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$Y_2O_3:Eu^{3+}$ (5 mol%) with Ag nanoparticles prepared by citrate precursor

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ABSTRACT

$Y_2O_3:Eu^{3+}$ (5 mol% Eu^{3+}) and $Y_2O_3:Eu^{3+}$ (5 mol% Eu^{3+}) containing 1 mol% of Ag nanoparticles were prepared by heat treatment of a viscous resin obtained via citrate precursor. TEM and EDS analyses showed that $Y_2O_3:Eu^{3+}$ (5 mol% Eu^{3+}) is formed by nanoparticles with an average size of 12 nm, which increases to 30 nm when Ag is present because the effect of metal induced crystallization occurs. Ag nanoparticles with a size of 9 nm dispersed in $Y_2O_3:Eu^{3+}$ (5 mol% Eu^{3+}) were obtained and the surface plasmon effect on Ag nanoparticles was observed. The emission around 612 nm assigned to the Eu^{3+} ($^5D_0 \rightarrow {}^7F_2$) transition enhanced when the Ag nanoparticles were present in the $Y_2O_3:Eu^{3+}$ luminescent material.

1. Introduction

Europium-activated Y_2O_3 ($Y_2O_3:Eu^{3+}$) has attracted much attention as a red-emitting phosphor for commercial use in fluorescent lighting and screen due to its high luminescence emission around 612 nm. Because of the fast development of nanotechnology, the optical properties of nanocrystalline $Y_2O_3:Eu^{3+}$ have also been extensively investigated for its potential application in high resolution imaging for flat plasma displays and in fundamental research [1,2]. Therefore, many researchers have already performed investigations related to this nanophosphor, such as the study of the influence of particle size on the intense luminescence of nanocrystalline $Y_2O_3:Eu^{3+}$ [3–12].

In order to achieve improved luminescent properties of $Y_2O_3:Eu^{3+}$ [13], the precursors as well as the synthetic route are very important factors. In the literature, many papers have reported different routes used to prepare this material, for example EDTA complex sol–gel process [14], combustion synthesis [15,16], flame spray pyrolysis [17,18], low temperature hydrothermal route [19], firing precursors prepared by urea thermal decomposition [20], microemulsion microwave heating [21], reverse micelles [22], sol–gel process [23–25], homogeneous precipitation technique [26], Au nanoparticles dispersed in $Y_2O_3:Eu^{3+}$ films [27], and the citrate method [30]. The use of citrate precursors has been reported as a way to achieve materials with excellent features [31]. The use of citric acid (alpha-hydroxycarboxilic acid) contributes to form the stable chelates through carboxylic groups with different metals and provides precursors with a high level of homogeneity.

Besides, nanostructured metallic surfaces appear as an alternative to enhance the luminescence of $Y_2O_3:Eu^{3+}$. Liu et al. [32] have assigned the luminescence enhancement of $Y_2O_3:Eu^{3+}$ to an energy transfer from Ag to this material. Metallic nanostructures have caused a drastic increase in the intensity of Raman scattering or luminescence ions in close proximity with the metallic surface [33]. $Y_2O_3:Eu^{3+}$ containing Au nanoparticles has also been reported with an increase of luminescence compared with the same materials without Au, which may have potential applications in biological detection and nanoreactors [34].

This notable enhancement phenomenon stems from a resonant excitation of surface Plasmon polarizations confined within a metallic nanostructure leading to a consequent enhancement in the induced dipole moment of the electronic transition responsible for the emission. Based on some studies, research on the fabrication of plasmonic nanomaterials and their high potential for various applications in photonics and surface-enhanced spectroscopy resulted in an increasing interest about the fundamental physics of the metal nanoparticles [35–39]. Moreover, many papers have been published regarding the effect of Ag metallic nanoparticles on the structure of annealed silica obtained by sol–gel method.

In this work, we have focused on an easy method to prepare the luminescent materials Y_2O_3 and $Y_2O_3:Eu^{3+}$ (5 mol% Eu^{3+}) using citrate precursors. Also, the effect of Ag nanoparticles on the spectroscopic and structural properties of the doped material was investigated.

