Morphology controlled hydrothermal synthesis processes and emission near 2 μm of Tm^{3+}- doped Lu_2O_3 nanostructures

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Due to the conjunction of excellent thermo-mechanical properties, high optical cross-sections and high doping potential for rare-earth laser cations, the sesquioxides Sc_2O_3, Y_2O_3 and Lu_2O_3 are attractive hosts for high power solid-state lasers [1]. Giving its very similar mass and size the latter is the choice material for the favorable incorporation of the highest concentration of Tm^{3+}. The 1.95 μm eye-safe laser emission operating in the $^3F_4 \rightarrow {}^3H_6$ of Tm^{3+} can advantageously replace the traditionally used Ho^{3+}-doped analogue crystal, in the same spectral range, when pumping with high power AlGaAs diode lasers.
However, the high melting temperature, ~2500 ºC, of Lu_2O_3 supposes serious difficulties for the production of bulk crystals. As an alternative, diverse low temperature methodologies have been extensively applied to prepare nanocrystals of this phase, mainly intended for fabricating transparent laser ceramics [2]. Another possibility to be explored is the incorporation of these nanoparticles in hybrid composites. A first step in this direction is the synthesis of Tm^{3+}-Lu_2O_3 nanocrystals with size and morphologies suitable for dense sintering or for infiltration or merging with other materials also transparent in the mid-infrared.

In this work a simple hydrothermal route to synthesize nanoparticles of $Lu_{2-x}Tm_xO_3$ is presented. Hydrothermal processes benefit not only of much lower temperatures than other preparation methods but also of being advantageous for homogeneous nucleation of nanocrystals with well-defined morphologies. Two distinct shapes such as micron size rods with ~ 90 nm ∅ and nanosquare sheets have been obtained for Tm^{3+} concentrations ranging from 50% mol to 0.2% mol Tm (i.e., $1.0 \geq x \geq 0.004$) by choosing the starting reagents and adjusting the pH value, 7.5 and 12 respectively, of the reacting solution, which lasted in all cases the same time, 24h. Powder X-ray analyses indicate that both prepared structures are the pure cubic $Ia\bar{3}$ phase, see Figures 1a and 2a, while FESEM and TEM images confirm the formation of different morphologies, as shown in Figures 1b-c and 2c-d. The photoluminescence at ~1.95 μm of Tm^{3+} and emission lifetimes in these materials have been measured, and the dependence with the concentration and morphology is analyzed.

Consequently, the control of the hydrothermal reaction conditions open the possibility for obtaining the most adequate morphology for a same $Lu_{2-x}Tm_xO_3$ material to be incorported in a given hybrid composite: given the near uniform distribution of sizes for nanosquare sheets they can be the choice for dispresing in transparent polymers, or used as precursors for transparent laser ceramics, while micron size rods will allow their incorporation in 2D and 3D patterned structures.

References:

[1] A. Giesen, H. Hügel, A. Voss, K. Witting, U. Brauch, H. Opower, Appl. Phys. B **58** (1994) 365.
[2] M. Tokurakawa, K. Takaichi, A. Shirakawa, K. Ueda, H. Yagi, S. Hosokawa, T. Yanagitani, A.A. Kaminskii, Opt. Express **14** (2006) 12832.

Figures:

