Synthesis of LaF₃ inorganic nanoparticles: Er³⁺, Yb³⁺ by the coprecipitation method and characterization by optical spectroscopy and electron microscopy

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Abstract. It has been possible to synthesize LaF₃: Er³⁺, Yb³⁺ nanoparticles, which are light emitters by upconversion, using the co-precipitation method followed by a thermal treatment at temperatures of 400°C, 500°C and 600°C. In these nanoparticles, luminescence is attributed to upconversion process, where green and red radiative transitions emissions are observed under NIR irradiation of 980nm. The upconversion results reveals the emission dependence with Er³⁺ and Yb³⁺ concentrations in the synthesis of these nanoparticles, as well as their dependence on temperature as a result of the applied thermal treatment, being in all cases the most intense at 525nm, 546nm and 668nm. By means of diffuse reflectance spectra, the absorption bands of Er³⁺ ions were obtained. On the other hand photoluminescence measurements were made for the identification of emission bands in Er³⁺, in the visible range. Furthermore, data and additional information about crystalline nature of the material were obtained using the electron microscopy technique, in order to confirm the presence of LaF₃, the obtained samples showed a good correspondence with the hexagonal phase. Thus, from the electron microscopy and optical spectroscopy results, it was verified that temperature increment in the thermal treatment of the nanoparticles, significantly influenced their morphology and luminescent intensity.

Keywords: Nanoparticles, wet chemistry, upconversion, nonradiative transitions

1. Introduction
Recently, there is great interest in certain luminescent inorganic multifunctional materials such as nanoparticles doped with lanthanide ions (Ln³⁺), which have been extensively investigated for their potential optical applications [1], [2]. The interest in this type of nanoparticles is due to the fact that, under excitation of 980nm, it presents emissions in the visible range due to the phenomenon of upconversion. The benefit of using inorganic matrices of LaF₃ lies in the structural flexibility, an important factor that allows the assembly to easily host various types of dopants, especially other rare-earth ions [3]. Also the advantage of this host is that their low phonon energy could reduce the probability of non-radiative transitions, achieving a good luminescent efficiency [4]. These nanoparticles have a great potential in biological studies due to their good dispersibility in aqueous solutions [5]. This is not the case of conventional nanomaterials such as luminescent quantum dots (QD) applied in biological analyzes, These could have certain disadvantages, due to the use of short wave (high energy) as well, for example, if the cells were subjected to high doses of light, especially at short wavelengths, these would suffer a process called phototoxicity which can lead to cell death, these disadvantages include low depth of penetration and possible damage of living organisms [6]; so that, if we
compare the luminescent quantum dots with the nanoparticles based on lanthanides by upconversion, the lanthanide nanoparticles have several remarkable advantages, such as sharp emission bands, long photoluminescent lifetimes, and large anti-Stokes changes, as well as high resistance to photobleaching [7]. Considering their attractive characteristics, the luminescent nanoparticles of LaF₃ are a promising class of luminescent markers, thus, they have been investigated for applications in bioimages [8]. Therefore, the study of the optical properties of nanoparticles with optically active ions of rare earths, would allow a better knowledge of these materials, in order to be able to use it in applications that include visualization devices.

2. Experimental procedure

For the preparation of LaF₃:Er³⁺,Yb³⁺ nanoparticles we use the following chemicals. Lanthanum Chloride LaCl₃ (99.9%), ammonium fluoride NH₄F (99.9%), erbium chloride hexahydrate ErCl₃. 6H₂O (99.9%) and ytterbium chloride hexahydrate YbCl₃. 6H₂O (99.9%) were obtained from Sigma Aldrich.

2.1 Synthesis of nanoparticles LaF₃: Er³⁺, Yb³⁺

Initially for the first solution, 0.312mmol (76.520g) of LaCl₃ was mixed with 0.011mmol (4.229g) of ErCl₃.H₂O and 0.111mmol (43.007g) of YbCl₃.H₂O in 50ml of distilled water with ethanol. In another beaker, 3mmol (111.108 g) of NH₄F was dissolved in 5ml of distilled water, then the first solution was in fast magnetic stirring for about 12 minutes. Subsequently the second solution is added, by a slow process (drop by drop) and immediately the mixture was heated, maintained at 65°C for 4 hours. After this procedure was completed, white precipitated powders were formed in the beaker, which were placed for 8 minutes at centrifugation (5500 rpm), then it was washed with distilled water and ethanol several times; the obtained substance was dried at about 62°C. Then, thermal treatment was carried out, the material obtained was heated in the oven at about 600°C for 2 hours, the resulting product was extracted from the oven where a total of 0.211g was obtained. For its spectroscopic test the nanopowders were bombarded with IR laser (980nm) where a high fluorescence was observed. Following the previous procedures, they were synthetized several more times but the temperature of the thermal treatment was modified, heating to 500°C, 400°C and 200°C.

