Sol–gel Pechini synthesis and optical spectroscopy of nanocrystalline La$_2$O$_3$ doped with Eu$^{3+}$

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**Abstract**

Europium-doped La$_2$O$_3$ nanocrystalline powders with sizes in the range of 50–200 nm have been obtained by the modified sol–gel Pechini method. Differential thermal analysis, thermogravimetric analysis, infrared spectroscopy and X-ray diffraction were used to study the evolution of the precursor powders towards the desired crystalline phase. We determined the size and the morphology of the nanoparticles by electronic microscopy. Finally, we studied and analyzed the luminescence properties of the trivalent europium in the hexagonal La$_2$O$_3$ nanocrystals by photoluminescence and cathodoluminescence. The luminescence spectrum of Eu$^{3+}$ in these nanocrystals is dominated by the $^5$D$_0$ → $^7$F$_2$ transition with its maximum intensity peak located at 626 nm, which makes these nanocrystals promising nanophosphors emitting in the red region of the electromagnetic spectrum.

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1. Introduction

Research and development of nanoscale rare earth (RE) doped luminescent materials are part of the quickly advancing nanoscience and nanotechnology [1]. The size of these materials affects their physical properties such as emission lifetime, luminescence quantum efficiency, and concentration quenching [2]. Nanocrystalline materials with particle diameters of 100 nm or less may show increased luminescence efficiency as compared to their bulk counterparts [3].

RE sesquioxides (La$_2$O$_3$, Y$_2$O$_3$, Lu$_2$O$_3$, etc.) are known as excellent optical host materials for lanthanide active ions [4] because, among others, they are transparent for visible and infrared light, the effect of the matrix on the spectroscopic properties of the RE ions does not shift significantly the position of the emission bands of these ions, and the lanthanide luminescence can be efficiently sensitized by means of optical pumping [5,6]. Nanocrystalline RE sesquioxides doped with lanthanide active ions allow developing nanophosphors for various applications such as solid-state lasers, luminescent lamps, flat displays, optical fiber communication systems, and other photonic devices.

Lanthanum oxide (La$_2$O$_3$) is a semiconductor material [7] with the largest band gap among RE sesquioxides, with a value of 4.3 eV [8]. La$_2$O$_3$ crystallizes in the hexagonal system structure with space group $P$6$_3$m1 [9]. This compound has numerous industrial applications, as a component of catalyst supports and ceramics, as a strengthening agent in structural materials, as part of optical waveguide filters, and as part of automobile exhaust-gas convectors [10–14]. Trivalent europium (Eu$^{3+}$) activated phosphors have been extensively investigated due to their application as red phosphors [15]. Furthermore, Eu$^{3+}$ is often used as a structural probe [16], because of the relative simplicity of its energy-level structure and the fact that it possesses non-degenerate ground ($^7$F$_0$) and excited ($^5$D$_0$) states, and because the absorption and emission spectra of this ion show marked dependence on its site symmetry in the host material [17]. It has been previously introduced in several materials, including La$_2$O$_3$ using different synthesis techniques such as calcination methods [15], solutions combustion synthesis [3, 18, 19], conventional hydrothermal [20] and microwave hydrothermal methods [21].

In this paper, we propose a new method to synthesize Eu:La$_2$O$_3$ nanoparticles by using the modified Pechini method, which is an alternative to the conventional sol–gel method [4]. This method allows a molecular mixing of constituents, leading to a good chemical homogeneity, an increase in the reaction rate and a decrease of the temperature of crystallization [22,23].

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The luminescence properties of these nanoparticles have been characterized by photoluminescence (PL) and cathodoluminescence (CL).

2. Experimental procedures

La$_2$O$_3$ nanocrystals doped with 5 mol% of Eu$^{3+}$ (due to the concentration quenching effect, 5 mol% is the optimum for this material [15]) were prepared using the modified Pechini method [24]. Two reactions are involved in this process: the formation of a complex between an organic acid, such as citric acid or EDTA, with the precursor metals, and an esterification reaction with ethylene glycol (EG). The aim of the polymeric organic net produced by esterification is to reduce any segregation of the cations [25].

First, Eu$_2$O$_3$ was dissolved in hot HNO$_3$ (Merck, 65% weight per volume) under stirring to generate Eu(NO$_3$)$_3$. This was mixed with La(NO$_3$)$_3$$/\text{C}_1$$\text{H}_2$$\text{O}$ and dissolved in distilled water. We added EDTA to this solution with a molar ratio [EDTA]/[Metal] = 1 were [Metal] is the concentration of lanthanum and europium in the solution. The esterification agent, ethylene glycol, was added with a molar ratio [EDTA]/[EG] = 2, while stirring and heating the solution. The precursor resin generated was calcined at 573 K for 3 h to obtain the precursor powders. Finally, the precursor powders were calcined at different temperatures, between 573 and 1273 K, in air atmosphere for 2 h to obtain nanocrystals of Eu:La$_2$O$_3$ [4,23].

