**Synthesis and characterization of Tm doped $Lu_2O_3$ nanocrystalline powder**

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Rare earth (RE) doped materials are drawing much attention for many display and lighting devices such as plasma displays panels, electroluminescence and light-emitting diodes [1,2] since they can offer higher luminous efficiencies and lower manufacturing costs. On the other hand, the synthesis and preparation of RE doped nanocrystals of some laser materials is the first step in order to obtain their transparent laser ceramic. The use of ceramics as an alternative to single crystals is justified in some compounds, in which the crystal growth is difficult and has a high cost. Furthermore, the ceramics show better thermo-mechanical properties, such as the thermal shock parameter and resistance to the laser damage [1]. Highly transparent cubic ceramic materials $Y_3Al_5O_{12}$ (YAG) and RE sesquioxides $RE_2O_3$ have received great attention due to the improvement reached in nanocrystalline technology [2,3,4]. The $RE_2O_3$ oxides are interesting as laser materials for high power applications due to their high thermal conductivity, low phonon energy values and strong crystal field for the active ion [5].

We focused our attention in $Lu_2O_3$ doped with thulium ($Tm^{3+}$). The tunable laser emission of $Tm^{3+}$ around two microns has many interesting applications such as remote sensing and medicine, for instance, based on the atmospheric transparency window and the absorption of water at this wavelength range, respectively. It is well-known that the $Lu_2O_3$ matrix is highly chemical and thermal stable and has a broad optical transparence from the visible to the NIR regions [6]. The synthesis of nanocrystals with high crystalline quality and narrow size distribution is an important first step towards obtaining transparent laser ceramic materials. These two factors allow a more dense packing of the particles and minimizing light scattering.

$Tm^{3+}$ doped $Lu_2O_3$ nanocrystals $Lu_{2-x}Tm_xO_3$ with x = 0.01 – 0.3 (i.e., 0.5 - 15 mol at. % $Tm^{3+}$) were synthesized by a modified Sol- gel Pechini method. The maximum temperature at which these crystals have been synthesized has been 1073 K. In all cases, the obtained nanoparticles crystallize in the cubic system, with the space group of symmetry $Ia\bar{3}$. The mean particle size in all the cases was below 100 nm. We studied the evolution of the grain size with temperature and linear thermal expansion coefficient has been determined, 7.5 x $10^{-6}$ $K^{-1}$, and a grain growth activation energy value 76 kJ/mol for x = 0.15. No grain growth was observed until sintering at 1073 K. It has been observed in literature that there is a dependence of the grain size growth in relation with the doping-$RE^{3+}$ concentration [7]. However, no dependence of the size was observed as a function of $Tm^{3+}$ content.

The photoluminescence spectra show the large crystal field splitting characteristic of sesquioxides. We have observed that the $^3H_4$ and $^3F_4$ luminescence decays after short pulse excitation at 800 nm with low enough $Tm^{3+}$ concentration exhibit non exponential kinetics, which can be analytically reproduced by the sum of two exponential regimes. The shortest one would correspond to the emission of $Tm^{3+}$ ions at the surface of the nanoparticles and the longest one to $Tm^{3+}$ ions in the body of the nanoparticles, which in principal should approach to the value obtained in Tm-doped $Lu_2O_3$ bulk single crystals. The fast and slow decay components decrease with increasing $Tm^{3+}$ concentration.

Cathodoluminescent properties of the thulium doped nanocrystals have been investigated. The blue emission of the thulium doped nanocrystals had a CIE chromaticity coordinates of x=0.200, y=0.156 with a dominant wavelength of 468 nm. A color purity of 54% has been obtained in comparison with CIE Standard Illuminant C. The excitation voltage for cathodoluminescence measurement was 15 kV and the probe current 20 nA. Besides the major blue emission peak at 457 nm, a few minor peaks at 362, 724 and 812 nm were identified. (there are peaks at other positions, which are attributed to other lanthanide elements contamination.) These peaks are characteristic of transitions between electronic energy levels of $Tm^{3+}$ ions. The major peak centered at 457 nm corresponds to the transition from

$^1G_4 \rightarrow {}^3H_6$, while the transitions from $^1D_2 \rightarrow {}^3H_6$, $^1G_4 \rightarrow {}^3F_4$, and $^1G_4 \rightarrow {}^3H_5$ of the $Tm^{3+}$ ion are related to the emission peaks at 364, 680 and 813 nm, respectively.

**References**


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**Figures**

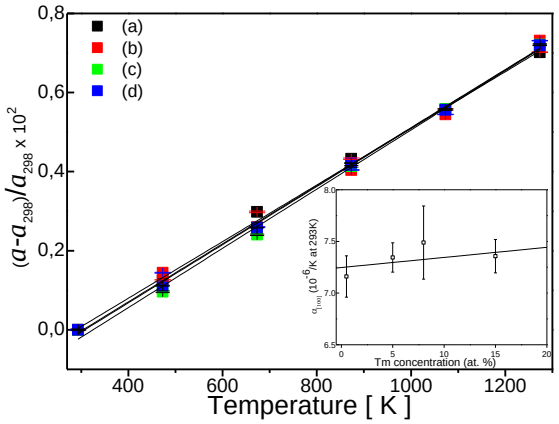


Fig. 1 Relative thermal evolution of the cell parameter a for $Tm:Lu_2O_3$ nanocrystals: (a) 0.5 at. %. (b) 5 at. %. (c) 8 at. %. (d) 15 at. %.

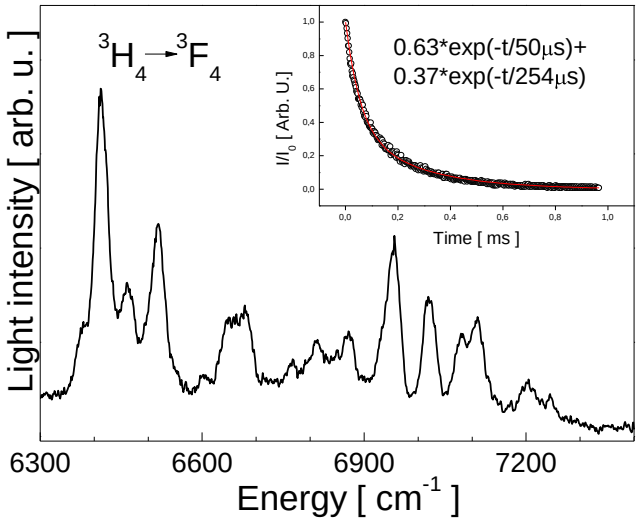


Fig. 2. 300 K $^3H_4 \rightarrow {}^3F_4$ photoluminescence of 5 at. % Tm nanoparticles excited at $\lambda_{EXC}$= 800 nm. Inset: Photoluminescence intensity decay of this transition at 300 K recorded at $I_{EMI}$= 1558 nm fitted with two exponential decays of the $(I/I_0)$ vs t dependency.