Up-conversion in Yb^{3+}-Ho^{3+}-Tm^{3+} co-doped $NaYF_4$ nano-crystals embedded in a silica glass synthesized by sol-gel route

A. Santana-Alonso[1], J. Méndez-Ramos[2,], A.C. Yanes[1], J. del-Castillo[1] and V.D. Rodríguez[2]*
[1]Dpto. Física Básica, Universidad de La Laguna, 38206 La Laguna, Tenerife, Spain
[2]Dpto. Física Fundamental y Experimental, Electrónica y Sistemas, Universidad de La Laguna, 38206 La Laguna, Tenerife, Spain
jmendezr@ull.es

$NaYF_4$ is an excellent host material for rare earth ions presenting very high efficiencies in up-conversion processes. Nano-glass-ceramics containing $NaYF_4$ nano-crystals emerge as promising candidates for general lighting appliances and integrated optical devices [1, 2]. Here we report highly transparent nano-glass-ceramics comprising rare-earth doped $NaYF_4$ nano-crystals prepared by adequate heat treatment of precursor glasses synthesized by the sol-gel technique. Thus, silica glasses with composition $95SiO_2$-$5NaYF_4$ co-doped with 0.3 Yb^{3+} and 0.1 Ho^{3+} and tri-doped with 0.3 Yb^{3+}-x Ho^{3+}-0.1 Tm^{3+} with x = 0.1, 0.05 and 0.025 (mol%) were obtained by sol-gel method as described in [3,4]. Subsequently, these sol-gel glasses were heat-treated in air at different temperatures ranging from 500 to 650 °C in order to achieve controlled precipitation of nano-crystallites, giving rise to transparent glass-ceramics. A structural analysis by means of X-ray diffraction measurements confirmed the formation of $NaYF_4$ nano-crystals analyzing the crystallization degree of nano-glass-ceramics as function of the heat treatment temperature. Luminescence features have been also related to the crystallinity degree of the samples. Red, green and blue up-conversion emissions were obtained under infrared excitation at 980 nm and corresponding mechanisms involved have been analyzed in terms of excited state absorption and energy transfer processes. A comparison between co-doped and tri-doped samples reveals that the introduction of Tm^{3+} ions, with appropriate heat treatment and doping levels, results in the addition of the blue up-conversion emission that along with the green and red ones, gives rise to an efficient white light generation that could be seen by the naked eye. High energetic up-conversion emissions and well-resolved Stark structure of emission bands support the conclusion of crystalline-like environment for the rare-earth ions into the precipitated nano-crystals. The total visible up-conversion emissions have been quantified in the CIE standard chromaticity diagram. Finally, bright white light generation has been achieved in Yb^{3+}-Ho^{3+}-Tm^{3+} tri-doped samples with appropriate choice of heat treatment temperature and adequate relative rare-earth doping level.

References:

[1] J. F. Suyver, J. Grimm, M. K. Van Veen, D. Biner, K. W. Krämer, H. U. Güdel, J. Lumin., **1** (2006) 117.
[2] F. Liu, E. Ma, D. Chen, Y. Yu, Y.Wang, J. Phys. Chem. B **110** (2006) 20843.
[3] S. Fujihara, C. Mochizuki and T. Kimura, J. Non-Cryst. Solids, **244** (1999) 267.
[4] A. C. Yanes, A. Santana-Alonso, J. Méndez-Ramos, J. del-Castillo and V. D. Rodríguez, **480** J. Alloys Compd. (2009) 706.

Acknowledgments:

The authors would like to thank Gobierno Autónomo de Canarias (PI042005/039), Consejería de Industria, Comercio y Nuevas Tecnologías (IDT-TF-07/077) and Ministerio de Ciencia y Tecnología of Spain Government (FIS 2006-02980) for financial support.

Figures:

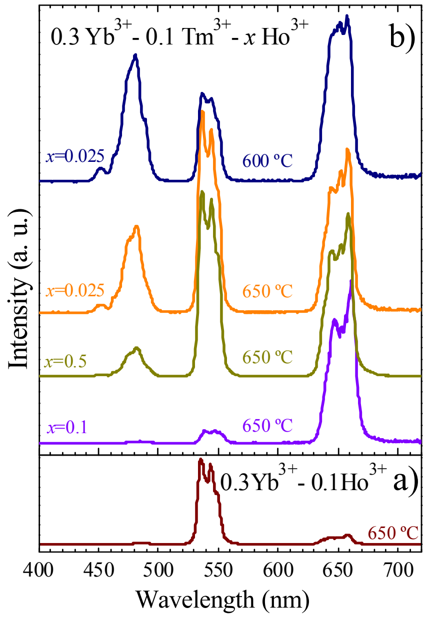

Figure 1. Up-conversion emission spectra under 980 nm excitation at 200 mW pump power corresponding to (a) $95SiO_2$-$5NaYF_4$: 0.3 Yb^{3+}, 0.1 Ho^{3+} (mol %); and (b) $95SiO_2$-$5NaYF_4$: 0.3 Yb^{3+}, *x* Ho^{3+} and 0.1 Tm^{3+} (mol %) nano-glass-ceramics, with *x* = 0.1, 0.05 and 0.025, heat-treated at indicated temperatures. Spectra in (b) have been normalized to the 640-660 nm band.

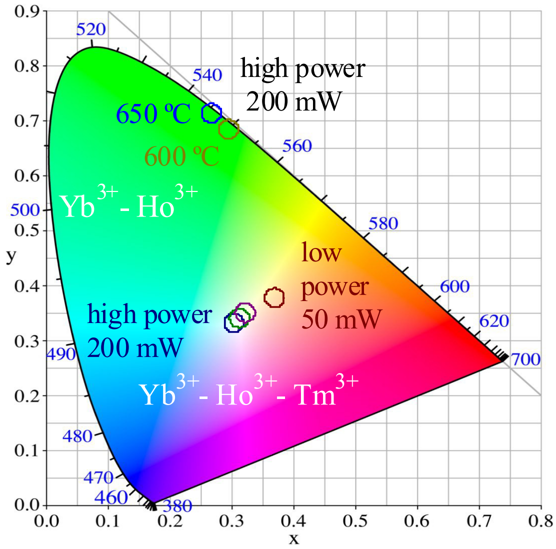

Figure 2. CIE standard chromaticity diagram with corresponding colour coordinates of total visible up-conversion emission under 980 nm pump power at 200 mW of $95SiO_2$-$5NaYF_4$ co-doped with 0.3 Yb^{3+} and 0.1 Ho^{3+} (mol %) nano-glass-ceramics heat-treated at 600 and 650 ºC, respectively. Additionally, colour coordinates of the $95SiO_2$-$5NaYF_4$ nano-glass-ceramics tri-doped with 0.3 Yb^{3+}, 0.025 Ho^{3+} and 0.1 Tm^{3+} (mol %) heat-treated at 600 ºC for different pump powers ranging from 50 to 200 mW are also presented.