Sol-gel derived nano-glass-ceramics containing Eu^{3+}- doped $NaYF_4$ nanocrystals

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Transparent glass-ceramics containing rare-earth doped nanocrystals emerge as new class of materials presenting enhanced physical and optical properties with potential applications in optoelectronic technology [1, 2]. On the other hand, $NaYF_4$ crystal is an excellent luminescence host material for rare-earth ions with relevance in a wide range of fields such as lighting, displays, photo-electronic devices, biological labels, solar cells and tuneable infrared phosphors for 3D optical recording [3, 4]. Furthermore, highly transparent nanostructured rare-earth doped glass-ceramics can be obtained by thermal treatment of precursor glasses prepared by the easy and low cost room-temperature sol-gel method [5]. In this sense nano-glass-ceramics containing Eu^{3+}-doped $NaYF_4$ nanocrystals have been successfully developed for the first time by thermal treatment of precursor sol-gel derived glasses with composition $95SiO_2$- $5NaYF_4$: 0.1 Eu^{3+} (mol %).

X-ray diffraction patterns of samples heat treated at temperatures ranging from 550 to 650 ºC confirmed the precipitation of $NaYF_4$ nanocrystals. Moreover, nanocrystal mean radii were calculated by using Scherrer's equation obtaining values ranging from 4.3 to 9.6 nm corresponding to treatment temperatures of 550 and 650 ºC, respectively. Addionally, TEM and HRTEM analysis were carried out for the 650 ºC heat treated sample, see Fig. 1. The precipitated nanocrystals are clearly visible as nearly spherical dark spots homogeneously dispersed in the amorphous silica network. Using HRTEM we can also observe a simple nanocrystal where direct image was filtered by using FFT pattern. A complete spectroscopic study has been carried out. Changes in the luminescence spectra with the temperature of the heat treatment have been analyzed and related to the degree crystallinity of the sample. Luminescence features are indicative of higher incorporation of Eu^{3+} ions into precipitated nanocrystals with increasing heat treatment temperature. In particular, emission spectra have been obtained for different excitation wavelengths discerning between the fraction of the rare-earth partitioned into $NaYF_4$ nanocrystals and those remaining in the amorphous silica glassy phase, see Fig. 2

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Figure:

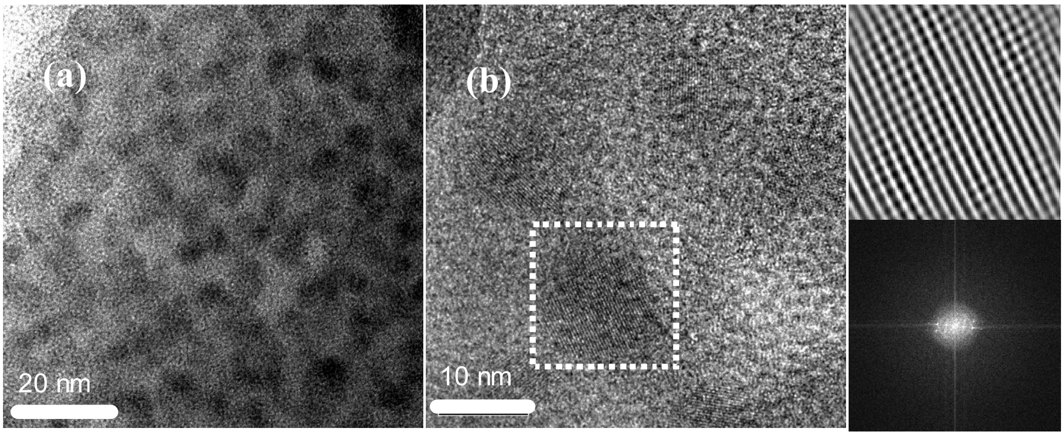

Fig. 1. TEM bright field image shows the presence of $NaYF_4$ nanoparticles in dark contrast (a). HRTEM microphotograph with $NaYF_4$ nanocrystals squared in white (b). The right-bottom image corresponds to the power spectrum obtained from the squared region. The right-up image shows a magnified detail of the same squared region revealing the crystalline pattern of a $NaYF_4$ nanoparticle.

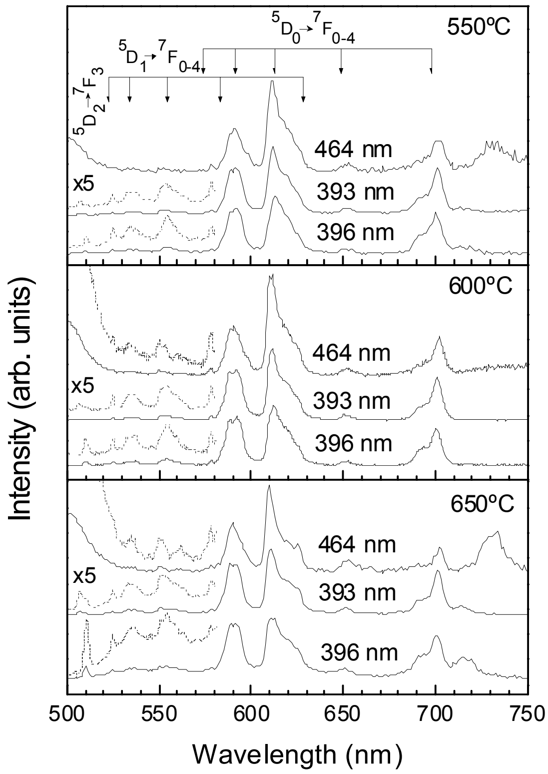

Fig. 2. Emission spectra exciting at 393, 396 and 464 nm, normalized to the maximum intensity at 590 nm. The intensity ratio R between the transitions at 590 and 613 nm increases with heat treatment temperature, indicative of a higher degree of crystallinity. Crystalline-like environment (higher R values) is favoured when exciting at 396 nm.