2.2 Characterization

For the measurements of the spectra by upconversion on the samples synthesized, a Science Surplus spectrophotometer equipped with a linear CCD sensor and a 980nm IR laser diode with power of 400mW was used. In the measurements of the absorption spectra, a UV-Vis-NIR Cary 5000 series Spectrophotometer was used, which was analyzed within the UV-visible, visible and part of the near-infrared UV range; While for the measurements of the fluorescence spectra a Perkin Elmer Fluorimeter was used model LS-55. TEM and HRTEM electron microscopy images were measured with an E1 JEOL 2010 FEG-TEM microscope.

Figure 1. (a) Experimental assembly of the components for the synthesis of LaF₃ nanoparticles doped with Er³⁺; Yb³⁺. (b) Fluorescence of LaF₃ nanoparticles: Er³⁺; Yb³⁺ dissolved in ultra-pure water, under 980nm laser excitation.

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3. Obtained results

3.1 Spectroscopy of emission by upconversion

In order to study upconversion emissions, LaF$_3$ nanoparticles doped with 20% mol Yb$^{3+}$ and 2% mol Er$^{3+}$ were excited with a 980nm laser diode. This was done for the samples with thermal treatment of 600°C, 500°C and 400°C, registering the emission spectra obtained by upconversion. To study the effect of the heat treatment on the synthesized samples, we compared the emission spectra, where we observed significant emission differences, stands out a higher luminescent intensity at a higher thermal treatment temperature.

Figure 2. (a) Emission spectra produced by upconversion (excited with a laser diode of 980nm with 400mW) of LaF$_3$ nanoparticles doped with 20% mol Yb$^{3+}$ and 2% mol Er$^{3+}$, with thermal treatment of 400°C, 500°C and 600°C. (b) Diagram showing the comparison of the total integral intensities of the LaF$_3$ nanoparticles: Yb$^{3+}$, Er$^{3+}$ (20/2)% mol at different temperatures of 400°C, 500°C and 600°C.

In figure 2, the presence of bands centered on green and red are observed in the three emission spectra. These bands present a series of peaks associated with the electronic transitions of excited states of the Er$^{3+}$ which are: $^3H_{11/2} \rightarrow ^4I_{15/2}$; $^3S_{3/2} \rightarrow ^4I_{15/2}$ visible green luminescence and $^4F_{9/2} \rightarrow ^4I_{15/2}$ visible red luminescence with wavelengths centered at 524.9nm, 545.8nm and 668.6nm respectively.

In the sample with heat treatment at 600°C, we see that the band formed by the radiative transition in the multiplets $^3H_{11/2} \rightarrow ^4I_{15/2}$ of Er$^{3+}$ has a higher luminescent intensity compared to the band formed by the transitions $^3S_{3/2} \rightarrow ^4I_{15/2}$. On the contrary, for the samples with treatment at 500°C and 400°C, the transitions $^3S_{3/2} \rightarrow ^4I_{15/2}$ are more efficient than transitions $^3H_{11/2} \rightarrow ^4I_{15/2}$.

In the luminescence spectra for upconversion of the LaF$_3$ nanocrystals: 20% Yb, 2% Er given by figure 3, the formation of bands coming from the strong emissions in the visible green corresponding to the electronic transitions can be seen $^3H_{11/2} \rightarrow ^4I_{15/2}$ and $^3S_{3/2} \rightarrow ^4I_{15/2}$ which are centered at 525.3nm and 545.9nm respectively, while the strong emission in the visible red is assigned to the transition $^4F_{9/2} \rightarrow ^4I_{15/2}$ centered at 667.5nm.

In the same way for the LaF$_3$ nanocrystals: 12% Yb, 3% Er, the bands formed presented the same characteristics as the concentration Yb, Er (20/2). As both samples were treated at 600°C, then the high temperature and the heating time favored the luminescent intensity, however, the most remarkable fact is that the LaF$_3$ nanocrystals with a concentration of 2% Er, 20% Yb, showed a greater intensity of emission both in their bands with visible green emission and in the band in the visible red, compared to the samples with concentration 3% Er, 12% Yb.
3.2 Diffuse reflectance spectroscopy

By this technique, the absorption spectra were determined. These spectra obtained allow the identification of the excited energy levels of the optically active Er\textsuperscript{3+} ion inside the LaF\textsubscript{3} nanocrystals.

In figure 4, a comparison between the absorption spectra of three LaF\textsubscript{3} samples is observed: Er\textsuperscript{3+}, Yb\textsuperscript{3+} (2/20)\% mol at different heat treatment temperature, where it is indicated for each band the centered wavelengths belonging to the excited states of the Er\textsuperscript{3+}. The spectra were taken between the ranges of 300 nm to 900 nm.

