

SYNTHESIS AND OPTICAL PROPERTIES OF RARE-EARTH-BASED LAMELLAR NANOHYBRIDS

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The actual requirements for phosphors demands for high emission efficiency and for lower energy excitation compared to standard materials used in luminescent lamps, flat screens, television and biological labelling. However, in order to comply with such requirements new materials are needed. In fact, standard phosphors are based on the absorption due to a charge transfer mechanism related to the excitation of an electron from the oxygen 2p orbital to the 4f orbital of a Eu (III) ion which generally takes place at around 250 nm (i.e. 5 eV).

In order to decrease the required excitation energy materials based on different absorption physical processes are needed. A good approach is to use the larger absorption cross sections and low energetic absorptions of organic molecules to absorb the incident radiation which will be further transferred to the emitting lanthanide ions (“antenna effect”). However, lanthanide (Ln) complexes are known to be unstable under a UV excitation.

In the last few years it was shown that non-aqueous sol-gel reactions of benzyl alcohol with different metal oxides precursors (alkoxides, chlorides, acetylacetonates...) allow the controlled and straightforward synthesis of various crystalline metal oxide nanoparticles [1]. Here we present a general non-aqueous sol-gel route for the preparation of rare-earth (RE) ordered nanocrystalline hybrid structures. In a simple one-pot reaction process, RE (III) isopropoxides (RE= Y, Er, Gd, Sm, Nd) were dissolved in different alcohols (benzyl alcohol or 4-biphenyl-methanol) and reacted in an autoclave between 250 and 300°C. This approach leads to very thin (~0.6 nm) crystalline rare-earth oxide layers regularly separated from each other by organic layers of intercalated organic carboxylate molecules derived from the oxidation of the alcohol used as solvent (the thickness of the organic part is typically between 1.2 - 2.0 nm) Fig.1 [2-5].

The optical properties of such nanohybrids doped with various lanthanides emitting ions were evaluated. It was found that an efficient charge transfer from the organic moieties to the Ln (III) emitting ion takes place. By following such an excitation path the energy required in order to sensitize the luminescent ions is significantly lower than the one needed by similar pure inorganic compounds (Fig. 2). In fact, because the absorption cross section of the intercalated organic molecules is much larger than the one of the charge transfer mechanism related to the excitation of an electron from the oxygen 2p orbital to the 4f orbital of a Ln (III) ion the radiance observed is larger (up to 50%) than the one observed in standard phosphors used in luminescent lamps, screens, etc. Finally due to the presence of organic molecules which naturally emit in the blue and green region of the visible spectrum the emission chromaticity can be tuned by the excitation energy without losing the high radiance values.

References:

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Figures:

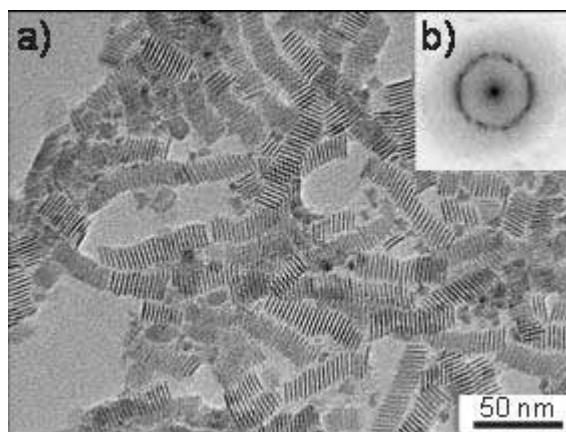


Fig.1: TEM image of Gd-based (a) based biphenolate nanohybrids and Fourier transform (b) show pairs of spots, organized in pseudo circles, which are due to the mesostructural order

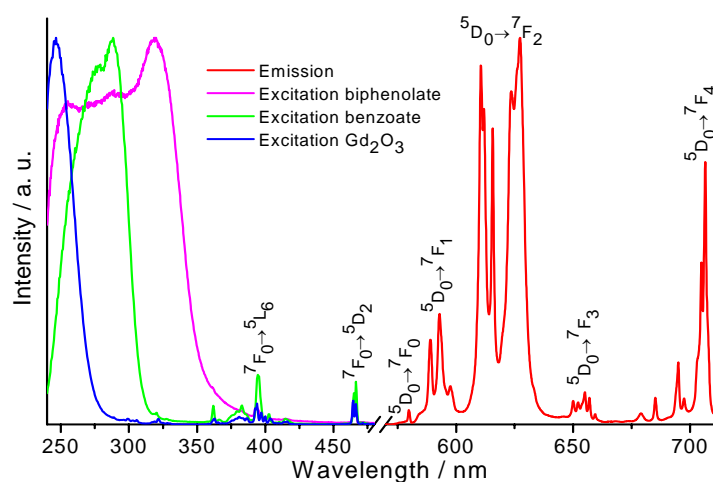


Fig. 2: Excitation (Ex) and emission (Em) spectra of gadolinium ($\lambda_{em} = 612$ nm, $\lambda_{em} = 320$ nm) based nanohybrids doped with Eu^{3+} . In the $\lambda_{em} = 320$ nm based nanohybrids doped with Eu^{3+} . In the excitation spectra of Eu^{3+} -doped Gd_2O_3 (blue line) and Eu^{3+} -doped gadolinium based benzoate nanohybrid (green line)