



Investigation of nanocrystalline zinc chromite obtained by two soft chemical routes

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ARTICLE INFO

Article history:

Received 28 February 2013

Received in revised form 20 August 2013

Accepted 25 August 2013

Available online 2 September 2013

Keywords:

A. Oxides

B. Chemical synthesis

C. X-ray diffraction

C. Photoelectron spectroscopy

D. Magnetic properties

ABSTRACT

Zinc chromite (ZnCr_2O_4) nanocrystalline powders were obtained by two different chemical routes: the precursor method and the solution combustion method involving glycine-nitrates. The complex compound precursors, $[\text{ZnCr}_2(\text{NH}_2\text{CH}_2\text{COO})_8] \cdot 9\text{H}_2\text{O}$ and $[\text{ZnCr}_2(\text{NH}_2\text{CH}_2\text{COOH})_{4.5}] \cdot (\text{NO}_3)_8 \cdot 6\text{H}_2\text{O}$, were characterized by chemical analysis, infrared spectroscopy (IR), ultraviolet–visible spectroscopy (UV–vis) and thermal analysis. The structure, morphology, surface chemistry and magnetic properties of ZnCr_2O_4 powders were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), infrared and Raman spectroscopy (RS), ultraviolet–visible spectroscopy (UV–vis) and magnetic measurements. X-ray diffraction patterns indicated the chromite spinel phase with good crystallinity and an average crystallite size of approximately 18–27 nm. The band gap values ranged between 3.31 and 3.33 eV. The magnetic measurements indicated an antiferromagnetic transition at $T_N \sim 17.5/18$ K.

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1. Introduction

Over the past 20 years, the nanosized ZnCr_2O_4 spinel has attracted considerable interest due to its various applications as pigments in high-temperature ceramics [1], catalysts [2–5], semiconductors [6] and sensors for toxic, hazardous and combustible gases [7,8]. ZnCr_2O_4 is a geometrically frustrated antiferromagnet (AFM) with a very high Curie–Weiss temperature ($\theta_{\text{CW}} = -390$ K) and relatively low first-order AFM transition ($T_N \sim 12.5$ – 16 K) which also generates a structural transition from cubic to tetragonal structure [9].

It is well known that the synthesis method has a crucial influence on the composition, structure, morphology, and, implicitly, on the properties of the spinel chromites [7,9–12]. At the same time, it is unanimously recognized that special conditions have to be satisfied in order to obtain nanosized spinel oxides [13]. Soft chemical routes play a very important role in the preparation of nanomaterials. New soft chemistry (“chimie douce”) synthesis routes have been developed to obtain ZnCr_2O_4 nanoparticles: sol–gel process [14], metal–organic solution evaporation/calcination

[15,16], self-combustion reactions [17,18]. The nature of the precursors plays an important role in the synthesis of nanocrystalline oxides. Multimetallic complex compounds are preferred as single molecular precursors because they ensure the stoichiometry of nanostructured oxides [13].

The goal of this research is to obtain ZnCr_2O_4 spinel nanoparticles through two different soft chemical methods: the precursor method (also named complexation method) and the solution combustion method. We want to emphasize the dual role of glycine amino acid as both chelating agent and combustion fuel.

2. Experimental

Chromium(III) nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), zinc(II) nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), glycine ($\text{NH}_2\text{CH}_2\text{COOH}$), all of reagent quality, were from Merck (Germany).

Zinc chromite powders were prepared through the precursor method (glycinate route) and through the solution combustion method (glycine-nitrates process – GNP)

2.1. Precursor method

For the synthesis of the complex precursor, the following system was investigated:

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Table 1
Chemical analysis of precursors.

Precursor	Cr (wt%)		Zn (wt%)		C (wt%)		N (wt%)		H (wt%)	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
I	11.26	10.97	7.09	6.89	20.79	20.93	12.13	12.95	5.41	5.09
II	9.36	9.28	5.90	5.82	9.72	9.60	15.75	15.95	3.10	2.95

I = $[\text{ZnCr}_2(\text{NH}_2\text{CH}_2\text{COO})_8] \cdot 9\text{H}_2\text{O}$.

II = $[\text{ZnCr}_2(\text{NH}_2\text{CH}_2\text{COOH})_{4.5}] \cdot (\text{NO}_3)_8 \cdot 6\text{H}_2\text{O}$.

$2\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} : 1\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} : 8\text{NH}_2\text{CH}_2\text{COOH}$.

The metal nitrates were dissolved together in the minimum amount of distilled water. An aqueous solution of glycine was mixed with the metal nitrates solution. The molar ratio of metal nitrates to glycine was 2:1:8 (Cr(III):Zn(II):glycine). Ammonia solution was added to adjust the pH to 6. The formed species are partially soluble in water. Acetone was added for complete precipitation. After 24 h at 4 °C, the lavender coloured precipitate was filtered and dried over P_4O_{10} . Table 1 shows the results of the chemical analysis for the resulting precursor (precursor I).

