Microfluidic synthesis of $NaYF_4$:Yb/Er nanoparticles

T. F. Amorim da Silva, C. H. Costa, A. S. Vianna Jr, W. de Rossi, V.L. Mazzocchi, R.E. Samad, N.D. Vieira Jr, S. L. Baldochi

tfasilva@ipen; cristhianoherrera@gmail.com; ardson@usp.br; wderossi@ipen.br; vlmazzo@ipen.br; resamad@ipen.br; nilsondv@ipen.br; baldochi@ipen.br.

Abstract:. *Synthesis of fluoride nanoparticles were studied using microfluidic devices. Experiments were performed in a glass microchip designed and produced at IPEN with femtosecond laser machining for nanoparticles synthesis and with commercial Asia chemistry modules system. $NaYF_4$ co-doped with Yb^{3+}/Er^{3+} were obtained in both systems but additional experiments for synthesis parameter optimization as well as in the IPEN microchip design are necessary to obtain single phase nanoparticles.*

Key-Words*: microfluidics devices, laser machining, nanoparticles; fluorides.*

Introduction: Recently, rare earth doped nanocrystals received great attention due to their application in high-resolution panels, integrated optical systems and biological labeling. 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 upconversion systems [2]. 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 the preparation of $NaYF_4$:Yb/Er upconversion fluorides nanoparticles using microfluidics devices, aiming a reproducible form to obtain these nanocrystals with well-defined size, shape and structure targeting biological and medical applications.

Experimental: Two-production process are under study: $NaYF_4$ co-doped with Yb^{3+}/Er^{3+} obtained by micro-flow reaction using a microchannel (microchip) and a micro capillary system (commercial Asia modules). The microchip designed and produced at IPEN with femtosecond laser machining (Fig.1) is a two-stage microfluidic reactor with one heated zone.

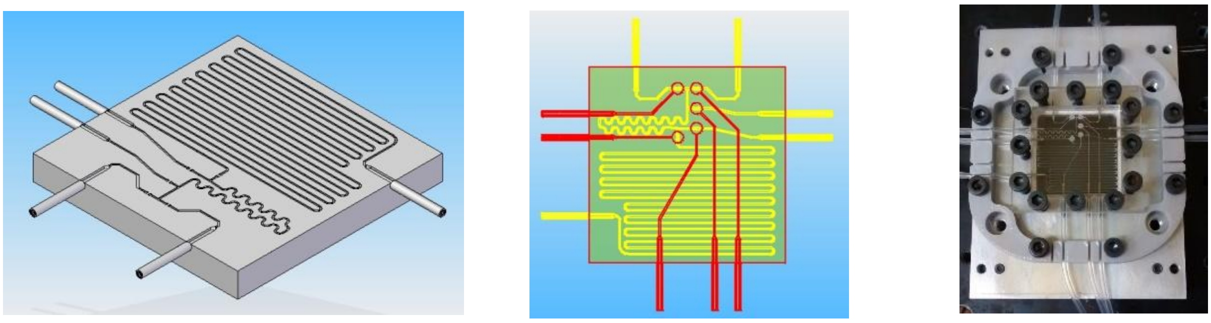
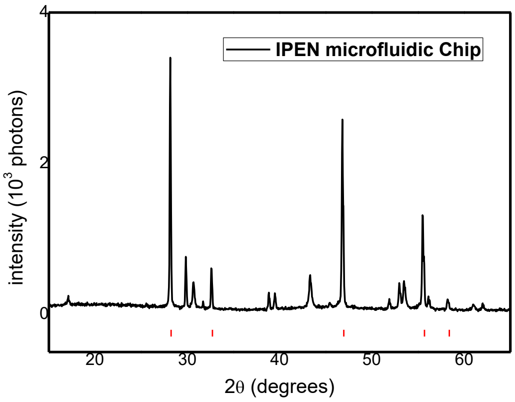


Fig 1. Microfluidics system designed and fabricated at IPEN for fluoride nanoparticles preparation.

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 60 to 100ºC). The main compounds are guided through the system with two syringes, with flow controlled by the applied pressure. In the Asia flow chemistry modules synthesis experiments were performed with flows on the range of 100 – 600µL/min, for NaF and $RECl_3$ solutions, at temperature of 120°C.

Results and discussion: Two chips with similar design were tested: one with ~200 microns micro-channels and a second one with ~400 microns micro-channels. Although no chemical reaction were observed between fluorides and the micro-reactor material (BK7 glass), in the first IPEN chip, with 200microns channels, clogging was always observed in the first stage of the chip. In the second chip fabricated with larger micro-channels this problem was not observed. No chemical reactions were observed between compounds and micro-tubes of the Asia modules either. The ideal solutions (concentration) for both devices were empirically defined for both components to obtain an uniform flow, without clogging, until the end of the synthesis. Nanoparticles of $NaYF_4$:10%Yb^{3+}/0,5%Er^{3+} were obtained with cubic phase, in the Asia modules and IPEN microchip synthesis, but others phases, not yet identified, were also observed in the X ray pattern as can be observed in Fig. 2.



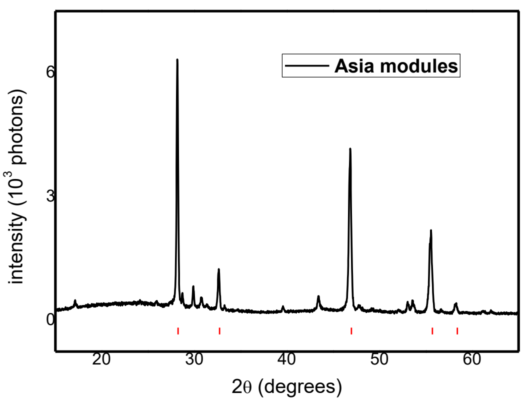


Fig 2. X-ray pattern of nanoparticles obtained by IPEN microfluidic chip and Asia flow chemistry modules. The red bars represents the cubic $NaYF_4$ phase.

Conclusion: Microfluidic were applied to obtain nanoparticles of rare earth doped $NaYF_4$. Synthesis using a commercial micro-flow reactor (Asia modules) resulted in nanoparticles with cubic structure but adjustment of reaction parameters as the residence rate and temperature are necessary for single-phase nanoparticles production. The microchip designed and fabricated at IPEN showed similar results of the commercial micro flow reactor and additional experiments for synthesis parameter optimization as well as in the microchip design are under development.

References and Acknowledgements:

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

[2] D. Vennerberg, Z. Lin. Upconversion Nanocrystals: Synthesis, Properties, Assembly and Applications. *Sci. Adv. Mat.*, 3 (2011) 26.

This work was supported by FAPESP - project nº 2013/261136 and CNPq INCT project nº 465763/2014-6.