Differential thermal analysis (DTA) and thermogravimetry (TG) were used to characterize the thermal evolution of the precursor powders with temperature using a TA Instruments Simultaneous Differential Techniques Instrument SDT 2960. The experiments were carried out in Pt pans using calcined Al$_2$O$_3$ as the reference material. The sample was heated at 10 K/min in the 300–1200 K range. We used synthetic air as the purge gas at a flow rate of 90 cm$^3$/min and the storage rate of data was 0.5 s per data point.

The crystalline structure of the nanocrystals was analyzed by X-ray powder diffraction using a Bruker-AXS D8-Discover diffractometer with parallel incident beam (Göbel mirror) and vertical goniometer, a 0.02$^\circ$ receiving slit and a scintillation counter as detector. The angular 2$\theta$ diffraction range was set between 5$^\circ$ and 70$^\circ$. Cu radiation was obtained from a copper X-ray tube operated at 40 kV and 40 mA. The data were collected with an angular step of 0.05$^\circ$ at 3 s per step for identification of the crystalline phases, and at an angular step of 0.02.$^\circ$ at 16 s per step for unit cell refinement. The lattice parameters of these crystals were calculated using the FULLPROF program [26] based on the Rietveld method [27]. The number of refined parameters was 10. The Scherrer’s formula was used to determine the average grain sizes of the Eu:La$_2$O$_3$ nanocrystals [28].

The characterization of the IR vibration bands of the Eu:La$_2$O$_3$ nanocrystals was carried out in the range 350–4000 cm$^{-1}$ using Fourier-Transformed Infrared spectroscopy (Bruker Equinox-55) equipped with a DTGS detector, and working in transmission mode. The frequency was set between 50 and 60 Hz and the current intensity at 0.8 A. The resolution of the measurements was 0.5 cm$^{-1}$.

To observe the distribution of size and the homogeneity of the nanocrystals, scanning electron microscopy (SEM) JEOL JSM6400 and transmission electron microscopy (TEM) JEOL JEM-1011 were used.

Photoluminescence (PL) was analyzed by steady-state fluorescence that was performed in an Aminco-Bowman Series 2 fluorescence spectrometer. The unpolarized emission spectrum was recorded between 560 and 750 nm in a 90$^\circ$ geometry with excitation by a Xenon lamp at 280 nm. The spectrum was recorded taking a measurement every 1 nm at a scanning rate of 10 nm/s.

Cathodoluminescence (CL) was performed at room temperature in a field emission scanning electron microscope (Zeiss Supra 55) using a Gatan Mono CL 2 System. The spectra and images were acquired using a Hamamatsu photomultiplier tube (R2228). The spectra were acquired at 3–10 keV using a probe current of 10 mA over a scanned area of 4000 mm$^2$. All the spectra were connected for the monochromator and detector response and normalised to maximum intensity. The images were recorded using a 5 keV electron beam with a probe current of 200 pA. For this characterization Eu:La$_2$O$_3$ samples were dispersed in an ethanol solution, and several drops of this dispersion were deposited on Si substrates, letting ethanol to evaporate.

3. Results and discussion

The DTA–TG thermograms of the precursor powders are shown in Fig. 1. Four regions (A, B, C, D), associated to weight losses, can
be observed. The first region, marked as A in Fig. 1 is associated with the evaporation of water formed during the esterification reaction between the EDTA and EG. This evaporation is produced in the temperature interval from 300 to 680 K with a weight loss of 3%. The second region, marked as B, corresponds to the evaporation of the organic molecule, EG, whose boiling point is 573 K [30,31,32]. The DTA curve also exhibits an exothermic peak at 614 K in this region. In the third region, C in the figure, between 700 and 900 K, DTA shows two exothermic peaks at 722 and 866 K that are attributed to the oxidation of the residual organic compounds, with a weight loss of 22%. Finally, the last region, marked as D in the figure, between 873 and 1200 K, corresponds to the crystallization of the two crystalline phases we observed by X-ray diffraction (see Fig. 2): Eu:La$_2$O$_2$CO$_3$ and Eu:La$_2$O$_3$, observed as two endothermic peaks in the DTA curve at 873 and 916 K, respectively. The weight loss associated to this interval is around 7%. From these results we concluded that the minimum calcination temperature of the precursor powders to obtain Eu:La$_2$O$_3$ nanocrystals must be higher than 916 K.

