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Structural properties of europia-doped-gadolinia synthesized through aerosol

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Abstract

High purity europium-doped gadolinia (Gd_2O_3:Eu^{3+}) have been prepared using spray pyrolysis technique yielding nanostructured non-agglomerated particles with spherical morphology. Comparative microstructural analysis was done for different europium concentrations. The particle homogeneity, crystallization and nanostructure development were analyzed using XRD, TEM-HRTEM and EFTEM. The existence of two different cubic phases has been identified in as-prepared samples: a bcc (SG *Ia*3) and a fcc (*Fm*-3*m*). After the thermal treatment only the cubic *Ia*3 phase has been observed with the cell parameters affected with Eu^{3+} doping concentration and temperature, followed with progressive increase in crystallite size.

Keywords: Powders-chemical preparation; Spray pyrolysis; X-ray methods; Electron microscopy

1. Introduction

The aerosol synthesis route offers many advantages for nanoparticle processing over more conventional synthetic procedures, especially when well controlled characteristics including size, morphology, non-agglomeration state and composition are considered.[1] These advantages are primarily related to the micrometer sized aerosol droplets evaporation/drying, precipitation and decomposition processes in a high temperature tubular flow reactor. Due to the time/temperature history, the amorphous, nanocrystalline, polycrystalline or even monocrystalline particles could be formed through the mechanisms of solute nucleation, crystallite growth, collision and sintering.[2] Since the precursors are mixed at the molecular level in a solution, a high degree of structural homogeneity is achievable. Doping through solution is effective and straightforward, so the dopant distribution is uniform overall the matrix material. Moreover, high heating and cooling rates and dispersion-state synthesis, associated with the aerosol processing route enable high surface reaction and even more, the metastable phases to be obtained. In addition, the solution based processing minimizes the potential for contamination, which is very important for the synthesis of phosphor materials that are sensitive to some of the impurities.[3]

Gadolinia-doped with europia has been used as an effective crystal phosphor for cathodoluminescence and laser action.[4–7] For effective luminescence, particularly when luminescence displays are considered, there is an increased interest for the uniform distribution of the luminescent center in the matrix of the host material, cubic crystal structure formation, narrow particle size distribution, large surface area, spherical particle morphology and the absence of agglomerates.[1]

In continuation of our previous studies on Gd_2O_3:Eu^{3+} phosphor material synthesis through the aerosol route [3,8] the goal of this paper was to evaluate the influence of the europium doping concentration on the particles structural and morphological properties, particularly emphasizing the primary nanoparticles evolution. The research is especially focused on the effects of Gd/Eu molar ratio on the cubic crystalline phase formation and the results obtained are discussed in the framework of the literature outputs.

2. Experimental

The processing route includes aerosol formation ultrasonically (resonant frequency ranging of 2.1 MHz) from common gadolinium and europium nitrate solutions. The aerosol was decomposed at 700 °C, after being introduced into a hot-wall

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Table 1
Structural parameters based on Rietveld Fullprof refinement for europium-doped Gd_2O_3 powder samples

	As-prepared	Annealing temperature (°C)			
		800	900	1000	1100
Gd_2O_3:Eu (0.01 M Eu)					
a (Å)					
*Ia*3	10.829 (3)	10.8187 (4)	10.8156 (4)	10.8166 (3)	–
Fm-3*m*	5.6242 (1)				
CS/PS (nm)	11 ± 1/800	21 ± 1	26 ± 1	50 ± 3	
Gd_2O_3:Eu (0.03 M Eu)					
a (Å)					
*Ia*3	10.833 (7)	10.8251 (7)	10.8235 (3)	10.825 (2)	10.820 (1)
Fm-3*m*	5.626 (5)	–	–	–	–
CS/PS (nm)	8 ± 1/700	26 ± 1	40 ± 1	64 ± 1	93 ± 3
Gd_2O_3:Eu (0.04 M Eu)					
a (Å)					
*Ia*3	10.838 (3)	10.835 (9)	10.828 (1)	10.8305 (2)	10.829 (6)
Fm-3*m*	5.633 (3)	–	–	–	
CS/PS (nm)	10 ± 1/600	14 ± 1	22 ± 2	40 ± 3	54 ± 2

tubular reactor by means of carrier gas (air). The gas flow rate was 1.5 l/min, and the corresponding droplet/particle residence time was 75 s.

