Optical properties of nanostructured particles synthesized by Spray Pyrolysis route

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Introduction

The investigations in the nanoscaled oxide materials doped with rare earths have received great attention in the recent decades because of their huge possibilities in application of Field Emission Displays (FEDs), Plasma Displays (PDs) and cathode Ray Tubes (CRT). The interest of such materials originates from their extraordinary luminescence, magnetic and catalytic properties.

The processing of europium-doped gadolinia (Gd_2O_3:Eu) nanostructured particles has been realized using the bottom-up chemical approache by a hot-wall spray pyrolysis technique (SP), starting from the aerosol of common nitrates precursors. This method offers the possibility for reaching high-purity nanostructured non-agglomerated particles having spherical morphology and high chemical homogeneity. Moreover, because of extreme synthesis conditions (high heating and cooling rates) the metastable structures can be obtained, as well.

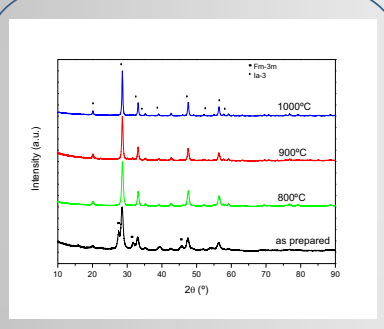
Objectives

The detailed study of the crystalline structure and luminescent properties were proceeded for the different europium concentrations (1, 2 and 6at%) by means of XRD, SEM and steady state-fluorescent spectroscopy. The phase development and structural changes implied the nanocrystalline inner structure (crystallites < 20 nm) and the coexistence of the following crystal phases for as-synthesized SP samples: two cubic phases, having either a bcc (SG: Ia3) or a fcc (SG: Fm-3m) structure, and a monoclinic phase with the space group (SG) C2/m. In the cubic Ia3 phase the cell parameter was affected by the europium concentration and the thermal treatment temperature, followed with progressive increase in crystallite size. On the other side, the monoclinic phase concentration decreased after additional thermal treatments. Luminescence measurements have detected the presence of divalent europium near to 480 nm, aside to the typical trivalent europium spectra. This behavior could explain the increase in the emission intensity in the blue spectral region due to the divalent europium.

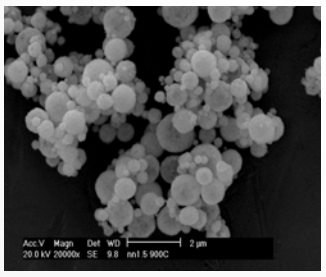
Experimental

Precursor common nitrates solution (0,1M) + Aerosol formation *via* ultrasonic atomization (Three piezoelectric transducers , 2.1 MHz) - 700ºC, air atmosphere ⇒ As-prepared nanoparticles + Thermally treated particles (800-1100ºC)

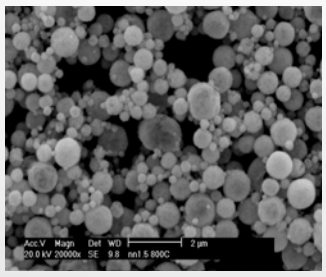
Results



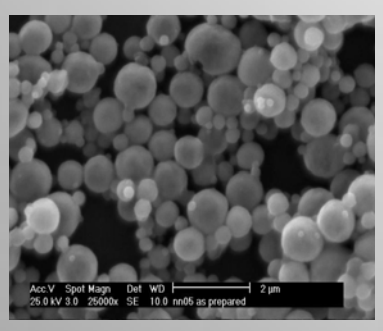
Two crystalline phases of cubic symmetry (Ia-3 and Fm-3m) have been identify in all as-prepared samples. Additional thermal treatment lead to the solely cubic Ia-3 phase.



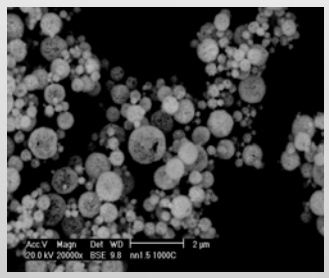
800 ºC



900 ºC

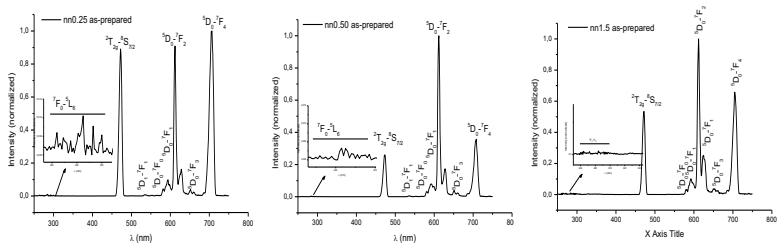


1000 ºC



The particles obtained have a spherical morphology with rough surfaces. The dense particles are non-aglomerated and have a mean crystallite and particle size of 20 and 500nm, respectevely.
With increasing temperature of thermal treatments, it is evident the increase the size of the primary particles.

Europium content (% at.)	Stoichiometry	Nomenclature	Heat treatment (ºC/12h)	Ia-3 a (Å)	Fm-3m a (Å)	Crystallite size (Å)
1	$Gd_{1.95}Eu_{0.05}O_3$	nn0.25	app	10.8156±0.0060	5.6129±0.0040	115±8
			800	10.8154±0.0090	--	164±14
			900	10.8135±0.0013	--	178±68
			1000	10.8140±0.0055	--	254±24
2	$Gd_{1.90}Eu_{0.10}O_3$	nn0.5	app	10.8448±0.0015	5.5978±0.0027	104±8
			800	10.8211±0.0026	--	154±15
			900	10.8176±0.0043	--	205±17
			1000	10.8140±0.0020	--	359±10
6	$Gd_{1.70}Eu_{0.30}O_3$	nn1.5	app	--	--	118±21
			800	--	--	253±95
			900	--	--	359±26
			1000	--	--	459±24



The emission spectra show typical Eu^{3+} ^5D_o-^7F_j (j=0,1,2,3,4) transitions with dominant red emission at 610nm in addition to a 480 nm peak attributed to a Eu^{2+} $^2T_{2g}$-$^8S_{7/2}$.

Fluorescence measurements have shown the existence of a crystallographic phase of monoclinic symmetry (C2 / m) centered around 629 nm, which did not appear in XRD measurements.

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Conclusions

• Hot-wall aerosol route (spray pyrolysis) is applied for the synthesis of nanostructured submicronic-sized spherical particles in the Gd_2O_3:Eu^{3+} system with 1, 2 and 6 atomic% of europium.

•Two cubic crystalline phases have been identified in all as-prepapred samples -Fm-3m and Ia-3; after additional thermal treatment remains only stable cubic phase with symmetry (Ia-3).

• The use of techniques of steady-state fluorescence emission indicates the coexistence of two different oxidation states for the europium (Eu^{2+} and Eu^{3+}), fassociated with the appearance of the monoclinic. Gd_2O_3:Eu phase that was not identified by XRD measurements. The amount of this phase decreases with the increase of the e of heat treatment temperature.

•The appearance of monoclinic phase is atributed to the extreme synthesis conditions (high heating/cooling rates and short residence time) .