The crystalline structure of the precursor powders used for the synthesis of Eu:La$_2$O$_3$ nanocrystals and calcined in the range between 573 and 1073 K, was studied by the X-ray powder diffraction technique. The results are shown in Fig. 2. X-ray diffraction patterns of the precursor powders were identified using the Joint Committee on Powder Diffraction Standards (JCPDS) files: 48-1113 for La$_2$O$_2$CO$_3$ [31] and 73-2141 [32] for La$_2$O$_3$.

The precursor powders are amorphous when calcined at temperatures in the range of 573–773 K. The first crystalline peaks were observed at 773 K and were attributed to lanthanum oxide carbonate according to the JCPSD file 48-1113 [31]. The diffraction peaks corresponding to this phase are marked as triangles in Fig. 2. The formation of the phase can be attributed to the presence of carbon rich species in the powders introduced by the organic molecules. At 873 K we observed the first diffraction peaks of the La$_2$O$_3$ phase, marked as stars in Fig. 2, according to the 73-2141 file of JCPDS [32]. At 973 K and above, only this phase remained and the La$_2$O$_2$CO$_3$ phase disappeared completely. Since measurements were taken every 50 K, it exists a discrepancy between the calcinations temperature determined by X-ray diffraction and that determined by DTA.

The size of the nanoparticles of Eu:La$_2$O$_3$ obtained by calcination at 1073 K for 2 h was calculated using the Scherrer’s formula, \[ L = \frac{0.9 \lambda}{\beta \cos \theta} \], where \( \lambda \), \( \beta \) and \( \theta \) are the wavelength (with a constant value of 0.15406 nm), the FWHM of the diffraction peak, and the Bragg angle for \( hkl \) peak considered, respectively. The validity of the Scherrer’s formula has been widely discussed in the literature [4]. It is valid for particles with sizes below 500 nm. We obtained a crystallite size of 50 nm calculated from the data corresponding to the (1 0 0) diffraction peak of Eu:La$_2$O$_3$ structure that is the one that showed the highest intensity for this structure.

The cell parameters of the sample calcined at 1073 K have also been determined by X-ray diffraction and refined using the FULLPROF program. The cell parameters calculated were \( a = b = 6.516 \) nm and \( c = 3.846 \) nm. These parameters are smaller than those of pure La$_2$O$_3$ ( \( a = b = 6.547 \) nm, \( c = 3.854 \) nm). This decrease in the unit cell parameters is attributed to the introduction of europium in the structure of the crystals, since the ionic radius of europium is smaller than that of lanthanum in a 7-fold oxygen coordination.

We also followed the evolution of the precursor powders towards the formation of Eu:La$_2$O$_3$ by infrared (IR) spectroscopy. The IR spectrum of commercial La$_2$O$_3$ (Aldrich, 99.9%) was used as reference. Fig. 3 shows the IR spectra of the samples calcined at 973, 1073 and 1173 K for 2 h, together with the IR spectrum of commercial La$_2$O$_3$. The IR characteristic band of La$_2$O$_3$ appears at 644 cm$^{-1}$ [33]. When we calcined the precursor powders of our samples to 1073 K or over for 2 h, a similar band appeared at 649 cm$^{-1}$. Taking into account the different atomic weight of La$^{3+}$ (138.91) and Eu$^{3+}$ (151.96), if Eu$^{3+}$ is substituting La$^{3+}$ in the structure, as we expect, this characteristic vibration band should shift towards larger energies, as we observed. Although the shift observed is small and may appear negligible, it constitutes a probe that we succeeded in the incorporation of Eu$^{3+}$ in the structure of La$_2$O$_3$.

If we compare the position of the v(La–O) in La$_2$O$_3$ at 644 cm$^{-1}$ with the position of the v(Eu–O) in Eu$_2$O$_3$, that appears at 753 cm$^{-1}$ [34], and we suppose, making a very rough approximation, that the position of this band will change linearly with the concentration of Eu$^{3+}$ in La$_2$O$_3$, the shift of 5 cm$^{-1}$ we observed would correspond to a sample of La$_2$O$_3$ doped 5 at.% Eu$^{3+}$. This
corresponds exactly to the concentration of Eu$^{3+}$ we introduced in our synthesis process.

