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Influence of pH and europium concentration on the luminescent and morphological properties of Y_2O_3 powders

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ABSTRACT

This work reports on the synthesis and characterization of Y_2O_3:Eu^{3+} powders obtained by the hydrothermal method. We studied the influence of different pH values (7–12) and Eu^{3+} concentrations (2.5–25 mol%) on the structural, morphological and luminescent characteristics of Y_2O_3:Eu^{3+} powders. The hydrothermal synthesis was performed at 200 °C for 12 h by employing Y_2O_3, HNO_3, H_2O and $Eu(NO_3)_3$ as precursors, in order to obtain two sets of samples. The first set of powders was obtained with different pH values and named Eu5PH*x* (*x* = 7, 8, 9, 10, 11, and 12), and the second set was obtained by using a constant pH = 7 with different Eu concentrations, named Eu*x*PH7 (*x* = 2.5, 5, 8, 15, 20 and 25). The XRD spectra showed that the Y_2O_3:Eu^{3+} powders exhibited a cubic phase, regardless of the pH values and Eu^{3+} concentrations. The SEM observations indicated that pH influenced the morphology and size of phosphors; for instance, for pH = 7, hexagonal microplatelets were obtained, and microrods at pH values from 8 to 12. Doping Y_2O_3 with various Eu^{3+} concentrations (in mol%) also produced changes in morphology, in these cases, hexagonal microplatelets were obtained in the range of 2.5–5 mol%, and non uniform plates were observed at higher doping concentrations ranging from 8 to 25 mol%. According to our results, the microplatelets synthesized with a pH of 7 and an 8 mol% Eu^{3+} concentration presented the highest luminescence under excitation at 254 nm. All of these results indicate that our phosphors could be useful for applications of controlled drug delivery, photocatalysis and biolabeling.

1. Introduction

The down-conversion process in rare earth (RE)-doped nanomaterials has been widely studied, due to its applications for phosphors for lamps, lasers, displays and LEDs [1–4]. In such applications, the RE ions absorb energy, and their electrons move toward excited levels with energy comparable to the absorbed levels; then electrons are relaxed toward lower levels, due to cross relaxation or non-radiative energy transfer. As a result, the emission energy has a longer wavelength than that of the excitation source (typically UV) [5–7]. Many efforts have been made to develop methods of synthesis in order to control or improve the characteristics of nanophosphors [8]. Therefore, there is a wide variety of matrices used as hosts for RES, such as Gd_2O_3, YAG, $BiPO_4$, Al_2O_3 and ZrO_2 [9–22]. In particular, Y_2O_3 is an excellent host matrix due to its chemical and thermal stability, and it is considered one of the best inorganic red-emitting phosphors when it is doped with Eu^{3+} (Y_2O_3:Eu^{3+}) [10,23,24]. Solid state reaction, spray pyrolysis and hydrothermal methods are commonly used to synthesize Y_2O_3:Eu^{3+} [23,25,26]. Among these methods, the hydrothermal method is preferred because with it, it is possible to produce nanoparticles with high crystallinity, controlled morphology and excellent reproducibility [5,10,27–29]. Zhu et al. [2] obtained Y_2O_3:Eu^{3+} homogeneous particles after 800 °C thermal treatment, via the hydrothermal method, using nitrate precursors containing HMT (hexamethylenetetramine), with different morphologies such as submicron spheres, microflower-like structures and microplates, with each particle shape associated with a pH in the reaction, obtained by controlling HMT/M molar ratios. In addition, there has been increasing attention to synthesizing other morphologies; for example, platelets, microrods, microcubes, microwires and microprism structures have been obtained [5,23,30–32]. Red phosphor exhibits a substantial morphology-

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dependent intensity of photoluminescence, produced by Eu^{3+}; in fact, the recommended morphologies for producing high red luminescence are platelets and microrods [5,23,30–32]. Furthermore, it has been reported that the dopant concentration, annealing temperature, pH values, precursors and time of reaction influence the optical properties of Y_2O_3:Eu^{3+} micro- or nanoparticles [2,5,23,26,32–34]. However, the reported structures have not presented a porous surface, which could be useful for controlled drug delivery [35–37] and photocatalysis [38–40]. Therefore, in this work, the authors have improved on previous work, synthesizing Y_2O_3 particles for systematic study. Different Y_2O_3 structures were synthesized using a hydrothermal procedure and adjusting the pH values of the original solution from 7 to 12. In this work, we synthesized porous microplatelets at pH = 7 without using organic additives, which allowed the formation of intermediate yttrium carbonate/nitrate-based compounds before reaching the Y_2O_3:Eu^{3+} phase via calcination at temperatures higher than 700 °C. To the best of our knowledge, the optical properties of synthesized Y_2O_3 platelets doped with Eu^{3+} concentrations from 2.5 mol% to 25 mol% have not been reported. Finally, this study reports on the remarkable changes in morphology, luminescence and crystallinity associated with changes in the pH values and europium content of synthesized Y_2O_3 powders.

