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Photo and cathodoluminescence characteristics of dysprosium doped yttrium oxide nanoparticles prepared by Polyol method

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ABSTRACT

The luminescent characteristics of Dy^{3+}-doped Y_2O_3 nanopowders synthesized using the polyol method are reported. The Y_2O_3 nanoparticles presented a cubic phase crystalline structure of Y_2O_3 after an annealing treatment in oxygen ambient at temperatures above 600 °C. The averaged crystallite size determined from the X-ray diffraction peaks width was in the 20–32 nm range depending on the annealing temperature. Scanning and transmission electron microscopy studies indicate the formation of nanoparticle aggregates up to 175 nm in diameter. Photoluminescence and cathodoluminescence measurements show a predominant emission at 573 nm, which is attributed to the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ of the Dy^{3+} ion. The luminescence emission dependence with the dopant concentration and post-annealing temperatures is discussed.

1. Introduction

Over the last few years there has been a great interest in the synthesis and characterization of nanostructured materials because of their unique properties, which are different from those exhibited by microscopic structured or "bulk" materials. Optical properties of rare-earth ions in nanostructured materials have also been extensively studied, the lifetime emission, the quantum-efficiency and the concentration quenching are some of the crystallite size-dependent properties in these materials [1–5]. The luminescent properties of these nano-materials make them attractive for many technological applications like display devices, up-conversion solar cells, white-light generation and detectors in medical diagnosis equipment among others [6,7]. Considerable efforts have been dedicated for the synthesis of rare-earth nano-phosphors with uniform size and shapes, by chemical means with techniques such as co-precipitation and polyol. In the co-precipitation case, the urea homogenous precipitation method and the co-precipitation method using $(NH_4)_2CO_3$ have been used to synthesize rare-earth doped Y_2O_3 nanopowders through a relatively clean and simple procedure [8,9]. In the case of the polyol method, initially developed for the preparation of metal nanoparticles [10], it has been used for the synthesis of nanopowders of inorganic compounds such as oxides, phosphates or sulfides with very successful results [11–15]. This technique is also simple and clean as the co-precipitation techniques mentioned above, although it allows for a better control on the nanoparticle size below 50 nm as shown in the present work. Yttrium oxide in its nano-crystalline form has been produced by many techniques and has been doped with several rare-earth ions; in its cubic phase, it has a large bandgap of 5.8 eV, a high dielectric constant of 14–18 and is also optically isotropic, with a refractive index of 1.91. It also has a high thermal stability and it has a dominant phonon energy of 380 cm^{-1}, which is one of the smallest phonon energies among metallic oxides; this low vibration energy is desirable for a host material as it improves the probability of radiative transitions among electronic energy levels of the rare earth ions [3,16]. Most of the studies reported for polyol-synthesized Y_2O_3 nanoparticles have been concentrated on Eu^{3+} and Tb^{3+} ions, making aside several interesting rare-earth ions [16–21], such as Dy^{3+} ion, which has been studied in materials synthesized by other techniques [4,22–24].

In the present work, the synthesis of Y_2O_3 nano-powder doped with the yellow emitting ion Dy^{3+} by the polyol method and its characterization are reported. In particular, the crystallinity, grain size and the photo and cathodoluminescent properties of the samples are discussed as a function of Dy^{3+} ion concentration and annealing temperature of the powders.

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2. Experimental details

The appropriate amounts of the precursor salts, yttrium (III) nitrate hexahydrate ($Y\ N_3O_9\ 6H_2O$, Alfa Aesar, 99.9%), and dysprosium chloride hexahydrate ($DyCl_3 \cdot 6H_2O$, MERCK, 99.99%) were dissolved in 100 ml of diethylene–glycol (Sigma-Aldrich, 99%) to form a solution with a total concentration of 0.078 M for the Dy^{3+} doped nano-sized powders synthesis by the polyol method. The Dy concentration was studied in the 0–4 at% range with respect to the Y content. The synthesis process consisted of three stages in which the solution was subjected to a continuous mechanical agitation and forced hydrolysis of the dissolved precursor was obtained by adding 2 ml of de-ionized water (18 MΩ cm) to the starting solution. The temperature of the solution in the first stage was elevated up to 60 °C and maintained for 1 h, to propitiate a good dilution of the precursor salts; in the second stage, the temperature was raised up to 120 °C and maintained for 1 h. The process of formation of the nano-sized powders occurs in the third stage, in which the temperature was increased up to 175 °C and the polyol method related evaporation/condensation cycles started, this stage lasts 2 h. The resulting powder was separated from the solvent by sedimentation and it was washed three times with methyl-alcohol. After each wash, the product was filtered in order to recover the powders. Then, the powders were dried at 300 °C for 12 h in air. The samples with different dopant concentrations were annealed at different temperatures in the 300–900 °C range in an oxygen atmosphere for 2 h. A 0.5 cm diameter pellet of these powders was used to facilitate the characterization.