Fig. 4 shows the SEM images of the Eu:La$_2$O$_3$ nanocrystals obtained after calcination at 1073, 1173 and 1273 K for 2 h. The SEM images indicate that the size of the nanoparticles increased when the calcination temperature increased.

Fig. 5(a) shows a TEM image of the Eu:La$_2$O$_3$ nanocrystals obtained by calcination at 1073 K during 2 h. To record this image the nanocrystals were dispersed in acetone and a drop of the dispersion was deposited on a cooper grid covered by a holey carbon film (HD200 Cooper Form-var/carbon). As we can see in the image the nanoparticles were agglomerated, which difficult the determination of their size. An approximate estimation of the size of the nanocrystals would be between 50 and 200 nm, which is in agreement with the crystallite size determined from the Scherrer’s formula. By electron diffraction we were able to show that each of these nanocrystals were a single crystal and corroborated that the structure of these nanocrystals was hexagonal, as can be seen in Fig. 5(b).

Fig. 6 shows the PL spectrum of Eu$^{3+}$ in La$_2$O$_3$ nanoparticles in the 550–750 nm range recorded at room temperature, after pumping into the charge transfer state band (CTS) at 250 nm. In this way, Oxygen 2p electrons are excited into 4f levels and subsequently the CTS relaxes to the 4f levels of Eu$^{3+}$. In this figure, the typical emission spectrum of Eu$^{3+}$ due to the $^5D_0 \rightarrow ^7F_J$ ($J = 0–4$) transitions was observed. The apparent broadness of the emission bands of Eu$^{3+}$ is due to the large spectral bandwidth (1 nm) we used to record this spectrum. The spectrum is dominated by the $^5D_0 \rightarrow ^7F_2$ transition which consists of two peaks at 613 and 626 nm, respectively. Park et al. [15] showed that the photoluminescence behaviour of Eu:La$_2$O$_3$ phosphors depends on the Eu$^{3+}$ concentration. They showed that while the spectra of samples doped with 0.01 mol Eu$^{3+}$ were dominated by the $^5D_0 \rightarrow ^7F_2$ transition, spectra of samples doped with a larger concentration of Eu$^{3+}$ were dominated by the $^5D_0 \rightarrow ^7F_2$ transition. The maximum emission intensity of this last transition was observed for samples doped with 0.05 mol Eu$^{3+}$. Park et al. [15] attributed this effect to an increase of the degree of covalency when the concentration of Eu$^{3+}$ ions increased (nephelauxetic effect), and to the interaction between Eu$^{3+}$ ions at long distances in this structure. Our sample was doped with 0.05 mol Eu$^{3+}$, and its emission spectrum is dominated by the $^5D_0 \rightarrow ^7F_2$ transition, in good agreement with the results of Park et al. [15]. The fact that the spectrum is dominated by this transition also
indicates that europium is located in a structural site without an inversion center \([35]\), such as the crystallographic site occupied by La\(^{3+}\) in this structure (C\(_{3v}\)).

The \(^5\)D\(_0\) \(\rightarrow\) \(^7\)F\(_1\) transition can be seen as two peaks located at 587 and 595 nm, respectively. It is well known that the electric dipolar \(^5\)D\(_0\) \(\rightarrow\) \(^7\)F\(_2\) transition (hypersensitive) is very sensitive to ligand field, and it is sensitive to small changes in the chemical environment around Eu\(^{3+}\) ions and the coupling strength of the host. Instead, due to the magnetic dipole transition, the \(^5\)D\(_0\) \(\rightarrow\) \(^7\)F\(_1\) transition is independent of the local environment of the europium, it does not depend strongly on coordination, and it hardly varies with the crystal field strength introduced by the matrix around the Eu\(^{2+}\) ion. So, it can be taken as a reference for different materials. Therefore, because of their different mechanism, the intensity ratio between the intensity of the \(^5\)D\(_0\) \(\rightarrow\) \(^7\)F\(_2\) transition at 626 nm and the intensity of the \(^5\)D\(_0\) \(\rightarrow\) \(^7\)F\(_1\) transition at 595 nm, can be used as a spectroscopic probe for evaluating the asymmetry of the coordination polyhedron of the Eu\(^{3+}\) ions, and gives a measure of the degree of distortion from the inversion symmetry of the local environment of the Eu\(^{3+}\) ion in the matrix \([2,36]\).

A large value of this ratio, means that the electric dipole interaction is enhanced, associated to a stronger crystal field in the short range, that can be related to an increase of the covalency of the structure or to a distortion of the bonds surrounding the active ion. In our case this ratio is 4.04. Compared to other ratios reported in the literature \([2,18,35]\), this value is within the maximum values reported, indicating that europium in the host lattice is located in a low symmetry site, as was expected after observing the high intensity of the peak corresponding to the \(^5\)D\(_0\) \(\rightarrow\) \(^7\)F\(_2\) transition.

