Structural, morphological and spectroscopic properties of upconversion Yb^{3+}/Er^{3+} co-doped $NaYF_4$ nanoparticles

Silvana R. Oliveira[1], Rafael R. Pereira[1], Rogéria Rocha Gonçalves[1*]

[1] *Departamento de Química, FFCLRP – USP, Ribeirão Preto – SP, Brasil*

*e-mail: rrgoncalves@ffclrp.usp.br

Rare earth (RE) fluorides are important compounds in the material field due to their unique applications in optical communications, three-dimensional displays, solid-state laser, photocatalysis, solar cells, biochemical probes and medical diagnostics.[1] Among them, sodium yttrium fluoride ($NaYF_4$) is one of the most noteworthy host lattices for multicolor upconversion (UC) luminescence of the doped RE ions. At ambient pressure, $NaYF_4$ exists in two polymorphs: a cubic phase and a hexagonal phase, depending on the synthesis conditions.[2] The hexagonal phase (β) exhibits considerable enhanced UC emissions compared with the cubic one and then, how to obtain pure β - $NaYF_4$ is crucial in successfully achieving high luminescence performance. Although there are many excellent routes to the synthesis of β - $NaYF_4$ nanoparticles with various sizes and shapes, these often require the use of toxic and/or expensive precursors and an organic phase at high temperature. Hydrothermal and microwave hydrothermal syntheses were investigated aiming to obtain simple, low-temperature and fast (MW synthesis) synthetic pathways to fabricate water-soluble Er^{3+}/Yb^{3+} co-doped $NaYF_4$. In both cases, syntheses were done in ethanolic medium and chlorides of rare earth ions were used. Sodium acetate and ammonium hydrogen difluoride were used as the sodium and fluorine sources. EDTA was used to tune the size and morphology of the products. A pure cubic phase (α) and a mixture of phases (α and β) were obtained by hydrothermal syntheses in ethanolic medium (24 h), at 180 and 200 ^{o}C, respectively. These nanoparticles were spherical with average diameter around to 150 nm and 100 nm, for 180 and 200 ^{o}C, respectively. The NIR emission spectra of the pure cubic phase and of the mixture of phases were similar, presenting a broadband with a maximum around 1531 nm corresponding to $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ions when excited at 980 nm radiation. The observed broadband is due to different symmetry sites of the cubic and hexagonal phases of $NaYF_4$. Furthermore, a strong and naked-eye upconversion luminescence upon direct 980 nm excitation was obtained for the mixture of phases (α and β) which makes it a promising material for many applications. Upconversion dynamics were determined by the photons number, evidencing that ESA or ETU mechanisms are probably taking place. After annealing at 400 ^{o}C for 5 h, the mixture of phases enhanced the proportion of the hexagonal phase demonstrating the partial conversion of the (α) to the hexagonal phase (β). The same hydrothermal synthesis was done changing the autoclave by the microwave oven. At 200 ^{o}C, a mixture of phases was found in a much shorter time, 20 minutes. After annealing at 400 ^{o}C for 5 h, the major component was the hexagonal phase but the mixture of phases still remains.

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