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2. Experimental procedure

As reported by Ferrari et al. [30] in previous work based on spectroscopic properties, the best concentration of Eu^{3+} in the Y_2O_3 host matrix prepared by citrate precursor is 5 mol%. Y_2O_3, Y_2O_3:Eu^{3+} (5 mol% Eu^{3+}) and Y_2O_3:Eu^{3+} (5 mol% Eu^{3+}) containing 1 mol% of Ag were prepared by citrate method [27–29]. Yttrium oxide (Aldrich 99.999%), europium oxide (Aldrich 99.999%) and silver nitrate (Acros Organic 99%) were used to obtain the respective nitrate solutions with concentration of metals of 9.95×10^{-3}, 1.3×10^{-2} and 0.01 mol L^{-1}, respectively, to obtain the stock solution. The volume of nitrate metal solutions and the amount of citric acid (Vetec, P.A.) (the number of moles of citric acid was 20 times that of the number of moles of metals) to prepare each material were added in the beaker and deionized water was added to complete 50 mL of final solution. Stoichiometric amounts of the reagents were used to obtain 1 g of Y_2O_3, Y_2O_3:Eu^{3+} (5 mol% Eu^{3+}) and Y_2O_3:Eu^{3+} (5 mol% Eu^{3+}) containing 1 mol% of Ag of final product. The amount of citric acid changes for each samples, because the amount of metals also changes. Then, ammonium hydroxide solution (0.01 mol L^{-1}) was added drop by drop to adjust the pH to 4 to facilitate the formation of homogeneous solution and to avoid possible metal hydrolysis reaction, and the solution was slowly evaporated upon 80 °C until the formation of a viscous resin. For the obtainment of the resin, the solutions were prepared in dark environment to avoid the reduction of silver by light. After that, the resins were fired in an oven at 800 °C for 4 h to give the three materials. The powder samples were characterized by X-ray diffractometry (XRD) using a Rigaku RINT 2000 (copper target, $\lambda=1.5406$ Å) at a scanning rate of 0.03°/2 s (15–70°, 2θ range). High resolution transmission electron microscopy (HRTEM) and energy-dispersive X-ray spectrometry (EDS) analyses were acquired using a Philips CM 200 transmission electron microscope in order to study the morphology, grain size and composition of the particles. HRTEM images were also used to determine an average particle size as well as the size distribution and to build the histograms. The nanoparticles were suspended in isopropyl alcohol and added onto copper grade to support the samples the during analyses. Photoluminescence (PL) spectroscopy measurements were carried out using a Fluorolog SPEX F212/Jobin-Yvon fluorescence spectrometer equipped with an R928 Hamamatsu photomultiplier. A 450 W ozone-free Xenon lamp was used as the excitation source equipped with a cooled Hamamatsu R928 photomultiplier with excitation and emission slits fixed at 0.3 and 0.5 mm, respectively. Emission spectra in the range between 575 and 700 nm of Y_2O_3:Eu^{3+} (5 mol% Eu^{3+}) and Y_2O_3:Eu^{3+} (5 mol% Eu^{3+}) containing 1 mol% of Ag were obtained at room temperature with excitation at 261 nm, in the region of the charge-transfer band related to the excitation of an electron from the oxygen 2*p* state to Eu^{3+} 4*f* state [32,40–42].

3. Results and discussion

Fig. 1 shows the XRD patterns of Y_2O_3, Y_2O_3:Eu^{3+} (5 mol% Eu^{3+}) and Y_2O_3:Eu^{3+} (5 mol% Eu^{3+}) containing 1 mol% of Ag prepared from citrate precursors. The cubic structure of Y_2O_3 appears as the main phase and is present in all the formed materials. Jung et al. [12] observed that the pure cubic phase of Y_2O_3 is obtained from spray pyrolysis in the temperature range from 800 to 1300 °C without transition to the monoclinic phase.

