Synthesis of NaYF₄: Yb, Tm Nanoparticles by Solvothermal Method and Characterization by Upconversion Visible Radiation Fluorescence

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Abstract. We report the synthesis of NaYF₄ nanoparticles doped with rare earth ions Yb³⁺, Tm³⁺, using the solvothermal method. These nanoparticles were synthesized varying the concentration of Tm³⁺, considering 0.5%; 1.0%; 1.5% and 2.0% of Tm³⁺ instead of the Y ions in NaYF₄ in order to study variations in their emissions around 480 nm. The results show a better performance of 1% Tm³⁺ doped nanoparticles. We report emission spectroscopy results using a 980 nm diode laser.

1. Introduction

Lanthanides are a special group of chemical element of the periodic table, because of the particular characteristics of their 4f orbitals. These inorganic materials with interesting fluorescent properties, when combined with a host, as in the case of Tm³⁺ and Yb³⁺ in NaYF₄, present the phenomenon known as upconversion [1] where an Yb transition is transferred to increase the energy of an excited electron in Tm³⁺ atom. This array of doping ions in a host is known as Upconversion nanoparticles (UCNPs).

Figure 1. Schematic of the Upconversion process as in NaYF₄ matrix with its doping ions Yb³⁺, Tm³⁺.

In these UCNPs one of the doping Ln³⁺ ions acts as a sensitizer, absorbing light. The sensitizer emits light, which is absorbed by the other Ln³⁺ doping ion (activator). This activator emits light at a wavelength greater than the absorbed light [2]. In addition, the inorganic matrix NaYF₄ is useful because of its low vibrational energy and high refractive index [3].

The NaYF₄ matrix has two polymorphic crystalline structure, the α-phase that is a cubic structure and the β-phase that is a hexagonal structure; these appear depending on the synthesis method and conditions [4]. Previous research showed that the β-phase presents a better crystalline for the different doping ions, in addition, the formation of the NaYF₄ matrix can be done with various synthesis methods such as coprecipitation, hydrothermal and solvothermal, the latter is developed...
when a chemical compound in liquid mixed placed in a closed container and heated above its boiling point, generating a pressure above atmospheric, with the objective of a better dissolution between the mixed chemical compound [5]. Finally, the characterization of these nanoparticles is carried out with the luminescence of Upconversion, using diode laser of 980 nm for its good affinity to be absorbed, and analyzing its fluorescence spectrophotometer.

2. Method of synthesis and characterization NaYF₄ nanoparticles

The method used for the synthesis of the nanoparticle NaYF₄ was solvothermal method. The chemical compounds were initially separated into three beakers of 100ml. The 1st beaker with 3.6 mmol of NaCl (Sigma Aldrich), 1.431 mmol of YCl₃.6H₂O (Sigma Aldrich), 0.0324 mmol of YbCl₃.H₂O (Sigma Aldrich) and 0.036 mmol of TmCl₃.6H₂O (Sigma Aldrich), the 2nd beaker with 27 ml of polyethyleneimine and 17 ml of ethylene glycol and the 3rd beaker with 0.027g NH₄F and 17ml of ethylene glycol, then homogenous mixing was carried out with the aid of a magnetic stirrer [Figures 2a and 2b]. The mixed sample was poured in a Teflon and sealed with an autoclave for its respective solvothermal process, for this we heated it to 170°C for 6 hours in an oven and the temperature was controlled by a Eurotherm 2408f [Figures 2c and 2d].

After this process, the heated sample in centrifuge tubes was placed in a centrifuge equipment (universal centrifuge PLC-012E) for its respective precipitation. After this process 3ml of residual liquid was to remove, then 2ml of ultrapure water and 2ml of ethanol were aggregated to clean the sample and it was centrifuged again. This process was repeated three times [Figure 2e]. After this, the sample was separated in a 25ml crucible and taken to an electric oven to perform the drying of the sample [Figure 2f], the dry sample was again taken to the oven to carry out a heat treatment. This consisted of taking the NaYF₄ sample at 400°C with two different time periods of 2 and 3 hours, this was in order to study dependence of the characterization of the sample with the periods of heat treatment. [Figure 2g].

Finally, the sample was taken to an experimental arrange in order to visualize the luminescence it presented, and to carry out its characterization. This arrange included a 980nm laser diode, 2 lenses placed between the sample, a ramp to position the sample and a filter positioned in such a way to allow the luminescence of the sample to pass through.
way that it received the emission of the sample. This emission was taken to a spectrophotometer (Science-surplus), through its software the sample emissions peaks were analyzed [Figures 2h and 3].

![Image](image.png)

**Figure 3.** Characterization by emission spectrometry. On the left: the encapsulated sample, diode laser, spectrometer, lenses, and the optical fiber used in the experiment. On the right: the sample emission spectrum registered by the computer.

### 3. Interpretation and Discussion

The samples were placed in two groups. Each group had samples with different molar concentrations of thulium dopant ions at 0.5%, 1.0%, 1.5% and 2.0%. A different thermal treatment was applied to each group of samples. Emission spectra are shown in Figure 4 for both groups of samples. Spectra shown in Figure 4.1 have three prominent peaks (with a highest intensity of nearly 25 000 u.a.) at wavelengths of 450nm, 477nm and 645nm with the most prominent peak being at 477nm which corresponds to the $^1G_4 \rightarrow ^3H_6$ transition.

In Figure 4.2, the highest intensity is approximately 21 000 u.a., this also presented three prominent peaks and it is observed again that the molar concentration at 1.0% Tm has better intensity than the other concentrations.
Figure 4. Emission spectra of the 4 Tm samples (0.5%: 1%: 1.5%: 2%). (1) Emission spectra with heat treatment 2 hours at 400°C. (2) Emission spectra with heat treatment 3 hours at 400 °C.

An X-ray diffraction (XRD) spectrum was carried out to the sample of 1% Tm molar concentration with two hours of heat treatment. Figure 5 shows the XRD spectra of this sample. Spectra shows the presence of α-phase (in red) and the β-phase (in blue). In this Figure, in the small graph, we present the diffraction pattern obtained from the literature for NaYF₄ α-phase and β-phase.
Figure 5. X-ray diffraction spectrum of 1% Tm molar concentration of NaYF4; Yb, Tm, and its miller index of diffraction patterns, small graph shows the comparison between x-ray diffraction spectrum and diffraction patterns of inorganic matrix NaYF4 α and β-phase taken from references [6] y [7].

4. Conclusions

- Using the Solvothermal method it was possible to synthetize NaYF4 nanoparticles doped with Yb³⁺, Tm³⁺ ions and blue luminescent emission could be observed.
- For both heat treatments (by 2 and 3 hours at 400 °C), 1% Tm concentration samples shows to be the most efficient emission ones.
- Heat treatment at 400°C by 2 hours let us get a better contrast between the observed emissions.
- X-ray diffraction spectra for the 1% Tm molar concentration with 2 hours of heat treatment shows a good correspondence with X-ray patterns of β-NaYF4 and α-NaYF4 matrix.
- Future work with these nanoparticles will be performed using 1% Tm samples.

5. References

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