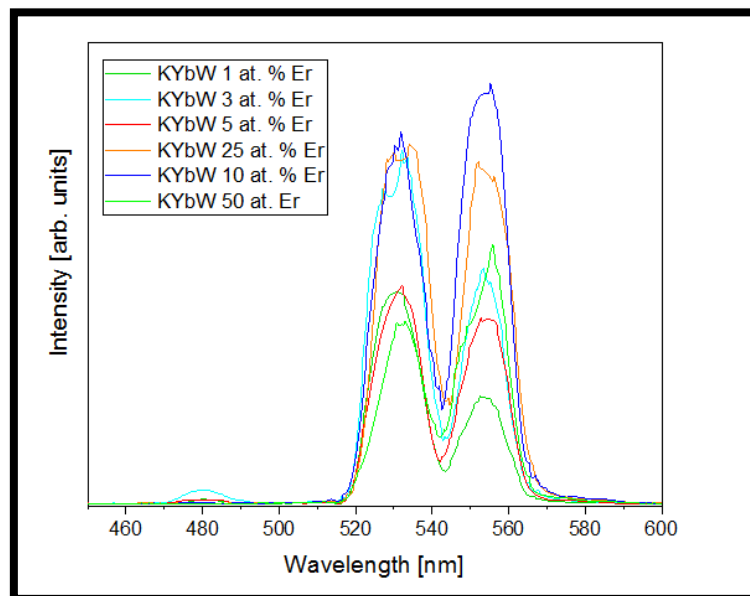


Figure 6.10 Full intensities of the synthesized samples

As can be seen in the spectrum obtained with the help of the Ocean View detector, the best sample for the project purposes was the KYb(WO₄)₂ 10 at. % Er³⁺. This result is in contradiction with previous studies realized in which the optimum concentration for obtaining green emission by upconversion in the KREW tungstates was between 3 and 5 at. % ^[5].

The spectroscopic studies for the thermal sensitivity calculation were carried with 10 at. Er :kYbW sample.

6.4 Photoluminescent thermometry in the 10 at.% Er: KYb(WO₄)₂

The calibration of a primary thermometer was performed by the variation of intensities $\frac{I_2}{I_1}$. The energetic difference that will be used come from the bibliographic parameter, and the K_B is the Boltzmann constant. Giving us the equation:

$$\Delta_p = B_p \times \exp\left(-\frac{\Delta E}{K_B T}\right) \quad (6.1)$$

Moreover, after that with variation of intensities in relation to the temperature and the equation 4.4, we can obtain a thermal calibration of our sample. From the plots of Δ_{exp} , and the help of the equation 4.4, the values for B experimental and ΔE experimental can be obtained. This will allow us to obtain also a calibration of the luminescent thermometer for temperatures.

For the variation of intensity, the sample behaviour was the expected one, given that as the higher the laser power projected on the sample was, an inversion of the picks could be seen, figure 6.11.

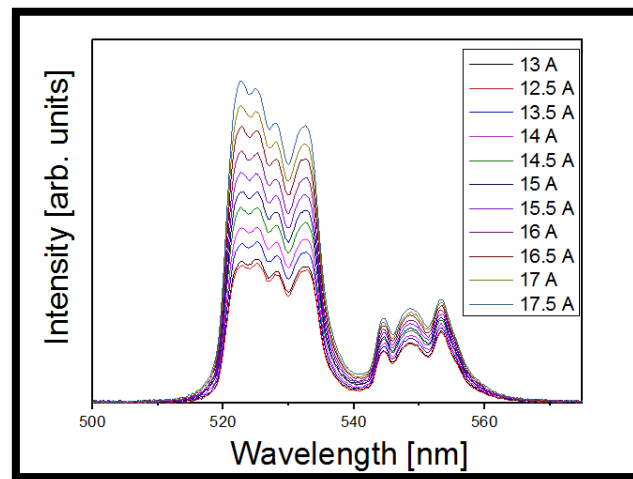


Figure 6.11 Intensity variation spectra obtained with OSA detector

Each spectrum of the figure 6.11 was treated with Origin software [24], in order to calculate the area of each peak by a fitting process was required, more specifically a Lorentz fitting. The value of this fitting allow to calculate the following function in order to obtain the delta parameter ;

$$\Delta = \frac{\sum \text{Peak area for the manifold } ^2H_{11/2}}{\sum \text{Peak area for the manifold } ^4S_{3/2}}$$