The complex precursor was calcined at 900 °C for 4 h in order to obtain a well-crystallized zinc chromite spinel.

2.2. Solution combustion method

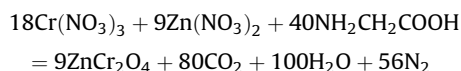
The following system was investigated:

$2\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} : 1\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} : 4.5\text{NH}_2\text{CH}_2\text{COOH}$

The ratio of chromium and zinc nitrates to glycine in the initial mixture was derived from the total oxidation number of the oxidizer and fuel, using concepts from the propellant chemistry. The stoichiometric composition of the redox mixture, $2(-15) + 1(-10) + n(+9) = 0$, requires $n = 4.5$. Thus, the reactants were combined in the molar proportion 2:1:4.5.

The reactants were mixed in an agate mortar until a concentrated homogeneous solution was formed. The hydration water from the nitrates was the only solvent. This solution was dried in a dessicator over P_4O_{10} for 48 h resulting in a blue grey compound (precursor II) (Table 1). The compound was placed on a heater and maintained at 250–300 °C. Initially it melted and then it decomposed by spontaneous self-ignition into a zinc chromite foam.

Under complete combustion the assumed chemical reaction can be written as follows:



The zinc chromite foam was calcined at 900 °C for 4 h.

2.3. Characterization techniques

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 Carbo Erba Model 1108 CHNSO elemental analyzer.

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 spectra were recorded with a JASCO V560 spectrophotometer with solid sample accessory, in the domain 200–850 nm, with a speed of 200 nm min^{-1} .

Photoluminescence spectra (PL) were recorded with a Perkin Elmer P55 spectrometer using a Xe lamp as a UV light source at ambient temperature, in the range 200–800 nm, with all samples

in solid state. The measurements were made with scan speed of 200 nm min^{-1} , slit of 10 nm and cut-off filter of 1%. An excitation wavelength of 350 nm was used.

The thermal behaviour of the precursors was followed by TG–DSC with a Netzsch TG 449 C STA Jupiter. Samples were placed in an open alumina crucible and heated with 10 K min^{-1} from room temperature up to 900 °C, under the flow of 20 mL min^{-1} dried air.

X-ray diffraction data were collected using parallel beam geometry on Rigaku's Ultima IV X-ray powder diffractometer, with $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$), CBO optics, operating at 40 kV and 30 mA, 0.02° step size and $5^\circ/\text{min}$. scan speed. Phase identification and Rietveld analysis were performed using Rigaku's PDXL software, with Whole Pattern Fitting (WPF) module, connected to ICDDPDF-2 database.

The microstructure of the complex precursors and final oxides was investigated by Scanning Electron Microscopy (SEM) in a FEI Quanta 3D FEG apparatus operating at 20 kV. The elemental chemical composition was determined with an Energy Dispersive X-ray (EDX) spectrometer.

Nitrogen sorption isotherms at 196 °C were recorded on a Micromeritics ASAP 2020 automated gas adsorption system. The samples were outgassed at 300 °C for 4 h under vacuum prior to N_2 adsorption. Specific surface areas (S_{BET}) were calculated according to the Brunauer–Emmett–Teller (BET) equation using adsorption data in the relative pressure range between 0.05 and 0.30. The total pore volume (V_{total}) was estimated from the amount adsorbed at the relative pressure of 0.97.

Surface analysis by X-Ray Photoelectron Spectroscopy (XPS) was carried out on a Quantera SXM equipment, with base pressure of 10^{-9} Torr in the analysis chamber. The X-ray source was Al $\text{K}\alpha$ radiation (1486.6 eV, monochromatized) and the overall energy resolution is estimated at 0.65 eV by the full width at half maximum (FWHM) of the $\text{Au}4f_{7/2}$ line. In order to take into account the charging effect on the measured Binding Energies (BEs) the spectra were calibrated using the C1s line (BE = 284.8 eV, C–C (CH) n bondings) of the adsorbed hydrocarbon on the sample surface.

Raman spectra (RS) were measured in a Horiba Jobin–Yvon LabRam HR microscope-spectrometer with acquisition time of 40 s; the green line ($\lambda = 514.5 \text{ nm}$) of an Ar^+ laser was used to excite RS with a power of $\sim 20 \text{ mW}$; measurements were carried out in the backscattering geometry, at room temperature, with a $50\times$ microscope objective; the laser spot size was around 1–2 μm ; RS covered the range between 50 and 1800 cm^{-1} .

Magnetic data were obtained with a Quantum Design MPMS SQUID susceptometer.

3. Results and discussions

3.1. Characterization of multimetallic compounds

The precursor method can be successfully applied to obtain spinel chromites if the multimetallic compounds generate only volatile products by thermal decomposition. The ligands that best satisfy this requirement are the anions of polycarboxylic/polyhydroxycarboxylic acids and the aminoacids. The precursor

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