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Simple preparation of fluorescent composite films based on cerium and europium doped LaF_3 nanoparticles

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A B S T R A C T

The combination of materials to form hybrids with unique properties, different from those of the isolated components, is a strategy used to prepare functional materials with improved properties aiming to allow their application in specific fields. The doping of lanthanum fluoride with other rare earth elements is used to obtain luminescent particles, which may be useful to the manufacturing of electronic devices' displays and biological markers, for instance. The application of the powder of nanoparticles has limitations in some fields; to overcome this, the powder may be incorporated in a suitable polymeric matrix. In this work, lanthanum fluoride nanoparticles, undoped and doped with cerium and europium, were synthesized through the co-precipitation method in aqueous solution. Aiming the formation of solid state films, composites of nanoparticles in an elastomeric matrix, the nitrile rubber (NBR), were prepared. The flexibility and the transparency of the matrix in the regions of interest are advantages for the application of the luminescent composites. The composites were applied as films using the casting and the spin coating techniques and luminescent materials were obtained in the samples doped with europium and cerium. Scanning electron microscopy images showed an adequate dispersion of the particles in the matrix in both film formation techniques. Aggregates of the particles were detected in the samples which may affect the uniformity of the emission of the composites.

1. Introduction

The formation of composites with nanostructures is one way to produce functional materials for specific applications. Initially, the formation of composites aimed, mostly, the production of structural materials. However, nowadays, the development of those materials is also related to improve and explore other properties, such as optical, magnetic and electric, among others [1].

The high ionic conductivity of lanthanum fluoride, especially in the nanoscale, is the property related to its application in chemical sensors [2]. Besides that, LaF_3 may be applied for biological markers and displays of electronic devices, when doped with rare earth elements that possess luminescent properties [3,4]. Other fluorides, such as CaF_2, are also used as host matrices for rare earth doping, aiming to produce materials for optoelectronic applications [5,6].

One of the simplest and fastest processes for the preparation of nanocomposites consists on the physical mixture of the inorganic particles in polymeric matrixes – this technique is the dispersion of nanoblocks. The main difficulties of the technique involve the high viscosity of the matrix, which may favor the agglomeration of particles, and the formation of heterogeneous composites [7].

However, using an adequate solvent to redisperse the nanopowder and, then, mixing this dispersion with the polymeric phase is a viable strategy to minimize those effects. In addition, it is possible to functionalize the nanoblocks to improve their dispersion in the solvent used in the process [7,8].

Different combinations of rare earth compounds in polymeric matrices for the preparation of fluorescent composites have already been reported. Many studies report the use of polymethylmetacrylate as a matrix for the composites [4,9,10], mainly due to its transparency and mechanical properties. Studies also report the use of other polymers, such as polystyrene [11] and perfluorocyclobutyl polymers [12] as matrices to rare earth composites.

Using rare-earth-doped nanocrystals is strategic due to their higher efficiency of emission, the possibilities of customizing the solubility and ease of functionalization of the particles' surface, especially when compared to the traditional chelates of rare earth used for optical applications [13]. However, the direct application of the powder has some restrictions for many purposes. In order to overcome that, some recent studies have reported the preparation of bulk fluorescent

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composites with those nanoparticles in their composition [4,14].

In this work, composites of lanthanum fluoride doped with cerium and europium were prepared in a nitrile rubber (NBR) matrix, *via* the simple incorporation of the nanoparticles in the matrix using xylene as a common solvent. The composites were applied in the form of casting and spin coating films. The elastomeric matrix is transparent in the regions of interest and is flexible, which could be valuable for some applications, such as electronic devices' displays.

2. Experimental section

2.1. Synthesis of the nanoparticles

The nanoparticles were synthesized through the co-precipitation method [15]. Solutions of lanthanum nitrate (0.08 mol L^{-1}) and cerium or europium chloride were added dropwise to a solution of ammonium fluoride (0.28 mol L^{-1}). The system was heated up to 343 K and left under mechanical stirring for two hours. After that, the dispersions of nanoparticles were purified by centrifugation and washing of the precipitate with deionized water. The purification process was repeated three times. The synthesis was performed several times to produce doped and undoped LaF_3 nanoparticles. The effectiveness of the route was confirmed by the characterization of the materials.

2.2. Purification of the nitrile rubber (NBR)

The commercial nitrile rubber NBR-608 (Nitriflex, 33% of acrylonitrile) was dissolved in 20 mL of chloroform (Synth, 99.8%) under magnetic stirring. After the complete dissolution of the rubber, the solution was transferred to an erlenmeyer with methanol so that the elastomer would precipitate. This procedure was repeated twice. Then, the rubber was dried under vacuum [16].

2.3. Preparation of the composites in NBR

The powdered nanoparticles were redispersed in a solution of purified nitrile rubber (NBR) in xylene, using different ratios of the nanoparticles and the polymeric matrix (1%, 5%, 10% and 25%). The films were prepared using a simple casting procedure, by drying a drop (50 µL) of the solutions on the substrate (glass or quartz) for 30 min at 40 °C; and the spin coating technique (*Spincoater Microtube Model A1V1.1.*) using the rotation of 2.000 rpm for 20 s, with acceleration and deceleration times of 5 s. The spin coating films were prepared with 5 layers.