The \(^5\)D\(_0\) \(\rightarrow\) \(^7\)F\(_0\) transition, that should be completely forbidden since the transition probability between \(J = 0\) and \(J = 0\) is zero at first order, can be seen as a small peak at 580 nm. Nieupoort and Blasse \([36,37]\) reported that the 0–0 transition might be partially allowed to the presence of a linear crystal field term in some lattice site symmetries such as \(C_2\) or \(C_{3v}\). So, the observation of the 0–0 transition agrees with the substitution of Eu\(^{3+}\) in the regular La\(^{3+}\) site in the structure of these nanocrystals.

This PL spectrum is in agreement with the PL spectra of Eu:-La\(_2\)O\(_3\) phosphors synthesized by other techniques \([3,15,18,19]\). When we compared the PL spectrum of the samples that we prepared by the Pechini method with those obtained in Ref. \([15]\), our spectrum corresponds exactly with that of the sample doped with 0.1 Eu mol\% La\(_2\)O\(_3\) in the range between 560 and 650 nm, even with the same intensity ratios. Park et al. \([15]\) were able to identify also the bands corresponding to the \(^5\)D\(_1\) \(\rightarrow\) \(^7\)F\(_0\), \(^5\)D\(_1\) \(\rightarrow\) \(^7\)F\(_1\), \(^5\)D\(_2\) \(\rightarrow\) \(^7\)F\(_2\), \(^5\)D\(_2\) \(\rightarrow\) \(^7\)F\(_1\), \(^5\)D\(_2\) \(\rightarrow\) \(^7\)F\(_0\) transitions, that appeared at shorter wavelengths, a range that we did not study. In addition to their bands, we were able to identify the bands corresponding to the \(^5\)D\(_0\) \(\rightarrow\) \(^7\)F\(_1\) and \(^5\)D\(_0\) \(\rightarrow\) \(^7\)F\(_2\) transitions that appeared at longer wavelengths, a range that was not previously studied by Park et al. \([15]\). Our PL spectrum coincides also with the spectrum obtained in 5 mol\% Eu:La\(_2\)O\(_3\) samples prepared by a solution
combustion synthesis procedure [3] in the 560–720 nm range. In this case, however, the intensity ratios changed slightly.

The cathodoluminescence spectrum of the Eu:La2O3 nanoparticles has been studied at room temperature. To the best of our knowledge this is the first time that cathodoluminescence has been used to characterize Eu3+ in this matrix. Fig. 7 shows the CL spectra recorded for the sample calcined at 1273 K for 2 h as a function of the accelerating voltage. As can be seen, the CL intensity increases with raising the accelerating voltage from 3 to 10 keV, keeping always constant the intensity ratios between the different peaks. All the peaks observed in these spectra correspond to the same transitions observed in the PL spectrum, indicating that Eu3+ in this matrix can be efficiently excited by means of electron bombardment.

Fig. 8 shows a SEM image of the Eu:La2O3 nanocrystals together with a panchromatic image and two monochromatic images of the same region of the sample taken at 594 and 626 nm, coinciding with the peaks corresponding to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transitions. These images confirm that the luminescence observed in the CL spectra arises from the Eu:La2O3 nanoparticles.

4. Conclusions

We have successfully synthesized europium-doped La2O3 nanoparticles by the modified Pechini method. The optimum range of calcination temperatures to synthesize these nanoparticles was between 1073 and 1273 K, obtaining nanoparticles with sizes ranging from 50 to 200 nm, depending on the calcination temperature. We investigated the luminescent properties of Eu3+ in the La2O3 nanocrystals by photoluminescence and cathodoluminescence. The spectrum of Eu3+ in these crystals is dominated by the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition with a maximum intensity peak located at 626 nm, which make of these nanocrystals promising nanophosphors emitting in the red region of the electromagnetic spectrum. Other peaks, corresponding to the $^5\text{D}_0 \rightarrow ^7\text{F}_j$ transitions from $j = 0$ to
$J = 4$ have been observed. A careful analysis of the relative intensities between the different spectroscopic bands observed for Eu$^{3+}$ in these crystals indicated that Eu$^{3+}$ is substituting La$^{3+}$ in the structure and it is not located in interstitial positions. A good agreement was found between the spectra collected by photoluminescence and cathodoluminescence, despite the different excitation mechanisms of both techniques.

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References