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journal homepage: [www.elsevier.com/locate/jmmm](http://www.elsevier.com/locate/jmmm)Structural and magnetic properties of  $\text{Fe}_{2-x}\text{CoSm}_x\text{O}_4$ —nanoparticles and  $\text{Fe}_{2-x}\text{CoSm}_x\text{O}_4$ —PDMS magnetoelastomers as a function of Sm contentMariano M. Ruiz<sup>a</sup>, José L. Mietta<sup>a</sup>, P. Soledad Antonel<sup>a</sup>, Oscar E. Pérez<sup>b</sup>, R. Martín Negri<sup>a</sup>, Guillermo Jorge<sup>c,d,\*</sup><sup>a</sup> Instituto de Química Física de Materiales, Ambiente y Energía (INQUIMAE), Departamento de Química Inorgánica, Analítica y Química Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Av. Cantilo s/n (1428), Buenos Aires, Argentina<sup>b</sup> Departamento de Industrias, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Av. Cantilo s/n (1428), Buenos Aires, Argentina<sup>c</sup> Instituto de Física de Buenos Aires, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Av. Cantilo s/n (1428), Buenos Aires, Argentina<sup>d</sup> Instituto de Ciencias, Universidad Nacional de General Sarmiento, J.M. Gutiérrez 1150 (1613), Los Polvorines, Buenos Aires, Argentina

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## ABSTRACT

We have synthesized magnetic  $\text{Fe}_{2-x}\text{CoSm}_x\text{O}_4$  nanoparticles (NPs) by means of the coprecipitation method, varying Sm content from  $x=0$  to  $x=0.5$ . Energy-dispersive X-ray spectroscopy showed agreement between the metal proportion of the obtained nanoparticles and the stoichiometric mixture of cations used for the synthesis. Part of the particles were heated at 800 °C, and both were characterized by X-ray diffraction, scanning electron microscope imaging and magnetization measurements. Physical and magnetic properties were analyzed as a function of Sm content, before and after the heating treatment. A phase segregation is found for the calcined nanoparticles with large Sm content. The magnetic remanence, saturation and coercive field were investigated as a function of Sm content for both heated and unheated (as-prepared) particles. Polydimethylsiloxane-NPs magnetoelastomers were prepared and cured under an external uniform magnetic field, obtaining structured anisotropic composites, in which inorganic needles (columnar micrometric structures) oriented in the direction of the magnetic field are formed. Young modulus and remanent magnetic moment were measured and magnetization time relaxation experiments were performed in the directions parallel and perpendicular to the needles in order to determine the magnetic and elastic anisotropy of the composites. The elastic modulus measured parallel to the needles resulted almost twice in magnitude with respect to the perpendicular modulus. The measured magnetic anisotropy of the composites is probably due to the enhanced interparticle interaction within a needle and the freezing of an preferred easy axis distribution among the particles at the curing process.

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## 1. Introduction

Magnetic nanoparticles have a wide range of applications in modern science. In medicine, for example, they have a potential use for cancer treatment therapy[1,2] and magnetic resonance imaging and drug delivery[3]. In addition, they are used in elaboration of ferrofluids and magnetorheoelastomers, in which the nanostructures are dispersed in an high viscosity fluid such as silicon oil[4], resins or polymers[5], which have important applications in stiffness suppressors[6], acceleration sensors[7], and valves for microfluidic[8,9]. The resin or polymer can be cured under a uniform magnetic field, producing an ordered uniaxial

magnetic structure of the magnetic material. The resulting composites hold very interesting structural and magnetic anisotropic properties[10].

In the design and testing of potentially interesting magnetorheoelastomers it is necessary to know the magnetic properties of the building magnetic nanostructures, as well as how they could be varied, in order to obtain the desired magnetic or elastic behavior. Particularly, in cobalt ferrites part of the Fe content can be substituted by samarium (Sm), changing their magnetic behavior. It could be a mechanism to tune magnetic properties in magnetoelastomers with potential technological applications. Nevertheless, up to our knowledge, there is no comprehensive study on the magnetic properties of Sm-substituted cobalt ferrites[11].

Many synthetic methods are reported in the literature as organic acid precursor [11], hydrothermal [12], and coprecipitation method [13–15]. In particular, the coprecipitation method is

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a very simple and clean way to synthesize nanoparticles, it does not involve organic compounds and the remaining salts can be easily removed by washing with deionized water.

In this work, we present an encompassing study of the structural and magnetic properties of  $\text{Fe}_{2-x}\text{CoSm}_x\text{O}_4$  with Sm content ( $x$ ) between  $x=0$  and  $x=0.5$ . The particles were prepared by the coprecipitation method, and were studied by means of X-ray Diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM) imaging, and magnetization measurements. With the obtained particles we develop anisotropic magnetoelastomers, dispersing the particles in uncured polydimethylsiloxane (PDMS) and curing under a uniform magnetic field. The elastic and magnetic anisotropic properties of the composites were studied in order to determine the magnetic and elastic anisotropies due to the spatial organization of particles within the composite.