2.4. Characterization techniques

The nanoparticles were characterized by means of dynamic light scattering (DLS) and zeta potential using the Zeta Sizer Nano ZS (Malvern Instruments) and deionized water as a solvent. UV–vis absorption spectra were collected on a Shimadzu Multispec 1501, in square quartz cells, from 200 to 800 nm; the nanoparticles were dispersed in water. Fluorescence spectra of the nanoparticles' dispersions in water were obtained with a Shimadzu 5301PC in 10 mm square quartz cells; the excitation wavelengths were the maximum absorption wavelengths from the photoluminescence excitation spectra. A Fluorog 3 equipment from Jobin Yvon was used to obtain the fluorescence spectra of the powdered nanoparticles; the excitation wavelengths were obtained from the excitation analysis with the same equipment. The powdered samples were also analyzed by X-ray diffraction, on a STADI P powder diffractometer, from STOE, operating at 40 kV and 40 mA, using $CuK\alpha_1$ radiation (λ = 1.54056 Å), from 20 to 70°, with step sizes of 0.015° and a counting time of 120 s at each 3.15°. The reference diffractogram of lanthanum fluoride was taken from the *Inorganic Crystal Structure Database (ICSD)*. The scanning electron microscopy (SEM) images of the composites were obtained using a Philips XL-30 microscope. The films were deposited on quartz substrates and their surface was metallized with gold. The fluorescence spectra of the films were collected using the Fluorog 3 equipment from Jobin Yvon.

3. Results and discussion

3.1. Doped and undoped LaF_3 nanoparticles

The average size of the nanoparticles dispersed in water (c = 0.5 g L^{-1}, for all samples) was determined using the dynamic light scattering technique. The dispersions of NPs doped with europium and cerium had average diameters of 123 nm and 95 nm, respectively. These dimensions are smaller than the average size obtained for the undoped LaF_3 nanoparticles (185 nm).

The polydispersity index (PDI), which is related to the dispersion of sizes of particles in each sample, was of 0.255 and 0.387 for the europium and cerium doped nanoparticles, respectively. These results indicate that the size distribution of the dispersions is not monodisperse, probably due to the presence of aggregates of nanoparticles in the samples.

Monodisperse size distribution of nanoparticles could facilitate the preparation of homogeneous composites after incorporation in the elastomeric matrix, avoiding shifts and intensity ratio changes in the emission pattern of the films, which may be attributed to different sizes and concentration of the particles in the matrix [8].

The zeta potential is positive and above 30 mV for all dispersions (ζ_{LaF3} = 44.2 ± 6.9 mV, ζ_{LaEuF3} = 41.5 ± 5.9 mV and ζ_{LaCeF3} = 49.2 ± 12.0 mV). This result is within the general stability range for the technique [17], meaning the samples do not present sedimentation of particles in this concentration.

The X-ray diffraction patterns of the powdered nanoparticles were used to confirm the formation of the lanthanum fluoride, based on the reference diffractogram obtained from ICSD (*Inorganic Crystal Structure Database* - ISCD 49721) [18]. Fig. 1 presents the X-ray powder diffraction patterns of the doped and undoped samples as well as the one used as reference.

On the basis of the XRD results, we used the Rietveld method [19,20] to further comprehend the crystal structure of the materials. The Rietveld refinement was performed using the software *Topas-Academic v. 5* [20,21]. Table 1 shows the crystallite sizes obtained from

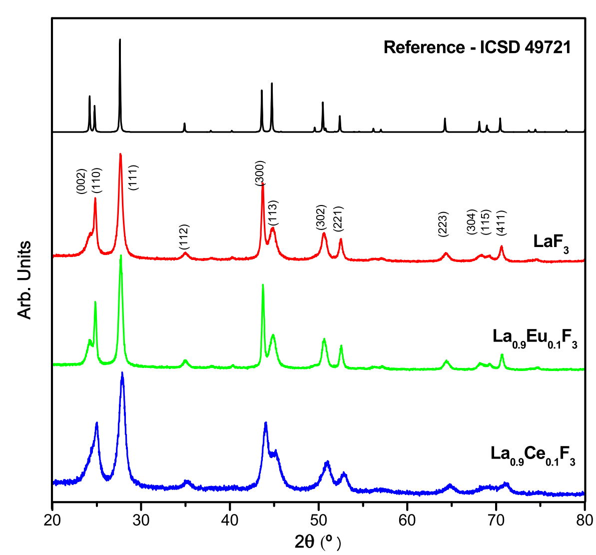

Fig. 1. XRD patterns obtained for the doped ($La_{0.9}Ce_{0.1}F_3$: blue line and $La_{0.9}Eu_{0.1}F_3$: green line) and undoped LaF_3 (red line) nanoparticles and the calculated one from the reference – ICSD 49271 (black line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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