A Spectroscopic Study of Er^{3+}/Yb^{3+} co-doped Nb_2O_5 and $SiO_2@Nb_2O_5$ for application as luminescent markers

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Luminescent markers are on the spotlight of new applications in the current biomedical panorama such as biodetection and cancer therapy.[1] Among the most used luminescent materials, certain rare-earth ions such as Er^{3+} and Tm^{3+} show upconversion properties, which are interesting for biological application. Nearinfrared-to-visible upconversion allows greater penetration of the excitation when compared with conventional ultraviolet (and visible) and still shows less harmful results.[2] The goal of the present work is the preparation of nanostructured $Nb_2O_5:Er^{3+}/Yb^{3+}$ powders and $SiO_2@Nb_2O_5:Er^{3+}/Yb^{3+}$ aiming NIR-to-visible upconversion emission of Er^{3+} for biological application as optical markers. The $Nb_2O_5:Er^{3+}/Yb^{3+}$ samples were prepared by dripping an ethanolic solution containing ethoxyethanol, niobium ethoxyde and the rare-earth chloride in a basic ethanolic solution, with further annealing at of 600, 900 and 1100 °C for 2 hours. The same procedure was adopted for the synthesis of *core@shell* $SiO_2@Nb_2O_5:Er^{3+}/Yb^{3+}$, which were obtained by the ethanolic solution being drippled in a basic colloidal dispersion containing silica nanoparticles. The obtained solid was then thermally treated at 900 ° C for 2 hours. Depending on the annealing temperature, orthorhombic or monoclinic Nb_2O_5 phase crystallize. The size and morphology of the *core@shell* nanoparticles were investigated by Scannig Electron Microscopy, which resulted in monodisperse with an average diameter of 500 nm. All $Nb_2O_5:Er^{3,}$ Yb^{3+} and $SiO_2@Nb_2O_5:Er^{3+}/Yb^{3+}$ nanoparticles presented emission in the near-infrared region under excitation at 980 nm, corresponding to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ emission of Er^{3+} ions. Broader band and high NIR emission intensity was evidenced for the $Nb_2O_5:Er^{3+}/Yb^{3+}$ annealed at 600°C, which has an orthorhombic crystalline phase. Concerning NIR-to-visible upconversion emission, all samples showed bands at 532, 545 and 672 nm, which correspond to the $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ emissions of the ion Er^{3+}, respectively. Upconversion dynamics were determined by the photons number, which evidenced that for the green emission, ESA or ETU mechanisms are probably taking place. Cross-relaxation process contributes to increase the red emission intensity, which is more significant for the monoclinic Nb_2O_5 phase. Higher visible emission intensity, evidenced by naked-eye, was observed for the orthorhombic Nb_2O_5 annealed at 900 °C, making them the most suitable candidate for the NIR-to-visible upconverters.

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2. Bünzli, J.C.G; *J. Lumin*, **170** (2016), *866-878.*

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