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Synthesis of europium orthochromites ($EuCrO_3$) nanoparticles by a combustion reaction method

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ABSTRACT

High purity powder samples of $EuCrO_3$ were produced by a combustion reaction technique. The crystalline structure, morphology and magnetic properties were investigated by X-ray diffraction, transmission electron microscopy, Fourier transform infrared spectroscopy, thermogravimetric analysis, differential scanning calorimetry and magnetization measurements. The average particle size was found to be about 30 nm. A weak ferromagnetism due to the canting of the Cr^{3+} spins was observed below a Néel temperature (T_N) of 172 K, yielding, for a formula unit, 0.01 μ_B, 2.0 kOe and 0.22 μ_B for the remanent magnetization, coercivity, and magnetization measured at the highest applied magnetic field (85 kOe), respectively, for $T = 5$ K. The Cr^{3+}–O^{2-}–Cr^{3+} bond angle was determined to be 156.3° being consistent with the lower value found for T_N.

1. Introduction

Multiferroics are materials that exhibit strong coupling between their electrical and magnetic properties. They have been receiving great attention due to their potential in applications such as memory storage devices, sensors and actuators [1,2]. The magnetoelectric coupling was found to be present in compounds with spin-induced ferroelectricity like orthoferrites and orthomanganites. More recently, a controversy has been raised about the existence of multiferroic behavior in polycrystalline samples of rare earth orthochromites ($RECrO_3$) [3–5]. Thus, these materials are also arising avid interest nowadays [3,4,6,7]. Besides, among the series of rare earth compounds, namely, chromites, manganites and ferrites, the chromites are the ones that exhibit the highest electrical conductivity, lowest activation energy and largest drift mobility [8].

One interesting member of the $RECrO_3$ family is the europium-orthochromite ($EuCrO_3$). It is crystallographically (and magnetically) isostructural with $GdFeO_3$ that crystallizes in a distorted orthorhombic perovskite structure (space group *Pnma*) [4,5,9]. Moreover, $EuCrO_3$ shows weak spontaneous magnetic moment below the Néel temperature ($T_N = 181$ K) [10] that has also been observed in other chromites [11]. The net magnetic moment in $EuCrO_3$ was associated to a small canting of the Cr^{3+} spins and to the Dzialoshinski-Moriya interaction [3,12,13].

Solid-state reaction has been one of the principal methods used to synthesize rare earth orthochromites [3,6,9]. However, for obtaining single phase materials by using this method it is required long periods of time (up to 70 h) and temperatures close to 1473 K. Orthochromites have also been prepared by using alternative synthesis such as micro-wave assisted [4], hydrothermal [14], wet-chemical [12] and combustion reaction [15]. Among these sample preparation techniques, the combustion reaction is the one that remains less used despite their simplicity, easy stoichiometric control, low cost, energy saving and environmentally friendly nature.

Thermochemical concepts used in propellant chemistry establish the principles for the combustion reaction synthesis. The reaction is characterized by being highly exothermic. Once the combustion reaction takes place, it becomes self-sustain yielding the final product in a short period of time. In some cases, it does not require subsequent heat treatment reducing considerably the length of the time for getting a single phase sample material [16,17]. However, calcination may be used for getting rid off some organic materials left in the synthesis process [16]. For instance, Taheri et al. [7,18] have synthesized europium orthochromites by using a combustion reaction technique and glycine ($NH_2 \cdot CHCOOH$) as fuel. Nevertheless, to obtain a single phase material they had to preheat the samples at 773 K for 5 h, followed by a 12 h calcination at

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1223 K, under an atmosphere of a mixture of argon and hydrogen.

In this work, a combustion reaction method was used to produce high purity nanopowders of $EuCrO_3$ without further requirement of high temperature heat treatments neither the use of special gases. The combustion reaction was done in air using urea as fuel. This procedure reduced substantially the time and the overall costs for synthesizing single phase sample materials. Furthermore, the morphology, the structure and the magnetic properties of the nanopowders were investigated by X-ray diffraction, transmission electron microscopy, Fourier transform infrared spectroscopy, thermogravimetric analysis, differential scanning calorimetry and magnetization measurements.

2. Experimental details

Europium orthochromites were synthesized by using analytical grade europium nitrate $Eu(NO_3)_3 \cdot 5H_2O$, chromium nitrate $Cr(NO_3)_3 \cdot 9H_2O$ and urea $CO(NH_2)_2$ as fuel. Using the thermochemical concepts of propellant chemistry [19], elements such as H, C, Eu and Fe are considered as reducing elements, O is an oxidizing element and N has a neutral valency. Taking this into consideration, the corresponding valency for each element are: Eu = +3, N = 0, H = +1, O = −2, Cr = +3, Fe = +3 and C = +4. Thus, the stoichiometric composition of the redox mixture for releasing the maximum energy during the reaction requires that $-30+6n = 0$ or $n = 5$ moles of urea. The reactants stoichiometrically combined were then hand mixed in wide-mouth vitreous silica basin and dissolved in deionizated water (10–30 mL) until an homogeneous solution was reached. Afterwards, the mixture was heated up around 673 K on a hot blanket inside a fume cupboard under air ventilation. A continuous raising in temperature in the aqueous solution causes an initial evaporation process. Subsequently, the thickened liquid began to frothing and ignition takes place in a non-centered focal point (Fig. 1a). The flame propagates through the surface of the capsule liberating a considerable amount of gases into the chamber. The whole process occurs between 20 and 30 min with the flame lasting for a few seconds, yielding a dry, very fragile foam which was transformed into a fine powder (Fig. 1b) with the help of a mortar and a pestle.

