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Cobalt chromite obtained by thermal decomposition of oxalate coordination compounds

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Abstract

Cobalt chromites ($CoCr_2O_4$) powders have been synthesized *via* thermal decomposition of oxalate precursor compounds $(NH_4)_4[CoCr_2(C_2O_4)_4(OH)_4]\cdot 7H_2O$ (**I**) and $(NH_4)_{12}[CoCr_2(C_2O_4)_8(OH)_4]\cdot(NH_4)_2C_2O_4\cdot 12H_2O$ (**II**). The oxalate precursors have been characterized by infrared (IR) and ultraviolet–visible spectroscopy (UV–vis), X-ray diffraction (XRD), scanning electron microscopy (SEM) and thermal analysis. The structure, morphology and magnetic properties of $CoCr_2O_4$ powders have been investigated by XRD, SEM, IR and Raman spectroscopy (RS), UV–vis and magnetic measurements. XRD patterns confirmed the formation of spinel-type cobalt chromite, with average crystallite sizes calculated from XRD patterns of 38 nm and 58 nm, for spinel chromites from precursors **I** and **II**, respectively. SEM micrographs revealed particle sizes between 30 and 130 nm, with a low degree of aggregation of primary nanocrystallites. Both $CoCr_2O_4$ powders presented ferrimagnetic ordering below the Currie temperature (T_c) and a phase transition at $T_s\sim 20$ K attributed to the onset of long-range spiral magnetic order.

Keywords: A. Powders chemical preparation; B. Spectroscopy; C. Magnetic properties; D. Spinels

1. Introduction

Spinel-type cobalt chromite ($CoCr_2O_4$) has been used as catalyst for the ortho-selective alkylation of phenol with methanol, for the removal of NO_x and diesel soot, for the oxidation of 2-propanol [1–3], and in the manufacture of industrial pigments [4–6].

Cobalt chromite is ferrimagnetic at low temperatures. It is also a multiferroic material in which the electric polarization is induced by spiral magnetic order [7,8]. The unique magnetic properties of $CoCr_2O_4$ arise from nanosize effects, lattice distortion and surface defects [9,10]. For this reason, besides classical ceramic and conventional coprecipitation techniques [1,2,11], new chemical synthesis routes have been developed, such as the sol–gel technique [3,6,12], hydrothermal/solvothermal processes [13–16], the sonochemical technique [17], solution combustion synthesis [18,19], and thermolysis of polymer metal/polynuclear metal precursors – also named as the *precursor method* [4,9,10,20–22].

The precursor method – a chemical route belonging to soft chemistry ("*chimie douce*") is preferred because multimetallic complex precursors can easily produce nanostructured mixed oxides by thermal decomposition [23–26]. These complex precursors should generate only volatile products during decomposition into oxides. Complexing agents that largely satisfy this requirement are the anions of polycarboxylic and polyhydroxycarboxylic acids: oxalate, citrate, tartarate, gluconate, *etc.* Different versions of this method are named according to the complexing agent (ligand) employed.

The aim of this research is to obtain $CoCr_2O_4$ nanoparticles with spinel-type strucure through the precursor method, using the oxalate anion as complexing agent.

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2. Experimental

2.1. Reagents

Chromium nitrate ($Cr(NO_3)_3 \cdot 9H_2O$), cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$) and oxalic acid ($H_2C_2O_4$) from Merck were used as reagents.

2.2. Precursor method

The polynuclear coordination precursors were prepared as follows: chromium(III) nitrate and cobalt(II) nitrate were dissolved together in the minimum amount of water. An aqueous solution of oxalic acid was mixed under continuous stirring with the metal nitrates solution. The molar ratios of metal nitrates to oxalic acid were $2Cr(NO_3)_3 \cdot 9H_2O{:}Co(NO_3)_2 \cdot 6H_2O{:}4H_2C_2O_4$ and $2Cr(NO_3)_3 \cdot 9H_2O{:}Co(NO_3)_2 \cdot 6H_2O{:}10H_2C_2O_4$. Ammonia solution (12.5%) was added to adjust the pH to 6. Gray–violet crystalline compounds were separated. After 24 h at 4 °C, they were filtered and dried over P_4O_{10}.

The metal content of the complex compounds was determined by atomic absorption spectroscopy with an SAA1 instrument and by gravimetric techniques; the C, N and H values were obtained using a Carlo Erba Model 1108 CHNSO elemental analyzer. Elemental chemical analysis was consistent with the formula

$(NH_4)_4[CoCr_2(C_2O_4)_4(OH)_4] \cdot 7H_2O$ (**I**) Anal.: Calcd.: Cr%: 13.32; Co%: 7.55; C%: 12.29; N%: 7.17; H%: 4.35; found: Cr%: 13.56; Co%: 7.70; C%: 11.81; N%: 6.70; H%: 4.35.