This crystalline system corresponds to a body-centered cubic structure with Ia_3 space group consistent with the JCPDS no. 43-1036 card [43]. It is well known that the Y^{3+} ions are accommodated in two different symmetries, i.e., the C_2 without inversion center and the S_6 with inversion center [26,44]. The Eu^{3+} ion might be replacing the Y^{3+} ions in the Y_2O_3 host lattice because no diffraction pattern characteristic of Eu_2O_3 phase is detected. This is an expected effect since the difference between the Y^{3+} and Eu^{3+} atomic radii is quite small (0.047 Å) [30,45]. Through careful examination of the powder XRD patterns of phosphors with Ag content, it can be observe the extra reflection peaks that are assigned to the metallic Ag phase, which are consistent with the JCPDS no. 04-0783 card [46]. The peak of Ag is localized around $2\theta=38.25°$ and assigned to the (1 1 1) plane. In addition, a comparison among the half-band widths of the diffraction peaks from the different samples (Fig. 1) suggests that the Ag nanoparticles lead to sharper peaks referent to the Y_2O_3 in the diffractograms, and this effect may be related to an increase of the system crystallinity. In accordance to Herd et al. [47] the addition of small amount of metals to some materials, the metal-induced crystallization effect occurs, contributing to increasing the crystallinity, or then, the formation of phases that are normally obtained at higher temperature. Using an XRD diffractogram, it was possible to estimate of the average nanocrystallite size by Scherrer's formula. The equation is described by the relation $t=0.89\lambda/B\cos\theta$, where t is an average nanocrystallite size, $\lambda_{Å}$ the X-ray wavelength, B the full width half-maximum (FWHM) and θ_{rad} the position of the peak used in calculus. The estimations were realized based on the reflection peaks localized near $2\Theta=29.28°$ assigned to the (2 2 2) main plane present in the diffractograms and the average nanocrystallite sizes for Y_2O_3, Y_2O_3:Eu^{3+} (5 mol% Eu^{3+}) and for Y_2O_3:Eu^{3+} (5 mol% Eu^{3+}) in the sample containing 1 mol% of Ag, were 9.6, 9.6 and 16.9 nm, respectively. According to Taxak et al. [22], the Y_2O_3:Eu^{3+} nanoparticles obtained via tartaric acid sol–gel method, depicted nanocrystallite with size around 20 nm for materials annealed at 500 °C and 45 nm for material annealed at 800 °C/3 h. Recently, Wang et al. [48] reported the obtaining of Y_2O_3:Eu^{3+} by homogeneous precipitation, and observed the formation of nanocrystallite size around 41 and 30 nm dependeing on the amount of europium and also the pH chosen in the reaction. As we can see, the method reported in this work contributes to obtaining Y_2O_3:Eu^{3+} material with smaller nanocrystallites size in comparison with other works reported in the literature.

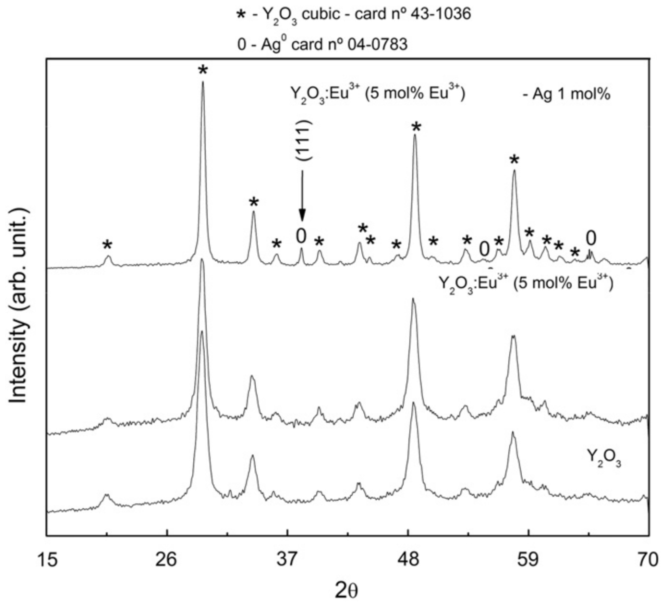

Fig. 1. X-ray diffraction patterns of Y_2O_3, Y_2O_3:Eu^{3+} (5 mol% Eu^{3+}) and Y_2O_3:Eu^{3+} (5 mol% Eu^{3+}) containing 1 mol% of Ag samples obtained by heat treating the resin prepared by citrate precursor at 800 °C for 4 h in static air atmosphere. The assignments of the indexed phases are also indicated (inset).