In the figure 6.11 it can be observed the variation of the delta as a function of the laser power intensity. By adjusting linear equation, it could be extrapolated the value of Δ_0 , that should allow as to calculate the B_p , using the expression 4.5. As can be seen from the figure, the extrapolated value is negative, so, this means that the sample is not following the physical behaviour described by the model of the equations 4.4 and 4.5. Further experiments should be performed to clarify why.

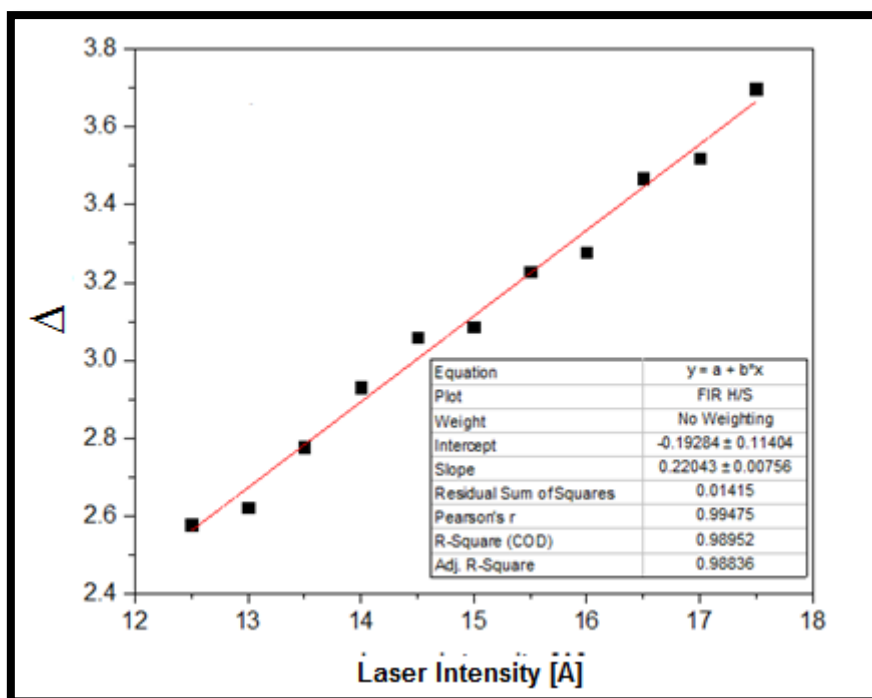


Figure 6.12 Linear fit for intensities variation

Figure 6.13 shows the variation of the emission intensity of the up conversion emission as a function of the temperature. The green emission gets higher values as the temperatures rises until the 107K after that temperature; the intensity values start to decrease.

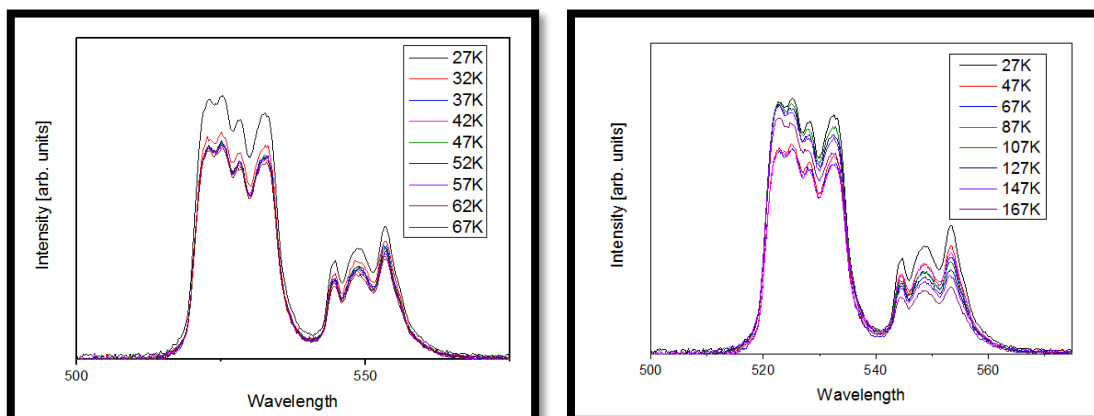


Figure 6.13 a) Spectra for the temperatures b) Spectra for the biological temperature range

In the figure 6.14 it can be observed the variation of the delta as a function of the temperature. As expected it can be seen that the intensity area ratio is increasing with the temperature, that reflects the fact that increasing the temperature the electronic population of the $^2H_{11/2}$ manifolds is increasing, as described by Boltzmann model.

