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Chromium substituted copper ferrites *via* gluconate precursor route

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Abstract

$CuFe_{2-x}Cr_xO_4$ spinel ($0 \le x \le 2$) powders were synthesized by a soft chemistry method—the gluconate multimetallic complex precursor route. The complex precursors were characterized by elemental chemical analysis, infrared (IR) and ultraviolet–visible (UV–vis) spectroscopy, thermal analysis and Mössbauer spectroscopy. The oxide powders were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), IR, Raman and Mössbauer spectroscopy. It was shown that the structure, morphology and magnetic properties of the obtained spinel powders depend on the concentration of Cr^{3+} ion. The XRD of the chromium substituted copper ferrite powders calcined at 700 °C/1 h indicated the formation of a cubic spinel type structure for $x=0.5$, 1.0 and a tetragonal structure for $x=0$, 0.2, 2. The crystallite size ranged from 19 nm to 39 nm. The Mössbauer spectroscopy revealed the site occupancy of iron ions, relative abundance and internal hyperfine magnetic fields in both tetrahedral and cubic $CuFe_{2-x}Cr_xO_4$ spinels.

Keywords: A. Powders chemical preparation; B. Spectroscopy; D. Ferrites; D. Spinels

1. Introduction

Cu-based spinel oxides CuB_2O_4 ($B^{3+}=Fe^{3+}$, Cr^{3+}) have attracted interest due to their technological and industrial applications. Copper ferrites have been commercially used as high-frequency devices such as radio frequency coils, transformer cores and magnetic cores of read-write heads for high speed digital tapes [1]. Copper chromites are versatile catalysts applied successfully in the oxidation, hydrogenation/dehydrogenation of hydrocarbons and the decomposition of organic compounds in the pollution treatment [2,3].

Substitution of Fe^{3+} ions with Cr^{3+} ions in $CuFe_2O_4$ to obtain copper ferrite–chromites $CuFe_{2-x}Cr_xO_4$ has been proposed as a method to induce interesting magnetic and electric properties. The magnetic properties of these ferrites arise from their structural characteristics which are due to the distribution of the ions in the sublattice [4]. These ferrospinels are known to have high oxygen overpotential.

$CuFe_2O_4$ crystallizes in either tetragonal (T) or cubic (C) symmetry. The tetragonal phase is an inverse spinel, stable at room temperature. The Fe^{3+} ions in this phase occupy both the tetragonal A and octahedral B-sites. The Cu^{2+} ions occupy only the B-sites, causing tetragonal distortion due to the cooperative Jahn–Teller effect. The cubic phase is stable at temperatures higher than 360 °C. At room temperature, it can be obtained as a metastable phase by quenching from high temperatures [5].

$CuCr_2O_4$ is a normal spinel which crystallizes in a tetragonal distorted structure. Such distortion is a consequence of the cooperative Jahn–Teller effect of Cu^{2+} ions in the tetrahedral sites [6].

When Fe^{3+} ions are progressively replaced by Cr^{3+} ions in $CuFe_{2-x}Cr_xO_4$ ($0 \le x \le 0.8$), the crystal structure becomes a cubic spinel structure [7].

It is well known that the synthesis method plays a crucial role on the composition, structure and morphology of the

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spinel oxides. The synthesis method is the key in obtaining ferrites/chromites with enhanced properties. Nanostructured ferrites/chromites have been synthesized by various methods such as the coprecipitation method [4,8], the citrate-gel auto combustion method [9], the sol–gel auto combustion method [10] and the thermolysis of multimetallic precursors–precursor method [11,12]. Gabal proposed a very simple sol–gel method to obtain $CuFe_{2-x}Cr_xO_4$ ($0 \le x \le 1$) using nitrates and freshly extracted egg white [13]. In order to synthesize $CuFeCrO_4$ and $CuFe_2O_4$, Costa applied a variant of the precursor method using gelatin and metal nitrates as raw materials [14].

In this paper, chromium substituted copper ferrites $CuFe_{2-x}Cr_xO_4$ ($0 \le x \le 2$) were obtained by a soft chemistry method—the gluconate precursor route.

The goals of this study were: (i) the synthesis and physicochemical characterization of polynuclear complex compounds containing anion of gluconic acid as ligand; (ii) the analysis of the thermal decomposition of these compounds used as precursors; (iii) the structural, morphological and magnetic characterization of the resulting spinel oxide crystalline powders.

2. Experimental

2.1. Reagents

Chromium nitrate ($Cr(NO_3)_3 \cdot 9H_2O$), iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$) and δ-gluconolactone ($C_6H_{10}O_6$) from Merck were used as reagents.

2.2. Precursor method

The following systems were investigated for the preparation of the complex precursors: Cu^{2+}:(Fe^{3+}_{2-x},Cr^{3+}_x):8$C_6O_7H_{11}^-$, where $0 \le x \le 2$ and $C_6O_7H_{11}^-$=gluconate anion.