X-ray diffraction measurements (XRD) were performed at room temperature using the CuKα radiation (λ=1.5418 Å), the $\theta-2\theta$ configuration, from 20° to 90° in steps of 0.005°, in a Shimadzu XRD-7000 diffractometer. Crystal structure refinements were made by using the Rietveld method and the MAUD software. The as-prepared sample was mixed with KBr and compacted into a pellet to be used in the Fourier transform infrared spectroscopy (FT-IR) studies. The FT-IR measurements were taken at room temperature from 4000 cm^{-1} to 400 cm^{-1} in a Shimadzu IRTracer-100 system, which has a signal-noise ratio of 60000:1. A SETARAM LABSYS Evo system was used to perform thermogravimetric (TGA) and differential scanning calorimetry (DSC) measurements in an atmosphere of O_2, using platinum crucibles and varying the temperature in the range 300– 1473 K at a rate of 10 K/min. The temperature rate of 10 K/min was also used in the cooling down procedure. The morphology, particle size distribution and chemical composition were analyzed by a transmission electron microscope (TEM) using a 200 kV microscope JEOL, model JEM 2100, equipped with an energy-dispersive X-ray (EDS) spectrometer. A small amount of the sample was dispersed in 3 mL of n-propanol and sonicated for 5 min. Droplets of the dispersion were placed on a copper grid coated with parlodion and carbon films and dried in air. Magnetization measurements were carried out in a broad range of temperature T (5–300 K) and of applied magnetic field H (±85 kOe) by using a PPMS (Physical Property Measuring System - Quantum Design) in the ACSM mode.

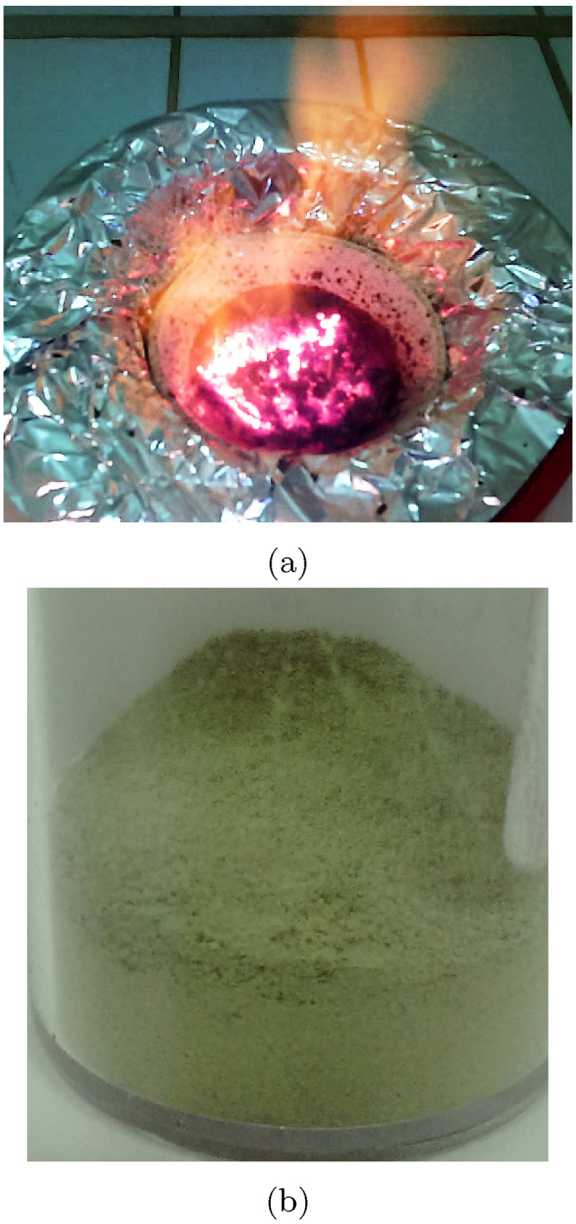

Fig. 1. (a) Flame produced during the combustion reaction synthesis of $EuCrO_3$ and (b) the final product.

3. Results and discussion

The XRD data for a powder sample of the as-prepared $EuCrO_3$ is represented by the black dots in Fig. 2a while the corresponding refined data is the represented by the red solid line. The goodness of the refinement is usually exhibited by a plot of the experimental data minus the refined data. This result is shown in the lower part of Fig. 2a. (blue solid line). The peaks in the diffraction pattern were indexed with the JCPDS PDF # 251053 data used for orthorhombic perovskite structures with space group *Pnma* [4] while the values for the occupancy numbers followed the ones currently used in the literature [20,21]. No extra diffraction peaks were observed. Thus, within the resolution of XRD the as-prepared sample is single phase without requiring any subsequent heat treatment. The lattice parameters $a = 0.553(2)$ nm, $b = 0.764(2)$ nm and $c = 0.535(2)$ nm obtained from the Rietveld analysis are close to the ones accepted for this sample composition [6,9,10,18]. The average crystallite size