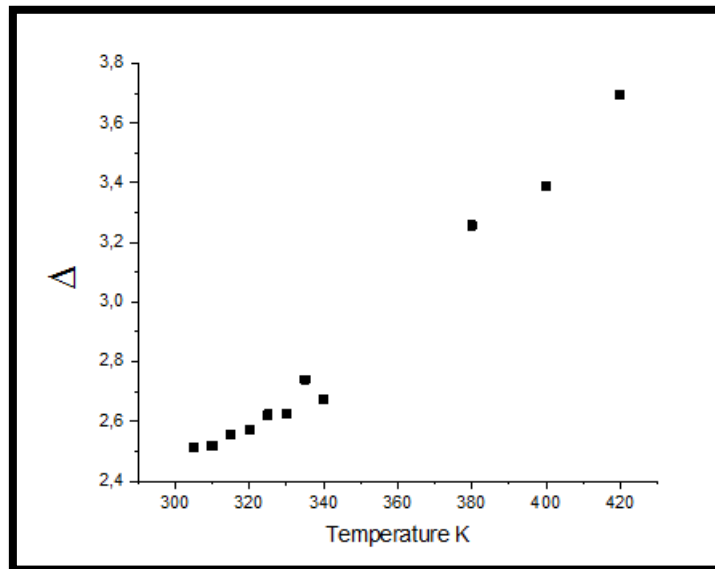


Figure 6.14 Plot of the peak variation vs Temperature

Expressing the equation 4.4, as $\ln \Delta = \ln B + \frac{AE}{Kb} \cdot \frac{1}{T}$, we can plot the data as shown in figure 6.15, and by adjusting to a linear equation, to obtain the experimental values of B_{exp} , and ΔE_{exp} . This experimental value enables as to obtain the experimental calibration of the 10 at. Er :KYbW nanocrystals as luminescent thermometer, with the following expression $B_{exp} = 10.31$, $\Delta E_{exp} = 307.2 \text{ cm}^{-1}$ ($\Delta E/Kb = 442.49$).

$$\ln(FIR) = \ln(B) + \left(-\frac{\Delta E}{k_B T} \right) = \ln(B) + \left(-\frac{C}{T} \right) \quad (6.2)$$

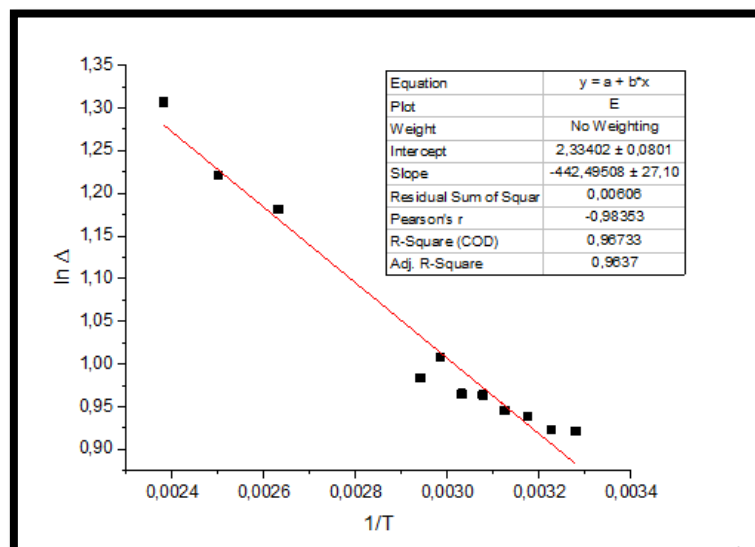


Figure 6.15 Linear fit for the experimental parameters

The value of ΔE obtained is much smaller than the absolute experimental value, as well as the value from the fitting at 300 K, this confirms that the Boltzmann model does not fully describe the experimental behaviour of the samples. It can be because other processes that depend of the temperature are affecting the populations of the starting levels of the measured emissions (those are no radiative processes, as others temperature excitations or cross relaxations processes).

