Optical Materials 84 (2018) 137–145

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Red phosphor based on Eu^{3+}-doped $Y_2(MoO_4)_3$ incorporated with Au NPs synthesized via Pechini's method

Airton Germano Bispo-Jr[a,b], Gabriel Mamoru Marques Shinohara[a], Ana Maria Pires[a,b], Celso Xavier Cardoso[a,*]

[a] São Paulo State University (Unesp), School of Technology and Sciences, Presidente Prudente, SP, 19060-900, Brazil
[b] São Paulo State University (Unesp), Institute of Biosciences, Humanities and Exact Sciences, São José do Rio Preto, SP, 15054-000, Brazil

ARTICLE INFO

Keywords:
Europium(III)
Molybdates
Luminescence
Au nanoparticles

ABSTRACT

Structural, morphological and spectroscopic characterization of the Eu^{3+}-doped $Y_2(MoO_4)_3$ red phosphor incorporated with Au nanoparticles (Au NPs) synthesized via Pechini's method is reported in the present study. In order to evaluate the Au NPs and Eu^{3+} ions influence on the molybdate structure, the $Y_2(MoO_4)_3$, $Y_2(MoO_4)_3$:Eu^{3+}, $Y_2(MoO_4)_3$/Au and $Y_2(MoO_4)_3$:Eu^{3+}/Au samples were produced and fully investigated. All samples obtained at relatively low temperature, i.e., 650 °C, show molybdate as the unique phase with high crystallinity assisted by both Eu^{3+} ions and Au NPs. Water molecules detected in the molybdate structure probably are distorting MoO_4, YO_6 and EuO_6 polyhedra similarly to the Au NPs incorporated in the same lattice. These Au NPs are spherical-shaped with a diameter near to 46 nm and they are located on the molybdate particle surface. The Eu^{3+}-doped phosphors, with or without the presence of Au NPs, exhibit intense red luminescence characteristic of the Eu^{3+} ion inserted in low-symmetry sites. However, the Au NPs increase the radiative emission rate and absolute quantum yield of the Eu^{3+} $^5D_0$ emitter state due to the excitation field enhancement caused by the local surface plasmon resonance absorption effect of gold nanoparticles, which was confirmed by diffuse reflectance measurements. Finally, the Eu^{3+} quantum efficiency enhancement to 92% played by the gold nanoparticles and the high red color purity qualify the obtained phosphor for photonic applications.

1. Introduction

Nowadays, the combination of Au nanoparticles (Au NPs) and phosphors has attracted a lot of attention in the photonic field due to their applicability as drug delivery, diagnosis, therapeutics, and fluorescent probes in the detection of metal ions, small molecules, and biomacromolecules. [1–5] This wide field of applications comes from the synergism between the phosphor luminescence and the AuNPs properties, such as good conductivity and favorable biocompatibility [6]. Therefore, in the present study, the $Y_2(MoO_4)_3$:Eu^{3+}/Au composite is introduced aiming to combine both phosphor's and Au NPs properties which can provide bifunctionalities for high sensitivity/resolution fluorescence imaging and high quality in the detection of different molecules [7].

Eu^{3+} ion, in its turn, is a well-know red activator due to its emission lines that arise from the $^5D_0$ excited level to the $^7F_{0-6}$ ground states. [8–10] Besides the efficient emission, the Eu^{3+} ion can also act as structural probe because its main emission lines are sensitive to the crystalline field around the metal ion [11]. Usually, the Eu^{3+} ion is inserted in a host matrix such as oxides [12] or silicates [13] in order to enhance the Eu^{3+} absorptivity due to the sensitization effect played by the matrix. In this context, yttrium molybdate, $Y_2(MoO_4)_3$, is a suitable host for the Eu^{3+} ion due to its low relative phonon frequency, high thermal and electrical stability, high UV absorption of the MoO_4 groups, and the similar radii between Y^{3+} and Eu^{3+} ions. [14,15] The synthesis of $Y_2(MoO_4)_3$:Eu^{3+} phosphor via solid-state [14] or co-precipitation [16] methods are already reported in the literature; however, to date, no reference has been found on the use of the Pechini's method to obtain such material. In this way, the Pechini method was chosen in this present study for the preparation of the red phosphor $Y_2(MoO_4)_3$:Eu^{3+} based on the fact that it is a simple, and low-cost methodology, that allows good structural and stoichiometric control in the synthesis of high purity metal oxide particles. [17,18].