Four water solutions having the same overall concentration of nitrates (0.1 mol/dm^3) were prepared by dissolving the appropriate amounts of $Gd(NO_3)_3{\cdot}6H_2O$ and $Eu(NO_3)_3{\cdot}5H_2O$ in order to obtain 0.09:0.01, 0.08:0.02, 0.07:0.03 and 0.06:0.04. Gd/Eu molar ratio ("as-prepared" samples are denoted nn1, nn2, nn3 and nn4, respectively) (Table 1). After synthesis, the powders were annealed isothermally at 800–1100 °C for 12 h in air

The morphology evolution and present phase identifications in all samples have been carried out by X-ray diffraction (XRD), and Transmission Electron Microscopy (TEM). XRD patterns were recorded with Cu Kα radiation in a X'Pert Philips automatic diffractometer. The 2θ range analyzed was 10–100° with a step scan of 0.02 and a counting time of 11 s for each step. The working conditions were 40 kV and 40 mA. A TEM 20 FEG Philips operated at 200 kV with a resolution of 2.0 Å was employed. TEM samples were prepared by disposing of small powder portion on a carbon coated cooper grid. The distribution of Eu and Gd in the particles was interpreted based on the energy filtered transmission electron microscopy (EFTEM) combined with electron energy loss spectroscopy (EELS) that were carried out using a LIBRA Microscope (Zeiss) operating at 120 kV, with a corrected 90° in column OMEGA energy filter.

3. Results and discussion

As-prepared particles ("secondary particles") derived from Eu-doped gadolinium nitrate precursor solutions are non-agglomerated, spherical, with smooth particle surfaces, as previously reported,[8] having the mean particle size (PS) based on SEM observations as follows: 800 nm (nn1), 700 nm (nn2), and 600 nm (nn3). The particle morphology implies composite structure representing an aggregate of "primary particles", arising during the thermally induced processes of nucleation, growth and collision at the droplet level.[8] After thermal treatment, the particle remains in un-agglomerated form and still with spherical shape (Fig. 1a). There is slight evidence about the decrease of the particle size with additional annealing (Table 1), caused by thermally induced primary particle combining and densifying to form aggregates holding together by necks resulting from intra-particle sintering. This is associated with increasing of the particle surface roughness due to thermally promoted crystallization.[9]

The distribution of the constitutive elements, gadolinium and europium, is uniform along the particles, as received in accordance to the EFTEM–EELS examination. Fig. 1b represents a low magnification image obtained with 0 eV where several filters were used to establish the chemical distribution. With the help of EELS spectrum, it was possible to make a mapping of the particles. Fig. 1c represents a false colour image of the same region after the application of several energy filters. As already, mentioned, both elements are homogeneously distributed along the particle, and the changes in intensities are indicating the changes in the thickness of the particle.

XRD patterns implied the presence of two cubic phases in all as-prepared powder samples formed during the process, a main *Ia*3 phase and a secondary *Fm*-3*m* phase. The content of the latter increases with europium content. Table 1 summarized cell parameter, crystallite (CS) and particle (PS) size. Only the *Ia*3 phase after the annealing was found.

It was found that the crystallite size increase with the annealing temperature. In all systems the cell parameter is higher in comparison to the c-Gd_2O_3 (a = 10.81 Å, file card 43-1014), indicating the incorporation of Eu^{3+} into the gadolinia matrix, since Eu^{3+} ionic radii is slightly larger than Gd^{3+} (Eu^{3+}: 0.095 nm; Gd^{3+}: 0.094 nm). The similar observation has been reported for the case of monodispersed c-Gd_2O_3 fine spherical particles derived from carbonate precursors.[10] The increase of

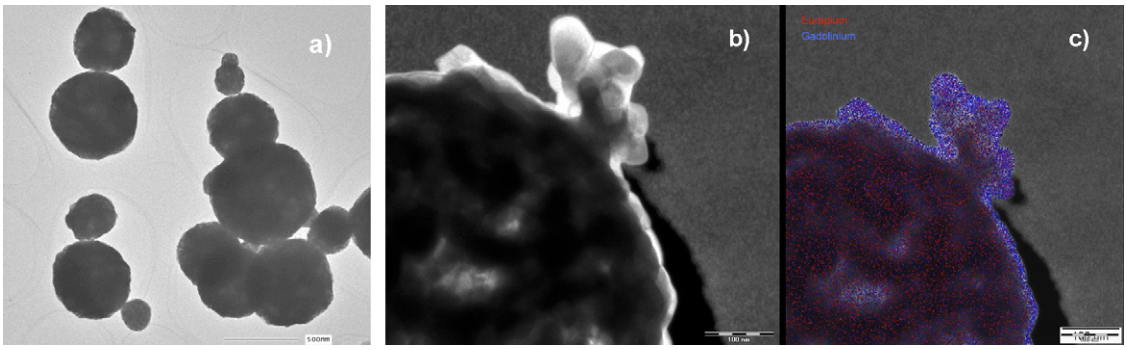

Fig. 1. The low magnification TEM (a), EFTEM image (b) and EELS spectra (c).

the cell parameter is in the same proportion as the gadolinium-to-europium molar ratio into the common precursor solutions. Following the tendency of the cell parameter-annealing temperature relationship, it is obvious that the mechanism of the Eu^{3+} ion incorporation obviously changed with annealing temperature, having a minimum at approximately 900 °C. After this temperature, there is a slight increase of the cell parameters with additional temperature increase. This behavior should be associated with the different mechanisms of europium ion diffusion into the gadolinia matrix, having different diffusion paths associated with the both lattice defects and the content of dislocations that are mostly affected with annealing temperature. The diffusion of Eu^{3+} into gadolinium matrix and substitution of Gd^{3+} lattice sites is additionally confirmed by thermoluminescence and radioluminescence measurements, as already reported.[3] The emission spectra of the annealed samples (nn1) exhibit the strong red transitions of the Eu peaking at 610 nm. Annealing at 1200 °C increases the luminescence efficiency by ~1000 in comparison to the as-prepared samples.