Copper, iron and chromium nitrates were dissolved together in a minimum amount of distilled water. The solution was mixed with an aqueous solution of gluconic acid in a suitable ratio. The gluconic acid ($C_6H_{12}O_7$) was obtained through the hydrolysis of δ-gluconolactone ($C_6H_{10}O_6$) at 80 °C. Grey-lavender compounds precipitated after adding methanol and raising the pH to 6 using $NH_4OH:CH_3OH$ (1:1). Acetone was added to achieve complete precipitation. After 24 h at 4 °C, the precipitates were filtered and dried over P_4O_{10}.

The elemental analysis was consistent with the formulae:

$(NH_4)_2\left[CuFe_{1.5}Cr_{0.5}(C_6H_{10}O_7)_4(OH)_2\right] \cdot 2H_2O$ **I**: Anal.: Calcd.: Cr%: 2.46; Fe% 7.95; Cu%: 6.01; C%: 27.28; N%: 2.65; H%: 5.11; found: Cr%: 2.61; Fe% 7.77; Cu%: 6.13; C%: 27.11; N%: 2.74; H%: 4.91.

$(NH_4)_2[CuFeCr(C_6H_{10}O_7)_4(OH)_2] \cdot H_2O$ **II**: Anal.: Calcd.: Cr%: 5.02; Fe% 5.41; Cu%: 6.13; C%: 27.81; N%: 2.70; H%: 5.02; found: Cr%: 4.95; Fe% 5.34; Cu%: 6.05; C%: 27.23; N%: 2.61; H%: 5.06.

$(NH_4)_2[CuFe_{0.5}Cr_{1.5}(C_6H_{10}O_7)_4(OH)_2] \cdot 6H_2O$ **III**: Anal.: Calcd.: Cr%: 6.94; Fe% 2.49; Cu%: 5.61; C%: 25.63; N%: 2.49; H%: 5.52; found: Cr%: 6.80; Fe% 2.44; Cu%: 5.50; C%: 26.00; N%: 2.50; H%: 5.12.

$(NH_4)_2[CuCr_2(C_6H_{10}O_7)_4(OH)_2] \cdot H_2O$ **IV**: Anal.: Calcd.: Cr%: 10.09; Cu%: 6.16; C%: 27.93; N%: 2.72; H%: 5.04; found: Cr%: 9.68; Cu%: 5.80; C%: 28.30; N%: 3.00; H%: 5.00.

The gluconate compounds were annealed at two different thermal treatments, 700 °C/1 h and 900 °C/4 h, in order to study the formation of $CuFe_{2-x}Cr_xO_4$ spinels.

2.3. Characterization techniques

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

The IR spectra of the complex precursors and spinel oxide powders were recorded on KBr pellets with a JASCO FTIR 4100 spectrophotometer in the 4000–400 cm^{-1} range.

The absorption spectra were recorded with a JASCO V670 spectrophotometer with solid sample accessory, in the range of 200–1400 nm.

The thermal behavior of the complex precursors was evidenced by TG–DSC data recorded with a Netzsch TG 449C STA Jupiter apparatus. The samples were placed in an open crucible made of alumina and heated at 10 °C min^{-1} from room temperature up to 900 °C, under a dried air flow of 20 mL min^{-1}.

X-ray diffraction data were collected using parallel beam geometry on Rigaku's Ultima IV X-ray powder diffractometer, with CuKα radiation (λ=1.54 Å), CBO optics, operating at 40 kV and 30 mA, 0.02° step size and 5° min^{-1} scan speed.

The microstructure of the spinel oxide powders was investigated by Scanning Electron Microscopy (SEM) using a FEI Quanta 3D FEG operating between 2 and 30 kV, equipped with an Energy Dispersive X-ray (EDX) spectrometer for elemental analysis.

The Mössbauer spectra were recorded at room temperature with WissEl—ICE Oxford Mössbauer spectrometer using a 20 mCi ^{57}Co(Rh) source. The sample thickness was ~7 mg Fe/cm^2.

The Raman spectra (RS) were measured using a Horiba Jobin-Yvon LabRam HR microscope-spectrometer with acquisition time of 40 s; the green line (λ=514.5 nm) of an Ar^+ laser was used to excite the RS with a power of ~20 mW; measurements were carried out in the backscattering geometry, at room temperature, with a 50× microscope objective; the laser spot size was around 1–2 μm; the RS covered the range between 50 and 2000 cm^{-1}.

3. Results and discussion

The concept of "*chimie douce*" – soft chemistry – was introduced by J. Livage [15–17]. All the methods belonging to the "*chimie douce*" are based on molecular precursors in which the distribution of chemical species is homogeneous at