Gd_2O_3:Eu System: Structural Study of the Influence of Luminescence Center Concentration

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Abstract

The influence of Eu^{3+} doping on the structural and morphological properties of the Gd_2O_3 :Eu^{3+} phosphor system, obtained ultrasonically via Spray Pyrolysis from common gadolinium and europium nitrate solutions, was studied. The particle morphology, crystalline and chemical structure were studied by XRD, SEM and EDS. TEM was applied in order to identify the structure and growth of "primary nanoparticles" and determine the presence of domains locally affected by "Moires Frames" and "Crystallite Size". The SADP allows determining the presence of a polycrystalline material with two phases in the "as-prepared" samples, and only an Ia3 phase along the thermal treatment.

Keywords : Nanoparticles, Spray Pyrolysis, phosphor materials

1. Introduction

Nanoparticles are of interest, because the chemical and physical behavior of the particles is different from those in bulk form. RE^{3+} doped phosphors play an important role for optical applications of field emission displays Spray pyrolysis process (SP) [1-4] is an efficient technique to prepare nano-scaled phosphors due to good mixing of starting materials, small limited space and relatively low reaction temperature. SP is based on the decomposition of micrometric drops of aerosol, generated by ultrasonic waves at intermediate temperatures (600-800ºC) in one step. Due to the precipitation, decomposition and chemical reaction in solid phase in one stage is easy to control important parameters as particles size, morphology, chemical composition, etc. In this work, the effect of changing doped Eu^{3+} amount in gadolinia matrix through the microstructural characterization of two samples, nn1 (Gd:Eu:0.09:0.01) and nn2 (nn2 Gd:Eu:0.08:0.02) will be studied.

2. Experimental

The processing route includes aerosol formation ultrasonically (resonant frequency ranging of 2.1MHz) from common gadolinium and europium nitrate solutions and control over the process of the aerosol decomposition in a tubular flow reactor at 700 ºC. Two water solutions having the same overall concentration of nitrates (0.1mol/dm^3) were prepared by dissolving the appropriate amounts of $Gd(NO_3)_3x6H_2O$ and $Eu(NO_3)_3x5H_2O$ in order to obtain either 0.09:0.01 or 0.080:0.020 Gd:Eu molar ratio ("*as-prepared*" samples are denoted nn1 and nn2, respectively). After synthesis, the powders were annealed isothermally at 800-1200^{0}C for 12 h in air [5]. The morphology evolution and present phase identifications in all samples have been carried out by X-Ray diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Selected Area Electron Diffraction (SAED).

3. Results

XRD and SAED allowed to identify the presence of two phases formed during the SP process, a main phase Ia3 (a: 10.829Å) and a secondary phase Fm-3m (a: 5.624Å) in as prepared nn1 and nn2. Only the Ia3 phase along the annealing was found. In table 1 is summarized the cell parameters calculated with respect to Ia3 phase (SG=206) by means of Rietveld based on *Fullprof* refinement and the chemical analysis obtained by SEM-EDS for nn1 and nn2 after annealing. Semiquantitative chemical analysis obtained by SEM –EDS shows a good agreement with theoretic proportion for nn1and nn2.

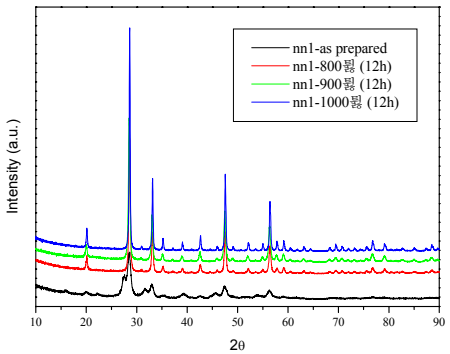

Fig. 1. Experimental X-ray diffraction patterns for as-prepared and thermally treated powder charges nn1 sample.

SEM images observations of nanoparticles indicate spherical, agglomerate-free with a mean particle size below 800nm and with the crystallite sizes below 20nm in both as-prepared samples (nn1 and nn2). Fig 2 shows spherical and hollow nanoparticles with narrow size distribution for both samples after the annealing treatment (900 ºC/12h).

