THE MORPHOLOGY, STRUCTURE AND LUMINESCENT PROPERTIES OF Gd_2O_3:Eu SYNTHESIZED BY AEROSOL ROUTE AND HIGH ENERGY BALL MILLING

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Abstract

The processing of europium-doped gadolinia (Gd_2O_3:Eu) nanostructured particles has been realized using the bottom-up chemical approaches either by a hot-wall spray pyrolysis technique (SP), starting from the aerosol of common nitrates precursors, or a high energy ball milling (HEBM) of common acetate precursors. The former one yields high-purity nanostructured non-agglomerated particles having spherical morphology and high chemical homogeneity. The HEBM-derived particles are with irregular morphology, submicronic in size, with amorphous structure after 12h of milling. The detailed study of the crystalline structure and luminescent properties were proceeded for the different europium concentrations (1, 2 and 6 at%) by means of XRPD, SEM, DSC, FTIR 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.

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), cathode Ray Tubes (CRT) etc. The interest of such materials originates from their extraordinary luminescence, magnetic and catalytic properties. Numerous processing routes have been developed in order to synthesize this kind of materials like sol-gel, coprecipitation and laser deposition route. These methods mostly lead to the material having low crystallinity and poor luminescent properties. In order to improve the particle properties and to provide more details regarding the Gd_2O_3:Eu particles formation mechanisms, here we have applied two basically chemical approaches in which the chemical reaction was promoted either thermally in dispersed aerosol system (SP) or mechanically, by HEBM. In both cases, the particles were analyzed by the same techniques: SEM/EDS, XRD, DSC, FTIR and steady state-fluorescent spectroscopy.

Experimental Procedure

Process I.- Spray Pyrolysis

Common nitrates precursor solution, (0,1 M; 1,2, 6 at% Eu) → Spray Pyrolysis: Ultrasonic Nebulizer f=1,7 MHz → Post-thermal treatment 800-1000°C/12 h

Process II.- High Energy Dry Ball Milling

Stoichiometric mixture of acetate precursors 2 at% Eu → Powder to balls mass ratio 1/10; Milling time: 0-12 hours; Pulverisette 6; Vessel and balls of agate → Post-thermal treatment 800-1000°C/12 h

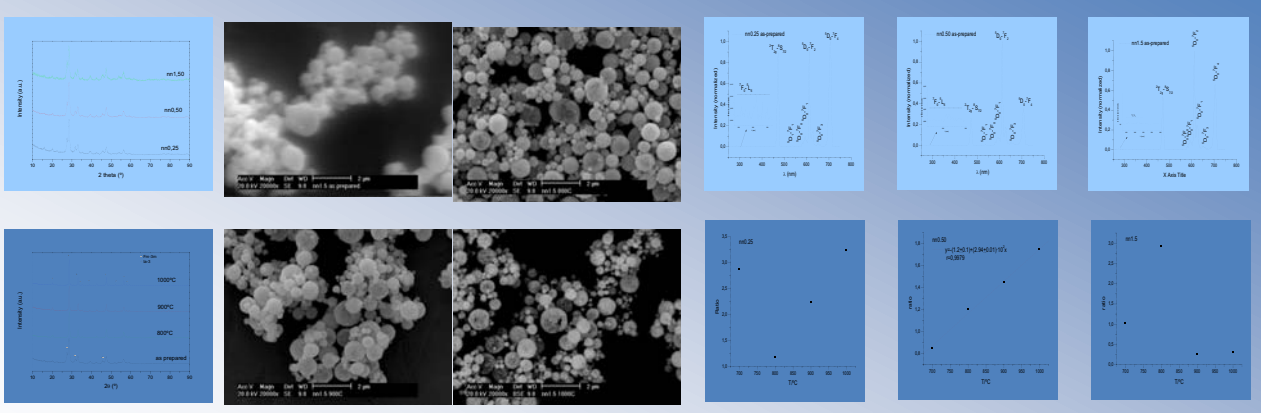
Characterization Techniques

XRD Philips X´Pert
SEM Philips XL 30
Perkin Elmer STA 6000
Edinburg Spectrofluorimeter
Perkin Elmer GX FTIR Spectrometer