By comparing the absorption spectrum of the sample at 400°C with the samples at 500°C and 600°C, we observed a significant decay of the intensity of absorption, as well as the decrease in the number of sharp peaks in certain regions of the spectrum, due to there is no formation of the bands corresponding to the multiplets \textsuperscript{3}H\textsubscript{9/2}, \textsuperscript{5}S\textsubscript{5/2}, \textsuperscript{5}I\textsubscript{9/2} of Er\textsuperscript{3+}.
In the absorption spectra with heat treatment at 600°C and 500°C, the number of peaks for both samples are the same, also the forms adopted by the bands are identical, as well the sample treated at 600°C has a slightly greater magnitude of absorption than the sample at 500°C, therefore, the heating temperature would significantly favor the relative intensity of absorbance and the formation of bands.

![Figure 5](image)

**Figure 5.** Spectra of absorption in the visible range of LaF$_3$ nanoparticles doped in molar ratio of Yb$^{3+}$, Er$^{3+}$ (20/2)% mol, and Yb$^{3+}$, Er$^{3+}$ (12/3)% mol, with temperature of thermal treatment at 600°C. The measurement conditions were the same in each one of the samples.

In the case of figure 5, absorption spectra given by two samples of LaF$_3$ at different molar concentration of Er$^{3+}$ and Yb$^{3+}$ are observed, but with the same thermal treatment temperature. We see that both spectra present identical acute band formation, where the variation occurs mainly in the order of magnitude of the absorption intensities. As the well-defined characteristic peaks, come from the excited levels of the Er$^{3+}$ ion. Although the concentration of (3%) Er$^{3+}$ in one of the samples is greater than the concentration (2%) Er$^{3+}$, it can be seen that the LaF$_3$ sample with dopant ratio Yb$^{3+}$, Er$^{3+}$ (20/2)% mol, it has a higher absorption capacity than the dopant ratio Yb$^{3+}$, Er$^{3+}$ (12/3)% mol, this according to the relative intensities of absorption.

### 3.3 Fluorescence spectroscopy

By means of this technique, excitation and emission spectra were recorded, thus by analyzing the light frequencies emitted together with their emission intensities, it was possible to determine different electronic states of the Er$^{3+}$ ion within the host of LaF$_3$, the measurements made they were within the range of the visible spectrum.

Spectra of LaF$_3$ crystallized nanoparticles with different molar concentration of impurities were registered, one with doping 20% mol Yb$^{3+}$: 2% mol Er$^{3+}$, the other sample were doped with 12% mol Yb$^{3+}$: 3% mol Er$^{3+}$ both treated at 600°C, these synthesized samples were excited at 378nm.

From figure 6, it was observed peaks distributed in five groups of bands, centered at 456nm, 487nm, 520nm, 548nm and 660nm, which comes from the transitions $^4F_{5/2} \rightarrow 4I_{15/2}$; $^4G_{7/2} \rightarrow 4I_{15/2}$; $^2H_{11/2}$, $^4S_{3/2} \rightarrow 4I_{15/2}$ y $^4F_{9/2} \rightarrow 4I_{15/2}$ respectively.

The results indicate that the luminescent intensity is better in the dopant relationship Yb$^{3+}$, Er$^{3+}$ (12/3) % than Yb$^{3+}$, Er$^{3+}$ (20/2) %, this is associated with the higher concentration of optically active ions of Er$^{3+}$. If compare the bands with the highest emission, we can see that the group of bands with peaks at 660nm and 674nm visible red band, is relatively more efficient than the emission in the visible green band with peaks at 520nm and 548nm.
3.4 Electron microscopy

In order to observe crystalline planes, the shape and size of the synthesized nanoparticles, it shows the results of the high resolution images obtained by transmission electron microscopy (TEM). The image of figure 7 allows observing the crystalline planes of the sample studied. In this region, the crystallographic parameters given in figure 8 were calculated, so the Fourier transform (FFT) in the selected area shows a hexagonal crystalline system for LaF$_3$, where a good crystallinity is observed.

In figure 7, a region of the studied sample is shown. This figure shows the reciprocal spaces for a certain region with values 8.13nm$^{-1}$, 7.71nm$^{-1}$ y 7.73nm$^{-1}$. Likewise, the FFT pattern is shown. The interplanar spacing of 0.33nm corresponds to the crystalline plane (111) of LaF$_3$; also the nanocrystals with interplanar spacing of 0.37nm correspond to the crystal plane (002) of LaF$_3$ given by reference [9].