In order to compare the behavior of these nanocrystals with other luminescent thermometers based on the Green emissions of erbium, the relative sensitivity expressed as equation 4.6 was calculate and plotted in the next figure 6.15. The value of the relative thermal sensitivity at room temperature is around 0.47 %/K.

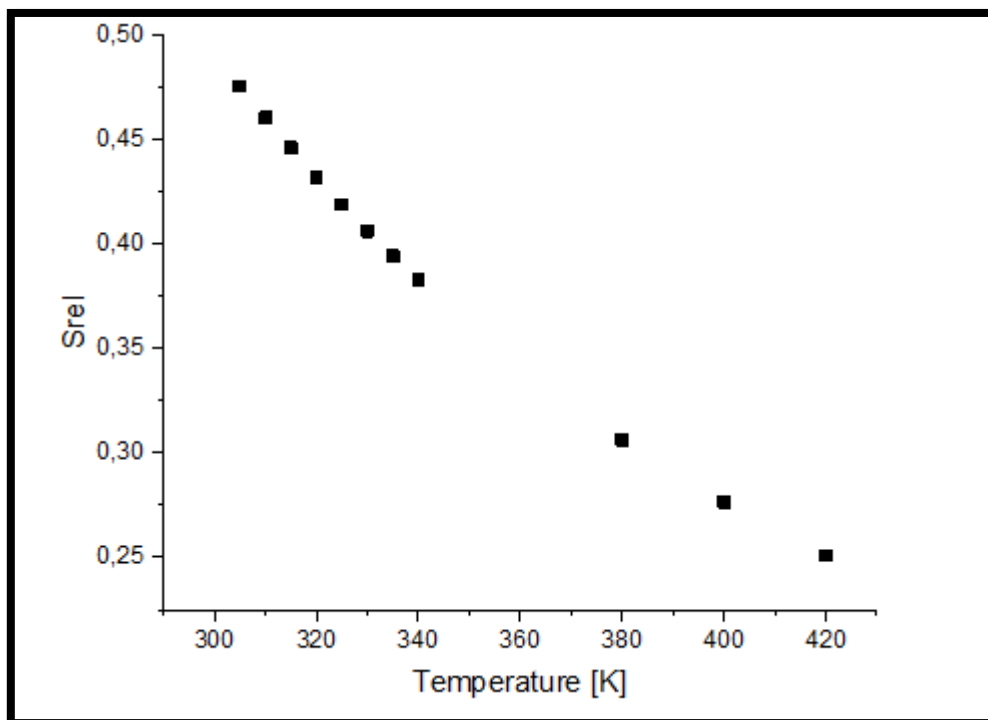


Figure 6.16 Srelative at various temperatures

6.5 Optical properties of the plants

The measurements were performed for the lentil's roots. As shown in the figure X, The lentil's root are almost transparent to the excitation wavelength (980 nm) and to the emission wavelength (green range) to be used in the luminescent thermometry. A weak absorption in the green is observed attributed to the presence of pigments of the plants, also in the roots. In the near infrared range, at 980 nm, maybe some slight absorption due to the water is observed (the band edge of the water absorption).