Results and discussion

Spray Pyrolysis

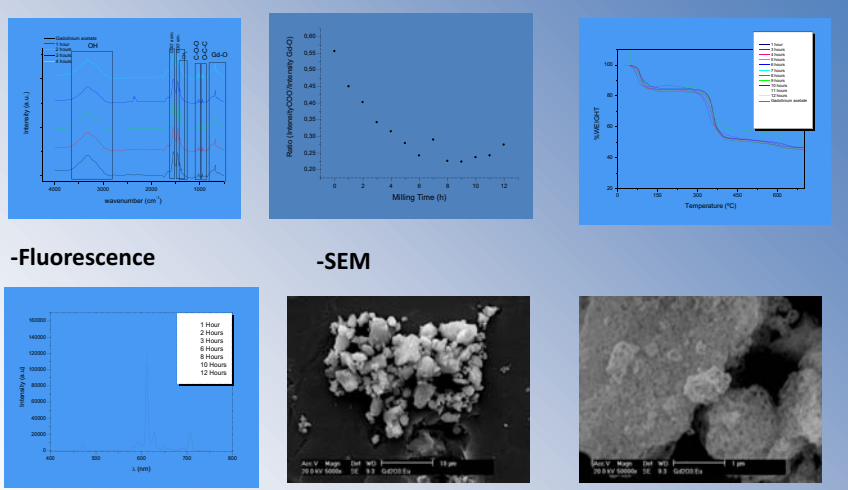
- XRD. -SEM -Fluorescence



Two crystallite phases of cubic symmetry (*Ia-3* and *Fm-3m*), have been identified by XRD, the former prevailing after heat treatments. SEM/EDS have identified spherical particles having high compositional homogeneity. The fluorescence measurements proved the presence of Eu^{2+} (fluorescence peak around 480nm) and imply the existence of a monoclinic *C2/m* phase ($^5D_0$-$^7F_2$ transition at 629nm), aside to the dominating $^5D_0$-^7F_J (J=0, 1 2, 3, 4) Eu^{3+} transitions in the region between 580 till 700nm.

HEBM

-FTIR. -TGA



-Fluorescence -SEM

Although XRD has not fully confirmed the appearance of the corresponding cubic (Gd_2O_3:Eu) phase after 12 hours of HEBM, the FTIR analysis revealed the Gd-O bonds decreasing with grinding time. Furthermore, TGA measurements indicate low loss in weight with milling time. The fluorescence spectra of the thermally treated samples imply the typical europium transition in a cubic symmetry, while SEM analysis indicates irregular particle shape, agglomerated in assembalge with a size close to microns.

Conclusions

•The dense spherical, nanostructured Gd_2O_3:Eu particles having cubic symmetry have been obtained by a SP route. Low temperature thermal treatment (800ºC/12h) led to the following crystalline phases formation: the principal *Ia-3* phase and a secundary *Fm-3m* phase. The fluorescence measurements additionally implied the existence of Eu^{2+}, as well as the presence of a monoclinic phase (*C2 / m*). On the contrary, a higher temperature thermal treatment influences on the cubic symmetry phase (*Ia*3) stabilization as well as prevailing of the Eu^{3+} typical transitions.

•By a HEBM technique has not been possible to obtain the Gd_2O_3: Eu particles with cubic symmetry (there are not evidence of new difracttion peaks during the milling process), but by means of FTIR it has been able to follow the evolution of the reaction depending on the time of grinding. TGA measurements showed no significant mass loss, although the calcined products showed the fluorescence emission spectra typical for the Gd_2O_3: Eu cubic symmetry., implying the temperature was the most influencing parameter in oxide formation. The particles obtained by this technique are of irregular size and morphology.

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