## 2. Materials and methods

### 2.1. Synthesis of $\text{Fe}_{2-x}\text{CoSm}_x\text{O}_4$ nanoparticles

The nanoparticles (NPs) were synthesized by the coprecipitation method. Adapting from Antonel et al. [14] and Mietta et al. [15], stock solutions of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (1 M) and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.5 M) were prepared, both in HCl 0.4 M. For every batch of synthesized particles a mixture solution was prepared using stoichiometric volumes of acidic Fe(III) and Co(II) solutions, and samarium (III) oxide ( $\text{Sm}_2\text{O}_3$ ) was dissolved in a stoichiometric ratio of concentrated HCl and filled with distilled water to complete a concentration of HCl of 0.4 M and final volume of 10 mL. The resulting acidic solution with the metals was slowly added (1 drop per 4 s) to 200 mL of 1.5 M NaOH solution at high speed stirring. The synthesis temperature (80 °C) was controlled by a water-jacketed reaction vessel with circulating thermostatic bath. Once finished the addition of the acidic solution, the system was left at 80 °C with high speed stirring in order to homogenize the particle size. The obtained particles were separated from the reaction medium by centrifugation (12,000 G for 10 min) and then washed with Milli-Q water. Centrifugation-washing cycles were repeated until the pH of the supernatant was nearly 7 (about 6 cycles). Finally the particles were dried in a vacuum oven at 40 °C for 24 h.

Part of the obtained particles were calcined for 2 h in a furnace at 800 °C (heat rate of 4 °C/min) in order to increase the crystallinity degree and study its influence in phase, size, morphology and magnetic properties.

### 2.2. Preparation of PDMS- $\text{Fe}_{2-x}\text{CoSm}_x\text{O}_4$ composites

Details of the synthesis of structured PDMS-nanoparticles were given in previous works [14,15]. The base polymer and the cross linker agent were mixed in 10:1 ratio, and then the inorganic nanoparticles were added (10% w/w). The obtained mixture, still fluid, was poured in a cylindrical mold (a specially designed device, 1 cm diameter  $\times$  3 cm long) and placed between the magnetic poles of a Varian Low Impedance Electromagnet (model V3703) [15]. This equipment provides an homogeneous magnetic fields (the magnetic field used in all the preparations was 3.5 kOe) as the mould was rotated at 30 rpm and heated at (75  $\pm$  5) °C for 4 h. Four different PDMS-NPs composites were prepared, using NPs of different composition ( $x=0.1$ ; 0.2; 0.3 not calcined NPs and  $x=0.1$  calcined NPs) in order to study the influence of the NPs composition and degree of crystallinity on the magnetoelastomer's properties.

### 2.3. Instrumentation

XRD analysis were performed with a Philips X-Pert diffractometer using Cu K $\alpha$  radiation ( $\lambda=1.54056$  Å). The average crystalline domain sizes were calculated with the Debye-Scherrer equation. TEM images were taken with Philips EM 301 equipment, SEM images and EDS analysis were obtained with a field Emission Scanning Electron Microscope (Zeiss Supra 40 Genimi). The average particle size was determined by counting 300 (or more) particles and the size distribution was fitted to log-normal curves.

Magnetic hysteresis curves and time relaxation of the remanent magnetization were measured with a Vibrating Sample Magnetometer (LakeShore 7400) at room temperature.

For elastic measurements and Young's modulus determination Stable Microsystems TA-XT2i Texture Analyzer equipment was used. This equipment compresses the sample at constant speed (0.1 mm/s) up to a given percentage of the initial thickness (usually 20 or 30%). A specially designed device was used for cutting the PDMS- $\text{Fe}_{2-x}\text{CoSm}_x\text{O}_4$  composites which allows obtaining axial and transverse slides with approximately the same area (0.83 and 0.79 cm<sup>2</sup> respectively) and equal thickness (3 mm).

## 3. Results and Discussions

### 3.1. SEM and TEM imaging

SEM images of the obtained particles before and after the heat treatment are shown on Fig. 1 (additional SEM images are shown in [supplementary material](#), available online). The morphology of the non-calcined particles resulted to be of irregular spheres for all Sm(III) proportions and the particles tend to form micrometric aggregates due to magnetic interactions. For the calcined particles the SEM images show sharp borders forming very well defined nanocrystalline structures.

The average particle size was determined using SEM and TEM images, and all the particles follow a log-normal size distribution. The average sizes obtained by TEM are in excellent agreement with the values obtained from SEM imaging (TEM images are not shown). In Fig. 2 we show the average sizes for both series of particles. For the non-calcined particles, compared to  $\text{Fe}_2\text{CoO}_4$  particles, the average particle size increases with small amounts of Sm(III) and reaches a maximum size of 36 nm when  $x=0.1$ . For higher Sm(III) contents ( $x=0.15$ –0.4) the average particle size decreases (except for  $x=0.5$ ). For the particles exposed to heat treatment there is a similar tendency: the largest size resulted to be for  $\text{Fe}_{1.9}\text{CoSm}_{0.1}\text{O}_4$  particles (32.5 nm), then the particle size became smaller when increasing Sm(III) content ( $x=0.15$ –0.5).

The average composition of all the synthesized particles was determined by energy-dispersive X-ray spectroscopy (EDS). The average proportion of Fe(III) and Sm(III) respect to Co(II) in all cases agrees with the stoichiometric composition. Only for large amounts of Sm(III) ( $x=0.5$ ), a deviation for Fe(III) content respect Co(II) in particles before and after calcination is observed (see [supplementary material](#)).

### 3.2. Structure analysis

On Fig. 3a we present the XRD patterns for the obtained nanoparticles without calcining. For all compositions ( $x=0$ –0.5) the diffraction peaks can be assigned to the inverse spinel structure of  $\text{Fe}_2\text{CoO}_4$  (JCPDF 22-1086). No other phases are observed even for large amounts of Sm(III). The XRD patterns of the calcined particles are shown on Fig. 3b. For small amounts of

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