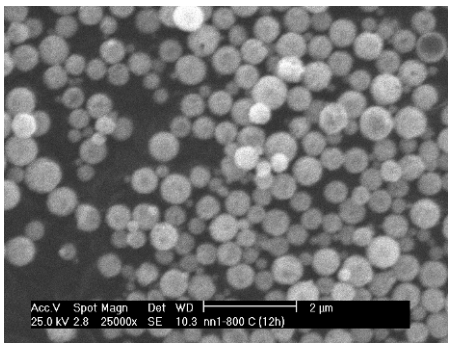

Fig. 2. SEM micrograph for nn1 sample 900 ºC/12 hour.

Table 1. Cell parameter calculated with respect to Ia3 phase (SG=206) by means of Rietveld based *Fullprof* refinement for nn1 and nn2 after annealing treatments and chemical analysis obtained by SEM-EDS.

Sample	Chemical analysis (EDS) (at %)		Annealing temperature (ºC)/12h	Cell parameter (Å)
	Gd	Eu		
nn1	90±1	9.7±0.5	800	10.8187(4)
			900	10.8156(4)
			1000	10.8166(3)
nn2	79.7±0.4	19.8±0.3	800	10.839(6)
			900	10.8261(4)
			1000	10.8373(3)
			1100	10.8180(1)
			1200	10.8360(4)

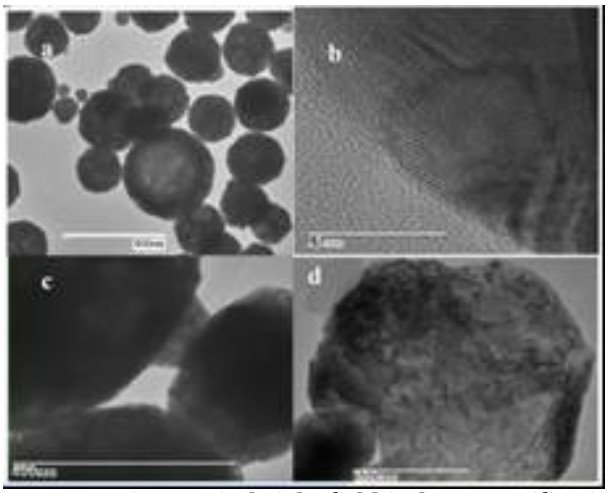

Fig. 3. TEM images in bright field in low magnification and high resolution of nn2 samples.

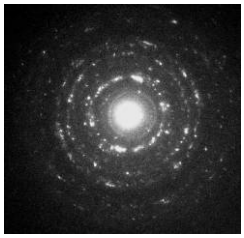

Fig. 4. SAED pattern of nn2 sample 900ºC/12 hour.

Fig 3 correspond to TEM images, (3a) is a low magnification bright field image from where it is possible to identify the particle structure aroused through the collision/coalescence mechanisms of primary nanoparticles; in 3b, a HRTEM image is showing the domains affected by Moirés Frames in primary nanoparticle. In 3c, the presence of sintering necks can be distinguished easily at higher temperatures (1100 ºC) and the beginning of the cohesion between the secondary particles can be observed at 1000 ºC (Fig 3d). Based on the presence of ring patterns in SAED patterns .the polycrystalline character was determined (Fig.4).

4. Summary

In this work, the synthesis of two earth rare oxides obtained by spray pyrolysis and its characterization using XRD data, SEM and TEM have been reported. These tools permit to identify the present phases in each sample. Microscopic observations indicate that obtained Gd_2O_3: Eu (0.09:0.010. and 0.08:0.02) solid solutions by this method correspond to nanoparticles formed from small primary nanoparticles which grow up sticking each other until they get bigger sizes. Hollow spherical nanoparticles are typical in "as prepared" samples and also after thermal treatments at low temperature (<1000 ºC). The presence of sintering necks can be distinguished easily at higher temperatures (from 1100 ºC). The beginning of cohesion between secondary particles can be observed at 1000ºC. In "*as prepared*" samples, XRD shows the presence of two polycrystalline phases, the main one is a cubic with Ia3 symmetry, and the secondary is a cubic with Fm-3m symmetry. However, in samples treated at temperatures between 800-1200ºC during 12h, only the cubic Ia3 phase has been observed. SAED pattern allowed confirming XRD results.

5. References

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