Metallic nanoparticles, as already mentioned, have been intensely used as active component in biosensors or drug delivery systems. [19,20] In this field, Au NPs have been highlighted because of their optical properties dependent on shape and size, and due to their quantum confinement effects [21]. For instance, due to their relative

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[*] Corresponding author. São Paulo State University (Unesp), School of Technology and Sciences, R. Roberto Simonsen, 305, 19060-900, Presidente Prudente, SP, Brazil.
E-mail address: xavier.cardoso@unesp.br (C.X. Cardoso).

https://doi.org/10.1016/j.optmat.2018.06.023
Received 26 April 2018; Received in revised form 30 May 2018; Accepted 14 June 2018

inertia and surface Plasmon absorption bands in the visible and near-infrared spectral regions, Au NPs have been used as SERS (surface-enhanced Raman scattering) substrates [22]. To the best of our knowledge, there is no report in the literature about the $Y_2(MoO_4)_3$:Eu^{3+}/Au composite synthesis. Furthermore, there is a challenge to be overcome in the synthesis of phosphors incorporated with gold nanoparticles in relation to the shape and size control of the metallic nanoparticles during the calcination step. Thus, the aim of this study is to synthesize the $Y_2(MoO_4)_3$:Eu^{3+}/Au composite applying an adapted Pechini methodology, in order to evaluate the effects of the Eu^{3+} ions and Au NPs in the structural, morphological, and luminescent properties of the produced composite.

2. Material and methods

2.1. Experimental

Rare earth oxides, (Y_2O_3 and Eu_2O_3, 99.99%, Sigma-Aldrich), ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}.4H_2O$, 99.9%, Sigma-Aldrich), gold (III) chloride trihydrate ($HAuCl_4.3H_2O$, Sigma-Aldrich), D-sorbitol ($C_6H_{14}O_6$: 99%, Sigma-Aldrich), anhydrous citric acid ($C_6H_8O_7$: 99.5%, Fluka Analytical), and nitric acid, (HNO_3, 65%, VETEC) were used as starting materials without further purification.

$Y_2(MoO_4)_3$, $Y_2(MoO_4)_3$:Eu^{3+}, $Y_2(MoO_4)_3$/Au and $Y_2(MoO_4)_3$:Eu^{3+}/Au powders were synthesized based on the modified Pechini's method reported to the preparation of Y_2O_3:Eu^{3+} phosphors [23,24] however, in the present case, using sorbitol as complexing agent instead of ethyleneglycol. The percentage of 2 at% of Eu^{3+} in relation to Y^{3+} ions was chosen to provide phosphors with good and comparable light-emitting properties [25]. Therefore, rare earth nitrate solutions (prepared by dissolving stoichiometric amounts of the rare-earth oxides in HNO_3) were added in citric acid (molar ratio of citric acid to rare earth of 3:1) in order to obtain 0.5 g of the final powder. The mixture was kept upon mechanical stirring until the acid dissolution at 80 °C for 10 min, and then stoichiometric amounts of ammonium molybdate tetrahydrate were added. At this moment, the solution acquired a yellow color. After 10 min, stoichiometric amounts of sorbitol (molar ratio of sorbitol to rare earth of 2:1) was added. After 20 min, just in the case of $Y_2(MoO_4)_3$/Au and $Y_2(MoO_4)_3$:Eu^{3+}/Au samples preparation, the gold (III) chloride trihydrate (in weight percent of 2 wt% in relation to 0.5 g of the final powder) was added. The solution was heated at 120 °C under mechanical stirring for 1 h until the polymeric resin formation. The polymeric resin was submitted to a pre-calcination at 400 °C for 5 h. After this treatment, the partial decomposition of the resin took place, yielding the so-called puff (expanded resin). This material was ground in a mortar and sieved in a 325-mesh sieve. Then, the powder was heated again at 650 °C in air atmosphere for 5 h [26]. The $Y_2(MoO_4)_3$:$Eu^{3+}$and the undoped matrix were also synthesized in order to evaluate the gold and europium impacts in the molybdate structure.

2.2. Characterization

Powder X-ray diffraction (XRD) was carried out in a SHIMADZU XDR-6000 diffractometer, step size of 0.02°, Cu $K\alpha_1$ radiation $\lambda = 1.5406$ Å. The crystallite size of the samples was calculated via Scherrer's method [27], equation (1).

$$\varepsilon = \frac{K\lambda}{\beta_p cos\theta} \tag{1}$$

Where βp is the width at half maximum in radians of a reflection peak; *k* is a constant that depends on the reflection symmetry, which usually is given as 0.9; ε is the grain size, and λ is the X-ray wavelength in nanometer.