![Emission spectra produced by photoluminescence of LaF$_3$ nanoparticles doped with 20% mol Yb$^{3+}$: 2% mol Er$^{3+}$ and 12% mol Yb$^{3+}$: 3% mol Er$^{3+}$, with thermal treatment at 600°C. The samples were excited at $\lambda = 378$nm.](image)

**Figure 6.** Emission spectra produced by photoluminescence of LaF$_3$ nanoparticles doped with 20% mol Yb$^{3+}$: 2% mol Er$^{3+}$ and 12% mol Yb$^{3+}$: 3% mol Er$^{3+}$, with thermal treatment at 600°C. The samples were excited at $\lambda = 378$nm.

![Figure 7.](image)

**Figure 7.** (a) Image (TEM) with unit of measurement at 5nm of nanoparticles LaF$_3$: Yb$^{3+}$; Er$^{3+}$ (20/2)% mol, with a heat treatment of 600°C. (b) Approach the region marked in figure (a). (c) The FFT pattern of the region indicated in (a) is shown.
The results of the high resolution images obtained by transmission electron microscopy (TEM). In figure 8, HR-TEM images of the LaF$_3$: Er$^{3+}$ nanoparticles are shown; Yb$^{3+}$ thermally treated at 200°C with units of measurement of 100nm and 50nm. These images show a greater contrast, which allows to see the agglomeration of the nanoparticles, despite that a certain distribution of particles. From this image, is observed a particle size of approximately 15 nm.

![Figure 8. Micrographs obtained by HR-TEM with unit of measurement 100nm and 50nm of the LaF$_3$ nanoparticles: Yb$^{3+}$; Er$^{3+}$ (20/2)% mol, with a heat treatment of 200°C.](image)

Figure 8. Micrographs obtained by HR-TEM with unit of measurement 100nm and 50nm of the LaF$_3$ nanoparticles: Yb$^{3+}$; Er$^{3+}$ (20/2)% mol, with a heat treatment of 200°C.

Figure 9 is a HR-TEM image, where the crystal planes can be observed. The crystalline system corresponds to the hexagonal structure, with well-defined crystallinity. Its structure corresponds to Lanthanum trifluoride (LaF$_3$) given by the reference [9], this can be corroborated with the pattern of the Fourier transform (FFT), which is located in the zone axis [1, -2, 1, -3]. Some crystal lattice planes are shown where the interplanar spaces are labeled in the image, which gave distances of 3.2 Å and 3.5 Å, which corresponding to the families of planes (111) and (110) respectively, with reciprocal spaces of 6.421nm$^{-1}$, 6.451nm$^{-1}$ and 5.751nm$^{-1}$. The doping of the trivalent ions Yb, Er, are within the structure of the host material, because the parameter of the crystal lattice of LaF$_3$ is not altered.

![Figure 9. High resolution image (HRTEM) of the LaF$_3$ nanoparticles: Er$^{3+}$; Yb$^{3+}$ (20/2)% mol, with thermal treatment at 200°C and unit of measurement 10nm in a certain region. The FFT pattern is indicated as well its interplanar distances of a single nanocrystal.](image)

Figure 9. High resolution image (HRTEM) of the LaF$_3$ nanoparticles: Er$^{3+}$; Yb$^{3+}$ (20/2)% mol, with thermal treatment at 200°C and unit of measurement 10nm in a certain region. The FFT pattern is indicated as well its interplanar distances of a single nanocrystal.
4. Conclusions
In the work presented in this paper, we were able to synthesize inorganic nanoparticles LaF$_3$: Er$^{3+}$ Yb$^{3+}$, effectively implementing a relatively practical chemical method.

- The emission spectra obtained by upconversion with dopant concentration Yb$^{3+}$, Er$^{3+}$ of 20%, 2% have greater luminescent efficiency with respect to the sample with concentration Yb$^{3+}$, Er$^{3+}$ of 12%, 2% respectively. In addition, the efficiency of the upconversion of nanoparticles is favored by increasing the heat treatment temperature.

- It has been determined that the most outstanding peaks in the absorption spectra are centered at 387nm, 521nm and 652nm. The formation of these bands presents relatively sharp lines.

- From TEM images, the existence of LaF$_3$ nanoparticles was verified: Er$^{3+}$, Yb$^{3+}$. The crystalline system corresponds to the hexagonal structure.

- The information obtained from the HRTEM images allowed to verify the estimated average grain size, which is around 15nm, belonging to the structure of LaF$_3$.

- In the future it is expected to be able to functionalize the nanoparticles by means of a nanostructured design from core to layer, covering the LaF$_3$: Er$^{3+}$, Yb$^{3+}$, in order to provide it with characteristics for possible applications in biomedicine, where these nanoparticles would produce emissions when placed inside cells.

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