Based on HR-TEM in the sample nn2, obtained at 800 °C (Fig. 2), the presence of microstrains is implied by the appearance of dislocations and locally Moire patterns, giving evidence for the defects associated both with the grain interior and grain boundaries. The diffusion of europium ions along gadolinia matrix is thus facilitated using the dislocation areas as the fast diffusion paths. Namely, several frames can be identified indicating imperfections and little misorientations amplified in the Moire patterns suggesting strain in the crystalline net. These Moire patterns are implying that defects are present and are modifying their periodicity. However, after increasing the annealing temperature above 900 °C, it is evident the better order related to the orientation in the atomic frames and a decreasing of defects content. Fig. 3 is showing a HR-TEM images where a single crystal *Ia*3 phase can be observed, thus supporting the XRD results.

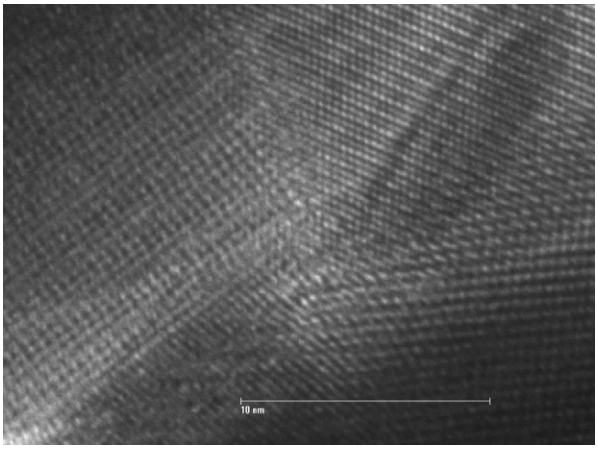

Fig. 2. HR-TEM image in bright field mode showing the intersections of several frames and Moire patterns in the sample nn2, annealed at 800 °C.

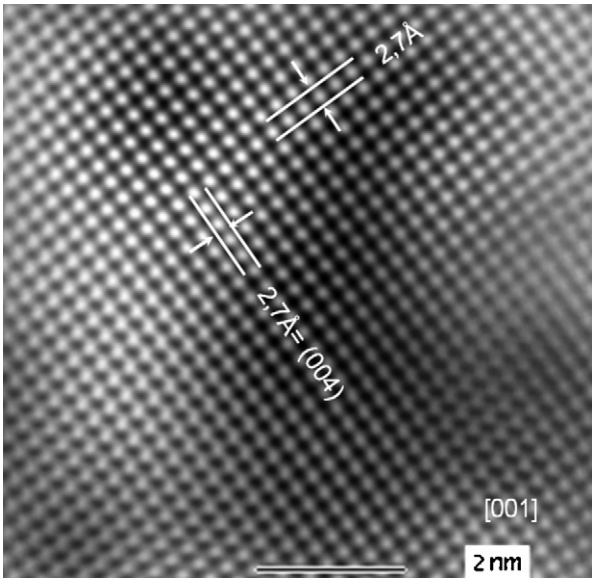

Fig. 3. HR-TEM showing a single crystal formed in the sample nn2 annealed at 1100 °C, 12 h.

4. Conclusion

Gd_2O_3:Eu^{3+} non-agglomerated spherical phosphor particles (<800 nm), having different doping concentration of europium, as a luminescence centre are synthesized from ultrasonically (frequency 2.1 MHz) generated common nitrates solution. Detailed phase and structural analysis were proceeded in accordance to XRPD, TEM-HRTEM and EFTEM analysing methods. EFTEM spectra proved uniform compositional distribution of the constitutive elements along the particles. XRPD revealed the presence of two crystalline cubic phases in as-prepared powders: a bcc phase with *Ia*3 space group ($a \approx 10.829(3)$ Å); and a fcc

phase with *Fm*-3*m* space group ($a \approx 5.6242(1)$ Å) for the Eu^{3+} less doping concentration. After the thermal treatment only the cubic *Ia*3 phase has been observed, with the cell parameters affected with Eu^{3+} doping concentration, followed with progressive increase in crystallite size. HR-TEM confirmed XRPD results and the presence of primary nanoparticles, associated with the defect structure both in the grain bulk and boundaries, as implied by the appearance of dislocations and locally Moire patterns. After annealing above 900 °C, it is evident the better order related to the orientation in the atomic frames and a decreasing of defects content.

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