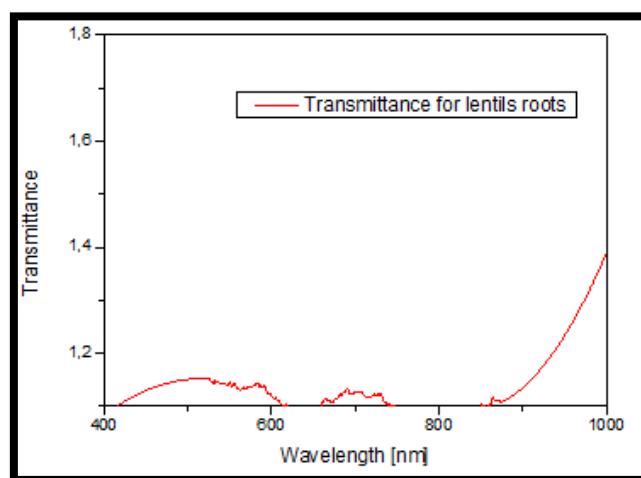


Figure 6.17 Transmittance for roots of lentils

So in conclusion the $\text{KYb}(\text{WO}_4)_2$ nanoparticles doped with Erbium, are a good choice for the emission study because, as can be observed there is poor pigmentation in the roots that could affect the results that obtained from the nanoparticles.

6.5.1 Laser effect on the plants

Previous to expose to the laser the lentil plant roots sprayed with the nanocrystal aqueous colloidal dispersion, a study of the plants behavior to the laser exposure was performed. The objective was establishing the experimental parameters, such as the transparency/scattering of the plant to the incident 980 nm laser and the lifetime of the plants, when getting exposed to the laser, without getting damaged or killed.

By a progressive increment of the laser intensities, the transmitted laser power through the lentil root plant was measured by an OPHIS II Powermeter; the values are reported in the table X. This value indicate us the laser power which transmits the roots, so it can be used as a reference value for the laser power which can be absorbed later on by the nanocrystals absorbed in the roots.

Table 6.2 Energy units for roots exposure to laser

Energy response for progressive variation of laser intensity			
Laser Intensity (A)	Powermeter result (mW)	Laser Intensity (A)	Powermeter result (mW)
4,5	0,8	11,5	359
5	0,9	12	401
5,5	1,4	12,5	448
6	2,5	13	499
6,5	15,2	13,5	578
7	39,8	14	631
7,5	70	14,5	699
8	100	15	760
8,5	133	15,5	833
9	169	16	892
9,5	196	16,5	994
10	233	17	1066
10,5	279	17,5	1182
11	313	18	1261

*after the 18 A, the roots looked dehydrated and also a burned smell came from the sample

The following table indicates intensity values, even though the actual selection of the optimal time was by visual observation.

Table 6.3 Energy units for roots exposure at various times

Laser Intensity (A)	Starting power (mW)	Ending power (mW)	Exposure Time (min)
7	35,6	1,235	15,36
11	298	1,538	7, 25
17	989	1,712	1,50

*the time coincided with the start of a dehydrated look of the plants.

Considering that the measurement of an emission spectrum, with the already described parameters for the OSA, takes between 3-5 minutes and that the emission detected needs to have a relative high response, the intensity chosen for the study of luminescence of the nanoparticles inside the roots was of 11 A.

6.5.2 Photoluminescence study of lentil roots

For the final step of the project, the 10 at. % Er. KYb(WO₄)₂ nanocrystals aqueous colloidal dispersion, both with coated and uncoated nanocrystals, were sprayed into the plants. The watering was done in the afternoon, to held after an overnight time of wait supposedly for the plants to absorb, by osmosis, the nanoparticles.

The plants roots after getting exposed to the laser, with a fixed intensity of 11 A, produce green emission that could be seen by naked eye, as shown in figure 6.18. The same behavior was observed with all of the samples. It was observed that the plants watered with the colloidal dispersion less diluted emits with the highest intensity, apparently.

As a first approach, it seems that the nanoparticles are biocompatible with the plants, and even the uncoated nanocrystals were absorbed.

Despite this emission was possible to be visualized by naked eye, it was not possible to record an emission spectrum due to the low intensity of the emission. Further experiments to be performed to record this emission spectrum, will be related to the improvement of the measuring set up increasing the threshold of sensitivity, or by other side, by increasing the signal (using the commercial fluoride or increasing further the quantity of the nanocrystals).