X-ray diffraction patterns of the powders were recorded using a SIEMENS, D5000 X-Ray diffractometer at a 1.540 Å wavelength. The morphology of the obtained powders was studied with both scanning and transmission electron microscopy (SEM and TEM). The SEM analysis was carried out using a JEOL, JSM-7401 F, field emission scanning electron microscope with an EDS attachment. TEM images were recorded using a JEOL, JEM-2010 transmission electron microscope. The photoluminescent (PL) characteristics of the powders were measured at room temperature with a spectrofluorometer HORIBA, FlouroMax-P operating on the phosphorescence mode with a 20 ms sampling window, a 0.01 ms delay time and a 50 ms time per flash. Cathodoluminescence (CL) measurements were carried out using a Relion CL system of electron beam in a vacuum chamber and it was spectrally resolved with the same spectrofluorometer on continuous (fluorescence) mode coupled with an optical fiber to the CL chamber. The CL measurements were carried out with an e-beam accelerating voltage of 5 kV and a current of 0.1 mA at room temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns of Y_2O_3:Dy^{3+} (0.3 mol%) annealed at 300, 500, 600, 700 and 900 °C. Powders with different doping concentrations annealed at 900 °C were also measured (not shown) but no evident variation in the diffraction patterns was observed in this case. The powders were amorphous up to 600 °C, at this temperature the formation of crystalline peaks associated with $Dy_2O_2(CO_3)$ and Y_2O_3 starts to be observed. The presence of the $Dy_2O_2(CO_3)$ is apparently associated with an incomplete dissociation of the organic components in the starting solution. At 700 °C and above, the diffraction pattern corresponding to a body-centered cubic phase of yttrium oxide with a lattice parameter $a = 10.5957$ Å is clearly defined (ASTM database card no. 01-071-0049). The crystallinity of the samples is enhanced as the annealing temperature increases, this is suggested by the increment on the diffraction peaks intensity [15,16,19,20,24].

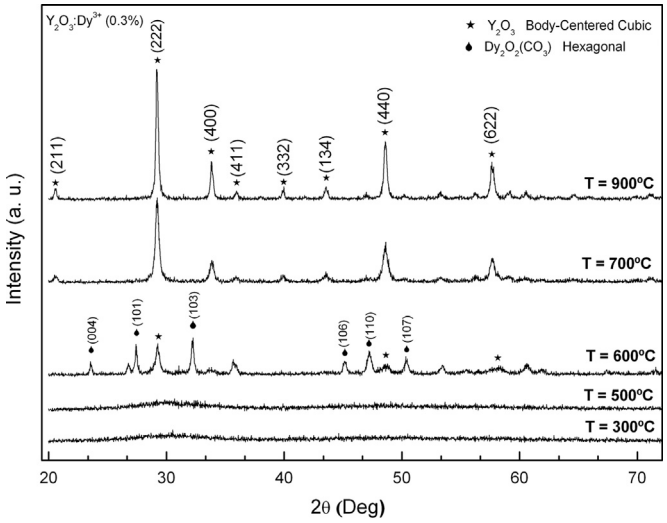

Fig. 1. XRD pattern of the Y_2O_3:Dy^{3+} (0.3 at%) for different annealing temperatures under an oxygen atmosphere.

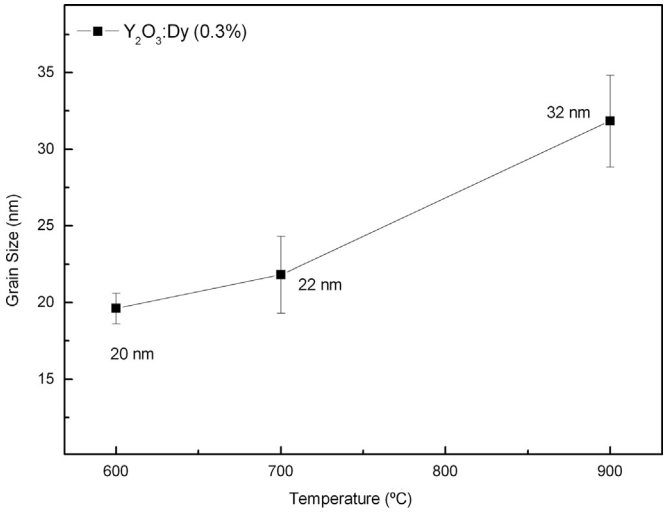

Fig. 2. Influence of the post-annealing temperature in the average grain size of the Y_2O_3:Dy^{3+} (0.3 at%).

The average nano-crystallite size was calculated from the [222] diffraction peak (in Fig. 1, at $2\theta = 29.173$) using Sherrer's equation. Fig. 2 shows the averaged crystallite size as a function of the annealing temperature, the average crystallite size grew from 20 nm at 600 °C to 32 nm at 900 °C.

The SEM micrograph shown in Fig. 3(a) and (b) illustrates the typical morphology of the powders and in this case, corresponds to Y_2O_3:Dy^{3+} (0.3 mol%) powder annealed at 900 °C. It is observed that the powder consists of agglomerated particles with quasi-spherical shape with an average diameter of 175 nm. The TEM micrographs shown in Fig. 3(c) and (d) for a similar sample at two different magnifications confirm that nano-crystallites of up to 50 nm cluster together in larger aggregates. The size of the observed nano-crystallites is of the order of that determined by Sherrer´s formula from the X-ray diffraction data (~32 nm).

Table 1 lists the results of EDS analysis for Y, O and Dy relative content in the powders annealed at 900 °C, these powders had an excess of oxygen content in relation to the 40–60 at% stoichiometry expected for Y_2O_3. The Dy content is found to increase proportionally to the content used in the starting solution. It is possible that the excess of oxygen in these powders is related to a