The thermal profile of the samples was checked through thermogravimetry (TG) and differential scanning calorimetry (DSC) using a TA Instruments, model SDT Q600, and heating ramp of 10 °C/min. The thermal treatment was performed from 25 ºC to 1000 °C, under a nitrogen atmosphere (100 mL/min). The vibrational profile of the samples was monitored by Fourier transform infrared spectroscopy (FTIR) in KBr pellets by using a SHIMADZU IRAFFINITY-1 spectrophotometer and by Raman spectra obtained in a RENISHAW IN-VIA spectrometer equipped with a LEICA DMLM optical microscope. The morphology was checked by scanning electron microscopy (SEM) measurements by using a CARL ZEISSEVO LS15 microscope and by transmission electron microscopy (TEM) in a JEOL microscope, JEM-2100 model. The samples were also characterized by UV–Vis diffuse reflectance measurements in a PERKIN ELMER LAMBDA 1050 spectrophotometer in order to evaluate the band gap of the phosphors through a graphic of $(\alpha h\nu)^n$ versus the energy of the incident photon (h), where *n* has a value equal to 2 for direct transition and 0.5 for indirect transition [28]. The α value is the ratio of the scattering and absorption coefficients according to the Kubelka-Munk's approximation [29], equation (2), where R is the reflectance observed for the different incident energies.

$$\alpha = \frac{K}{S} = \frac{(1-R)^2}{4R} \tag{2}$$

Photoluminescence (PL) spectroscopy, at room temperature, for all produced phosphors were measured under continuous Xe lamp (450 W) excitation in a HORIBA JOBIN YVON FLUOROLOG-3 spectrofluorimeter equipped with an excitation and emission double monochromator and a photomultiplier R 928 HAMMATSU. The slits were placed at 2.0 and 0.5 nm for excitation and emission, respectively. The emission decay curves were carried out in a phosphorimeter equipped with Xe (5 J/pulse) lamp. The Judd-Ofelt intensity parameters Ω_2 and Ω_4 were estimated for all Eu^{3+} phosphors from the emission data by using equations (3) and (4) [30], where $\langle {}^5D_0\|U^\lambda\|^7F_i\rangle$ represents the square reduced matrix elements which values are equal to 0.0032 to Ω_2 and 0.0023 to Ω_4 [30]; *h* is the Planck's constant, *e* is the electron charge, *c* is the speed of light in vacuum, ε_0 is vacuum permittivity constants. A_{01} can be estimated by the equation $A_{01} = 14.65\, n^3$ in s^{-1} [31], where *n* is the refractive index, equal to 2.031 for the molybdate [32]. I is the integrated area under the ${}^5D_0 \rightarrow {}^7F_j$ transitions in the emission spectra. *X* is the Lorentz local field correction equal to $n(n^2+2)^2/9$.

$$A_{0-\lambda} = A_{0-j} = A_{01}\frac{I_{0-j}}{I_{0-1}}\frac{h\nu_{0-1}}{h\nu_{0-j}} \tag{3}$$

$$\sum_{\lambda=2,4} \Omega_\lambda {}^5D_0\|U^{(\lambda)}\|^7F_j^2 = A_{01}\frac{I_{0-j}}{I_{0-1}}\frac{h\nu_{0-1}}{h\nu_{0-j}}\frac{3hc^3 4\varepsilon_0}{64\pi^3 e^2}\frac{1}{\nu_\lambda^3 x} \tag{4}$$

The emission decay curves were used to estimate the emission lifetime (τ) that were applied to evaluate the Eu^{3+} quantum efficiency (η_{Eu}). The quantum efficiency is calculated by applying equation (5), where A_{rad} and A_{nrad} are the radiative and the non-radiative rates for an emitting level, respectively.

$$\eta = \frac{A_{rad}}{A_{rad} + A_{nrad}} \tag{5}$$

The A_{rad} rate was estimated by equations (3) and (6), and the A_{nrad} from equation (7).

$$A_{rad} = \sum_J A_{0-j} \tag{6}$$

$$A_{total} = \frac{1}{\tau} = A_{rad} + A_{nrad} \tag{7}$$

Finally, the absolute emission quantum yield values (QY) were measured at room temperature by using a UV-NIR absolute PL quantum yield spectrometer C13534 from Hamamatsu under continuous Xe lamp