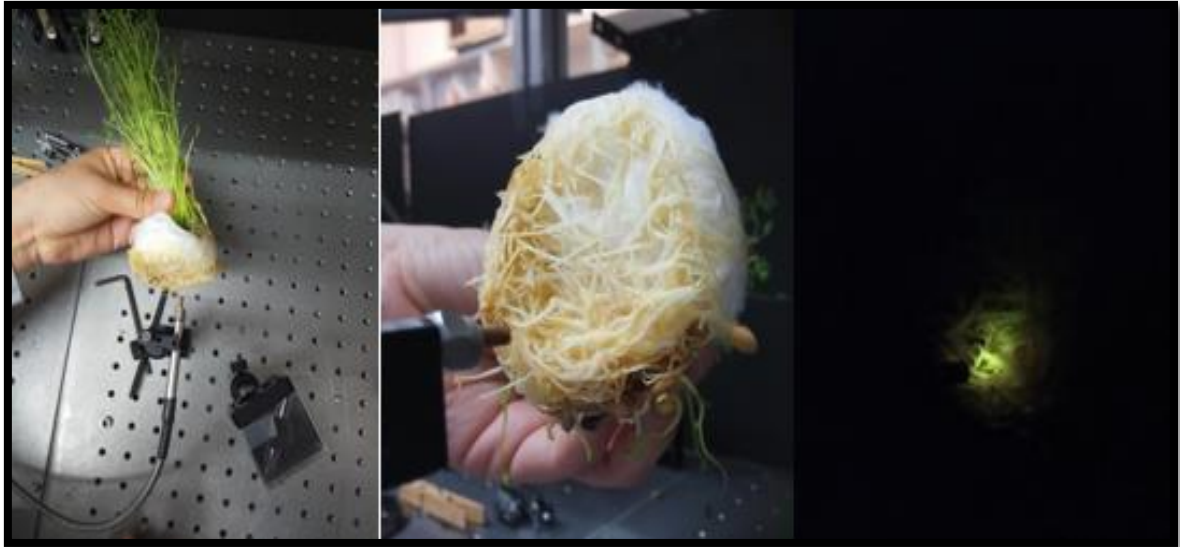


Figure 6. 18 Lentil plant root, and illuminated with the green emission

7 Conclusions

As a result of the project, the production of monoclinic Erbium doped $\text{KYb}(\text{WO}_4)_2$ nanocrystals with Erbium by modified Pechini method, is reproducible. These nanocrystals shown a green visible emission under near infrared emission, in efficient way, based in up-conversion processes. Even though that it could be seen that the Er,Yb:NaYF_4 commercial sample, as the used as reference, gave a more efficient emission.

The samples produced have optimal crystal sizes compared to actual nanoparticles; this means the size of the crystals was under 100 nm. Also a relevant point is that most of them are in agglomerates, which makes it look that there are particles bigger than it should be for a Nano material..

$\text{KYb}(\text{WO}_4)_2$; 10 at % of Er^{3+} have been calibrated as luminescent thermometer, with the expression . However, the values obtained indicate that their behaviors cannot be described solely on Boltzmann model and other processes are affecting. The S_r at room temperature was quite successful, given that the results obtained, made us possible to calculate the Δ , that will allow the temperature measurements inside the plants.

For the actual purpose of the project, the insertion of nanoparticles inside plants: The two aqueous colloidal dispersion of the nanoparticles were absorbed by the plants, meaning that even the uncoated ones, have, as a first approximation, a good biocompatibility. After several days of watering the plants, the nanoparticles didn't produce the death of the plant itself.

Finally, the green emission from the nanoparticles inside the plants could be seen by naked eye, but unfortunately, the intensity was so low that it could be not recorded with the used set-up. Further experiments are necessary to improve the sensitivity of the measurement set-up to check the viability of the Δ characterization to measure the actual temperature of the root plants.

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9 Annex 1

The following table shows the conversion from the intensity used in the head part of the laser to the laser power that excites the samples. The values of the laser power (W) that were detected by the OPHIS II Powermeter ^[19].

Table A.1. Correlation between the Excitation laser power focused in the set-up of the photoluminescence microscope

Intensity-Power value conversion			
Intensity (A)	Power (W)	Intensity (A)	Power (W)
5	0,007	16	3,428
6	0,087	17	3,863
7	0,192	18	4,256
8	0,495	19	4,646
9	0,815	20	5,03
10	1,166	21	5,26
11	1,534	22	5,67
12	1,916	23	6,04
13	2,316	24	6,45
14	2,708	25	6,85
15	3,095		