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Magnetic, electric and thermal properties of cobalt ferrite nanoparticles

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ABSTRACT

The electric and magnetic properties as well as the thermal stability of $Co_xFe_{3-x}O_4$ nanopowders, ($0.6 < x < 1.8$) were investigated. These powders were synthesized using a one pot solvo-thermal route with acetylacetonates as precursors. The properties were linked to the size, morphology, composition of the particles and to the cation distribution. With the exception of $x = 0.6$, the powders are stable up to 600 °C. Whatever the composition, Co^{2+} has a strong tendency to occupy tetrahedral sites, contrary to what occurs in bulk ferrites. The nanopowders display a semi conducting behaviour. Between ambient and 500 °C, conduction occurs between $Co^{2+} \leftrightarrow Fe^{3+}$ pairs, and intergrain conduction predominates. The conductivity is in the $10^{-7}\,\Omega^{-1}\,cm^{-1}$ range. The $Co_xFe_{3-x}O_4$ nanopowders behave magnetically as a superparamagnetic assembly of single-domain particles. The magnetocrystalline anisotropy constant is significantly higher for these nanoparticles than for bulk ferrites. $Co_{1.8}Fe_{1.2}O_4$ displays the lowest blocking temperature (200 K) and the highest anisotropy ($K = 21 \times 10^6$ erg/cm^3).

1. Introduction

Ferrites are materials which combine several remarkable physical properties along with chemical stability, low production cost, and have already many application fields [1]. In form of nanomaterials, ferrites may have superparamagnetic properties [2] and are currently used in magnetic data storage, magnetic imaging, drug delivery and microwave devices [3,4]. Recently, nano ferrites have shown gas sensing capability [5,6], as well as photocatalytic and catalytic activity toward the degradation of organic matters and oxidative reactions in presence of reducing gases [7–9]. This multifunctional character of ferrites has potential application in the field of sensors, transducers and actuators [10–14]. The control of the size, morphology and chemical composition of the spinel ferrite nanoparticles, should allow adjusting their various properties for specific needs.

In a previous work, the synthesis route of the $Co_xFe_{3-x}O_4$ nanoparticles and their catalytic response to methane were presented with an exhaustive structural characterization, including X-rays diffraction (XRD), transmission electron microscope (TEM) imaging and energy dispersive spectroscopy (EDS) analysis [7]. The elaboration route developed led to chemically homogeneous spinel cobalt ferrites, with mean size ranging from 4 to 7 nm, the smallest particles being obtained for $x = 1.8$. The morphology study of the particles evidenced a spherical form for low cobalt content, and a very irregular shape for high cobalt content. The highest conversion rate, at a given temperature, was obtained for $Co_{1.8}Fe_{1.2}O_4$. The role of the cation distribution and vacancies in the catalytic reaction was evidenced. The sensing properties of cobalt ferrite nanoparticles were investigated, and different resistance variations were noticed, depending on the cobalt amount [15,16]. $Co_{1.8}Fe_{1.2}O_4$ showed a *p*-type semi-conducting response to reducing gases, as $CoFe_2O_4$ showed a *n*-type behaviour. Like catalytic properties, magnetic and electric conduction properties of nanoparticles, are related to the mean size, the size distribution and the shape of the particles. In case of spinels, the cation distribution on octahedral and tetrahedral sites influences physical and chemical properties. The surface state of the nanoparticles plays also an important role in catalysis reactions as well as in magnetic phenomena. It is well known that the efficiency of a catalytic conversion increases with the amount of exposed surface, which is related to the size and the shape of the particles, with the nature of the exposed cation sites, and the number and type of defects at the surface [17,18]. In

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nanostructured magnetic materials, surface effects usually lead to increased magnetization or superparamagnetism [2]. Electric properties are also linked to the particle size, to the cation distribution and to the occurrence of vacancies [19,20].

Our work aims to investigate the influence of the composition, particle size and cation distribution of cobalt ferrites nanopowders on their thermal, electric and magnetic properties and to determine some characteristic values. The electric, magnetic and thermal properties of nanoparticles of cobalt ferrites for various cobalt contents were characterized and related to morphology, size, crystallographic structure and chemical composition. The composition dependence of these properties in very small nanocrystalline cobalt ferrites (less than 10 nm) has not yet been studied. Electric and magnetic properties of ferrites were already investigated but for particles in the 100 nm range [21]. The magnetic study of very small particles was done but for a low cobalt concentration ($x < 0.6$) [22]. The conductivity and Neel temperature dependence with grain size has been investigated in nanocrystalline cobalt ferrite powder for one composition only, namely $CoFe_2O_4$ [19,20,23,24]. Most of the magnetic or electric investigations of nanoparticles of cobalt ferrites in literature concern Cd, Al or Zn doped ferrites [25–27]. Magnetic properties and transport mechanisms of cobalt ferrites $Co_xFe_{3-x}O_4$ with various compositions were studied [28], but in that case the grain sizes were in the micronic range.

