3NANO-22
Nano Science/Technology/Biotechnology
6th Edition, Roma (Italy)

Synthesis and characterization of rare earth doped α-$NaYF_4$ nanoparticles: Crystal-Field Stark Effect on the upconversion light emission spectrum

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The crystal electric field (CEF) Stark effect affects the upconversion (UC) light emission of the NPs when doped with rare earth elements. Therefore, the knowledge of the CEF parameters, the wavefuncions and energy levels of the rare earth (RE) J-multiplet is expected to be of great help for the understanding and improvement of the UC light emission. In this work, α-$NaY_{1-x}RE_xF_4$ NPs (RE: Dy^{3+}, Er^{3+}, Yb^{3+}; nominal concentration x=0.02) were synthesized by the thermal decomposition method and characterized by means of X-ray diffraction, transmission electron microscopy (TEM) , photoluminescence, electron spin resonance (ESR) and magnetization (Figure 1). X-ray diffraction confirms the cubic crystal structure and TEM images display polyhedral morphology and narrow size dispersion (~8 nm) of the NPs. Fittings of the temperature and magnetic field dependent magnetization were performed in order to determine the 4th and 6th order cubic CEF parameters, B_4 and B_6. The ground state of Er^{3+}, Yb^{3+} and Dy^{3+} in these NPs was confirmed by low temperature ESR experiments. The obtained CEF parameters predict an overall CEF splitting around ~360 K and were used to write down a total Hamiltonian that allows to determine the CEF Stark splitting for all the energy levels of for Dy^{3+}, Er^{3+} and Yb^{3+}, respectively. Than, with the CEF parameters a was simulated the UC light emission line-widths for Er^{3+} doped NPs. The simulated spectrum are in good agreement with the experimental values.

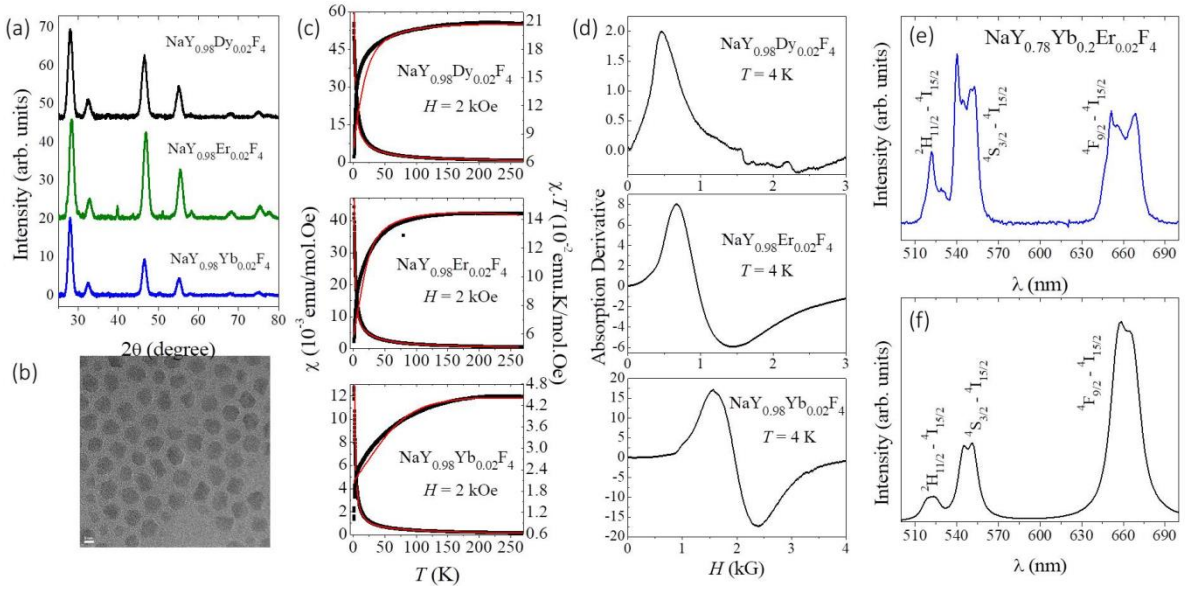

Figure 1: (a) X-ray diffraction, (b) TEM image, (c) magnetic susceptibility and (d) electron spin resonance for Dy^{3+}, Er^{3+} and Yb^{3+}-doped α-$NaYF_4$ NPs. (e) Experimental and (f) simulated upconversion emission spectra of Er^{3+}-doped α-NaYF4 NPs.