$(NH_4)_{12}[CoCr_2(C_2O_4)_8(OH)_4] \cdot (NH_4)_2C_2O_4 \cdot 12H_2O$ (**II**) Anal.: Calcd.: Cr%: 6.97; Co%: 3.95; C%: 14.48; N%: 13.14; H%: 5.63; found: Cr%: 7.00; Co%: 3.97; C%: 14.10; N%: 13.37; H%: 6.22.

In order to obtain well-crystallized $CoCr_2O_4$ spinels, the oxalate compounds were annealed at 800 °C/4 h.

2.3. Characterization techniques

The IR spectra of the polynuclear coordination compounds and spinel chromites were recorded on KBr pellets with a JASCO FTIR 4100 spectrophotometer in the 4000–400 cm^{-1} range.

Absorption measurements were recorded with a JASCO V-670 spectrophotometer in the domain 200–1800 nm.

Thermal measurements (TG, DTG and DTA) were performed using Mettler Toledo TGA-SDTA 851 equipment in static air atmosphere. Measurements were carried out in the range 25–1000 °C with a heating rate of 10 °C min^{-1}.

The structure was analyzed by X-ray diffraction using a Bruker-AXS tip D8 ADVANCE diffractometer. For powder diffraction, $CuK_{\alpha 1}$ radiation (wavelength 1.5406 Å), LiF crystal monochromator and Bragg–Bretano diffraction geometry were used. The data were acquired at room temperature, with a step-scan interval of 0.02° 2θ and a step time of 10 s. The powder diffraction spectra were analyzed and indexed using Crystallographica software. The crystallographic parameters and crystallite sizes were determined by quantitative phase analysis using MAUD (Materials Analysis Using Diffraction) software.

Raman spectra (RS) were measured in a spectrometer Horiba Jobin-Yvon LabRam HR using the green line (λ=514.5 nm) of an Ar^+ laser, with a power of ~20 mW and acquisition times of 40 s. Measurements were carried out at room temperature, in the backscattering geometry, using a 50× microscope objective and a laser spot size of 1–2 μm.

The morphology of the complex compounds and final oxides was analyzed by scanning electron microscopy (SEM) using a FEI Quanta 3D FEG apparatus. Micrographs were obtained from a secondary electrons detector working at accelerating voltages of 2 and 5 kV.

Magnetic measurements have been investigated using a superconducting quantum interference device (SQUID) at three different temperatures (5, 70 and 120 K) into a magnetic field of 6 T. Frequencies of 10 and 100 Hz were used.

3. Results and discussion

The selection of oxalic acid as complexing agent is justified by its coordination versatility, multiple coordination capacity, as a monodentate ligand (bonded to the oxygen atoms of the same carboxylic group), as well as a bidentate ligand (bonded to the oxygen atoms from each carboxylic group) or as a tetradentate ligand (double bridging between two or four metal ions) [27].

Several heteropolynuclear oxalate complexes have been reported as precursors for spinel-type oxides in the past decade. Wickham et al. [28] reported the first study concerning the synthesis of ferrites through thermal decomposition of oxalates. Paris and Paris prepared through this method the spinel aluminates and chromites [29]. Brezeanu et al. [30–32] synthesized and characterized three series of multimetallic oxalates as precursors for spinel ferrites

$(NH_4)_8[Fe_2M^{II}(C_2O_4)_8]$

$(NH_4)_2[Fe_2M^{II}(C_2O_4)_2(OH)_6]$

$[Fe_2M^{II}(C_2O_4)_2(OH)_4]$

where M^{II}=Mn^{II}, Co^{II}, Cu^{II}, Zn^{II}, Mg^{II}.

This research is focused on the synthesis of cobalt chromite through the thermal decomposition of oxalate compounds

$$(NH_4)_4[CoCr_2(C_2O_4)_4(OH)_4] \cdot 7H_2O \quad (I)$$

$$(NH_4)_{12}[CoCr_2(C_2O_4)_8(OH)_4] \cdot (NH_4)_2C_2O_4 \cdot 12H_2O \quad (II)$$

The molecular formulae were established by correlating elemental chemical analysis with physico-chemical measurements (IR, UV–vis spectra, and thermal analysis).

Data regarding the coordination of the ligand in these complex compounds were obtained by recording their IR spectra over the 400–4000 cm^{-1} range. Due to the fact that the $C_2O_4^{2-}$ anion can act as mono, bi, tri or tetradentate ligand, the assignation is more complicated. The splitting of ν_{asym} (OCO) and ν_{sym}(OCO) vibrations detected in both these spectra (Fig. 1) suggests two different coordination modes