2. Experimental

2.1. Preparation of Y_2O_3:Eu^{3+} (5 mol%) powders at different pH values

All reagents used for synthesis were purchased from Sigma Aldrich (99.99%) and used without further treatment. In a typical procedure, Y_2O_3 was dissolved in a mixture of HNO_3/H_2O in such a way that a molar ratio of $Y_2O_3/HNO_3/H_2O$ = 0.0011/1/3.5 was obtained. Then the solution was kept stirring at a temperature of 85 °C until the solution became transparent. Afterwards, 2.4×10^{-5} mol of Eu $(NO_3)_3$ were used to dope 5 mol% of Eu^{3+}. Subsequently the pH was adjusted from 7 to 11, using a solution of NaOH (1 M), in order to obtain six samples (named Eu5PH*x*, where *x* is the pH value). Each suspension obtained was transferred into a 50-ml stainless steel autoclave. Then each solution was autoclaved at 200 °C for 12 h. After this, the autoclave was allowed to cool down to room temperature, and the solutions were washed three times with distilled water in a centrifuge at 4000 rpm for 20 min. Thereafter, the samples were dried at 100 °C for 24 h and annealed at 700 °C for 2 h, using a heating rate of 10 °C min^{-1}. Finally, the products obtained were ground in an agate mortar to obtain fine powders.

2.2. Preparation of Y_2O_3 powders with Eu^{3+} concentrations

Another six samples of europium-doped Y_2O_3 were synthesized at a constant pH of 7 using a procedure similar to the one described above, except that the Eu^{3+} concentration (mol%) was adjusted over a range from 2.5% to 25%. Table 1 present a description of these samples, as well as those fabricated at different pH values.

2.3. Structural characterization and morphology

X-ray diffraction (XRD) patterns were obtained using Rigaku MiniFlex 600 equipment with a Cu tube and Kα radiation at 1.5405 Å, scanning in the 15–80° (2θ range) at increments of 0.02° with a sweep time of 0.2 s. Scanning electron microscopy (SEM) with a field emission gun was performed utilizing a JEOL JSM-7800F microscope operating at 15 keV, the particle specific surface area (SSA) was determined by the BET method.

Table 1
Y_2O_3 samples fabricated with different values of pH and concentrations of Eu^{3+} (mol%).

Sample	Eu^{3+} (mol%)	pH
Eu5PH7	5	7
Eu5PH8	5	8
Eu5PH9	5	9
Eu5PH10	5	10
Eu5PH11	5	11
Eu5PH12	5	12
Eu2.5PH7	2.5	7
Eu5PH7	5	7
Eu8PH7	8	7
Eu15PH7	15	7
Eu20PH7	20	7
Eu25PH7	25	7

2.4. Optical characterization

Photoluminescence (PL) characterization was performed using a Xenon lamp with 75 W of excitation power. The fluorescent emissions were analyzed with an Acton SP2300 spectrograph from Princeton Instruments and a R955 photomultiplier tube (Hamamatsu). The system was PC-controlled, and the emissions were recorded with Spectra-Sense software. All optical characterization was performed at room temperature, and the powders were compacted to make pellets to guarantee a consistent quantity of excited material. Special care was taken to maintain the alignment of the setup, in order to compare the emission intensities of different samples. The Fourier transform infrared (FTIR) spectra were recorded in a range of 4000 to 400 cm^{-1}, using a Perkin-Elmer Spectrum 65, and the samples were prepared with the KBr pellet method.

3. Results and discussion

3.1. The effects of pH on crystalline structure and morphology

Fig. 1 shows the X-ray diffraction patterns of the synthesized samples Y_2O_3: Eu^{3+} (5 mol%) prepared at different pHs, ranging from 7 to 12. We doped Y_2O_3 with 5 mol% of Eu^{3+} because it is

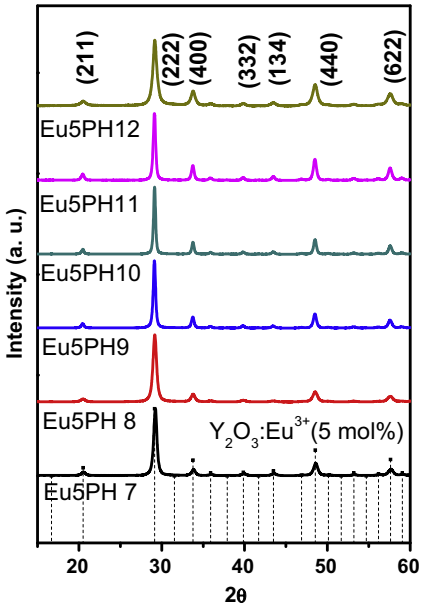

Fig. 1. XRD spectra of Y_2O_3:Eu^{3+} (5 mol%) powders at different values of pH.