Study of different production processes of doped rare earth fluorides nanoparticles: co-precipitation and microfluidics

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Recently, rare earth doped nanocrystals received great attention due to their application in high-resolution panels, integrated optical systems and biological labeling. For efficient application of such materials, it is important that they can be produced in a reproducible way. The controlled synthesis of nanoparticles with uniform size, shape, structure and rare earth doping became of fundamental importance once the final properties are directly related to these parameters [1].

The $NaYF_4$ is a very efficient host matrix for trivalent rare earth ions such as Yb/Er and Yb/Tm for up-conversion systems. This fluoride crystallize in different dimensions and shapes in both its cubic and hexagonal phases. There are several synthetic processes already reported in the literature for production of this material, involving different chemical routes and processing from organic and inorganic compounds, however, the reproducibility of these processes are not always achieved.

The objective of this work is to study different process for preparation of $NaYF_4$:Yb:Er up conversion fluorides nanoparticles aiming a reproducible form to obtain these nanocrystals with well-defined size, shape and structure targeting biological and medical applications.

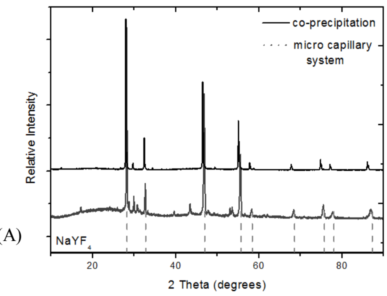
Two production process are under study: (1) $NaYF_4$ co-doped with Yb^{3+}/Er^{3+} obtained by co-precipitation with different fluorinating compounds and, (2) $NaYF_4$ co-doped with Yb^{3+}/Er^{3+} obtained by micro-flow reaction using a microchannel and a micro capillary system. The microfluidic circuit was designed and fabricated at the Center for Lasers and Applications at IPEN. The micro capillary system was a commercial Asia flow chemistry modules from Syrris Co.

Rietveld analysis of X-ray data showed that $NaYF_4$:10%Yb^{3+}/0,5%Er^{3+} were obtained by the co-precipitation method with cubic phase, presenting crystallite size in the range of 70 nm (Fig 1a). Routes using different fluorine sources were tested, and the best results were obtained from the addition of a NaF excess in the starting compounds.

Before the study of the synthesis process, the ideal microchannel architecture for the flow chemical reactions has to be defined. The microfluidic system designed at IPEN (Fig1b.) is a two-stage microfluidic reactor: in the first stage, the product stream (NaF solution) is combined with the second precursor stream ($RECl_3$ solution, were RE = rare earth). In the second stage the compounds flow through a heated zone (temperature range of 70 - 100ºC). The main compounds are guided through the system with two syringes, with flow controlled by the applied pressure (electronic controlled). Preliminary experiments are under way to analyze injection flow rates of the components, aiming to define the residence rate and temperature for desired nanoparticles production.

With the Asia flow chemistry modules different experiments were performed with flows in the range of 100 – 600 μL/min, for NaF and $RECl^3$ solutions, at temperature of 125°C. No chemical reaction were observed between fluorides and the microcircuit materials. The obtained material are under characterization to determine the efficiency of the experimental conditions adopted, in the size and phase of obtained NCs. Other experiments are in progress.

(A)



(B)

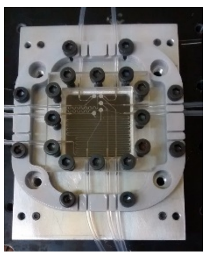


Fig.1: (a) X-ray pattern of nanoparticles obtained by co-precipitation and micro capillary system; (b) Microfluidic system designed and fabricated at IPEN for nanoparticles preparation.

[1] P.N. Prasad, Nanophotonics, Wiley, Hoboken, NJ, 2004.