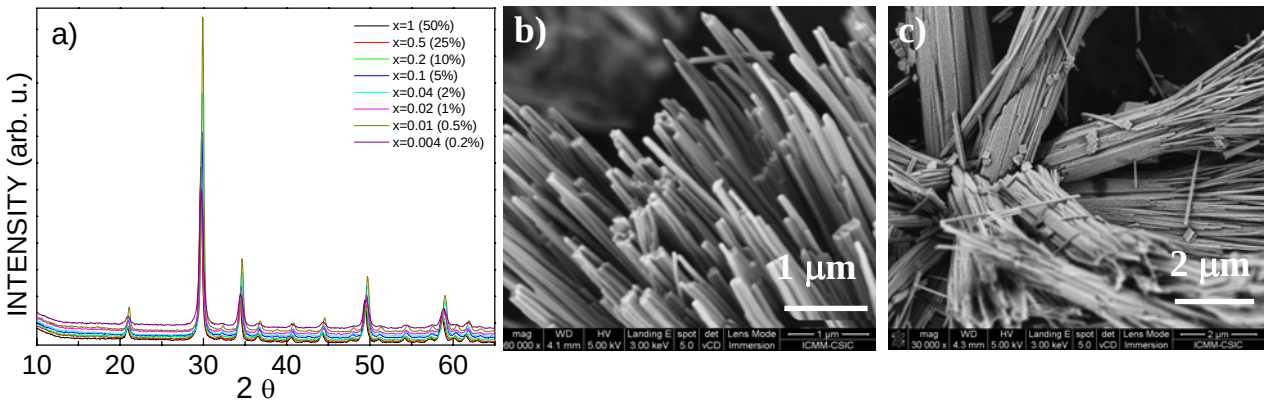

Figure 1. Hydrothermally prepared $Lu_{2-x}Tm_xO_3$ from chloride precursors (pH=7.5 and 185 ºC during 24 h, followed by annealing at 800 ºC during 30 min: a) XRD patterns showing the pure cubic *Ia*-3 phase for all Tm^{3+} concentrations, $1.0 \geq x \geq 0.004$, the FWMH of peaks indicating ~25 nm size for particles; b) FESEM image of micron size nanowires constituting the product of the hydrothermal synthesis (x=0.04); c) FESEM image of the final calcined product (x=0.04), where the predominant morphology consists of rods 15μm×90 nm ∅

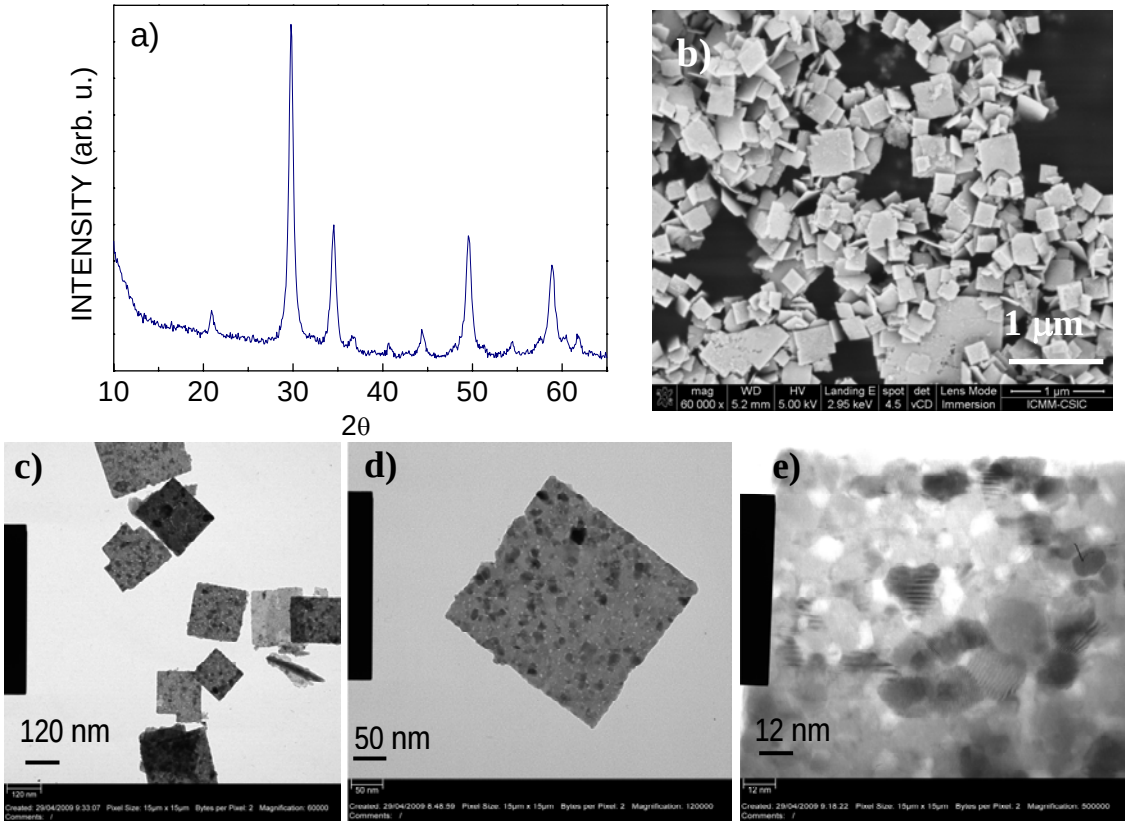

Figure 2. $Lu_{2-x}Tm_xO_3$ (x=0.1) hydrothermally prepared from nitrate precursors (pH=12 and 185 ºC during 24 h, followed by annealing at 600 ºC during 1 h: a) XRD pattern showing the pure cubic $Ia\bar{3}$ phase of the final product, the FWMH of peaks indicating ~10 nm size for particles; b) FESEM micrograph of final product consisting of ~150 nm square nanosheets; c), d) and e) TEM images of square nanosheets, the latter showing the elemental ~10 nm particles within square nanosheets.