2. Experimental procedures

2.1. Synthesis of $Co_xFe_{3-x}O_4$ nanoparticles

A series of cobalt ferrites nanoparticles samples with the general formula $Co_xFe_{3-x}O_4$, x varying from 0.6 to 1.8 ($x = 0.6, 1, 1.2$ and 1.8) were synthesized by a new one-pot solvo thermal route, using iron and cobaltacetylacetonates as precursors, dissolved in benzyl alcohol. Synthesis details can be found in a previous work [7].

2.2. Structural characterization

The detailed structural characterization, by XRD and TEM, of the as prepared cobalt ferrites nanopowders can be found in [7], for 3 compositions. The XRD diagram were collected in a classical θ–2θ angles coupled mode on a D5000 Siemens Bruker diffractometer operating with a copper X-rays source and equipped with a back monochromator, to avoid fluorescence. The diagrams were collected with a step of 0.04°, a time of 20 s per step, over a 2θ range from 15 to 115°. Rietveld refinement was done using the Powdercell software. Morphologies and crystal sizes of nanoparticles were determined by TEM, using a Tecnai 200 kV, with a point to point resolution of 0.25 nm. Images were recorded using a 1 K × 1 K slow scan CCD camera. The statistical studies on particle size were carried out over 500 particles for each composition. The powders were characterized after impedance spectroscopy measurements by XRD and TEM.

2.3. Thermal analysis

Differential thermal analysis (DTA) and thermogravimetric measurements (TG) were performed using a SETARAM TG–DTA 92 thermal analyzer. The experiments were carried out under static air up to 1200 K at a heating rate of 10°/min.

2.4. Electric impedance spectroscopy

The powders were compacted under a pressure of 140 MPa during 5 min, without any further sintering, and sandwiched between platinum electrodes. The porosity of the pellets was characterized by $P = 1 - \rho_{exp}/\rho_{theo}$, with ρ_{exp} and ρ_{theo} being the experimental and the theoretical densities of the pellets. Whatever the powders, the porosity was found to vary from 0.43 to 0.47. These porosity values are quite common for ferrites pellets [19,29]. The weak increase in porosity is linked to the small decreases in particles size [7]. conductivity measurements were performed under air, using a Solartron SI 1260 AC impedance analyzer working in the frequency range from 10^{-1} to 10^7 Hz. Data were analyzed using a non linear least squares (NLLS) fitting routine. Several heating and cooling cycles were performed from room temperature to 600 °C in order to check the reproducibility of the measurements, followed by a final heating up to 900 °C.

2.5. Magnetic measurements

The magnetic measurements, in the temperature range between 4 and 300 K, were performed using a physical property measurement system (PPMS) from Quantum Design. The specified resolutions are 210^{-5} emu in DC fields and 10^{-8} emu for AC magnetization. The collected data were corrected from the diamagnetic contribution and presented in CGS units. The samples were compacted in a plastic sampling tube in order to minimize dipolar inter-particles interactions and to keep the particles from rotating rigid-body like as the applied field changes direction. The zero-field cooling (ZFC) curves were obtained by cooling to 20 K the sample under zero applied field, then applying a field of 100 Oe and slowly warming the sample to around 300 K. The field cooling (FC) curves were obtained by cooling the sample from 300 K to 20 K under the same applied field.

3. Results and discussion

3.1. Structure and morphology of the cobalt ferrite $Co_xFe_{3-x}O_4$ nanoparticles

For the different compositions, the cobalt ferrites powders are single phased and have the expected spinel structure (space group Fd-3 m). Fig. 1a shows the XRD diagram corresponding to $Co_{1.2}Fe_{1.8}O_4$. Fig. 1b shows typical cobalt ferrite nanoparticles obtained for $x = 1.2$, along with the size distribution. The log normal function fitted very well the distribution size of the particles and led to somewhat smaller values that those obtained using the gaussian function [7]. The mean sizes and the associated standard deviation deduced from the log normal fits are given in Table 1. For $x = 0.6$, 1 and 1.2, the particles have an almost spherical and regular shape (see Fig. 1c for $x = 1$). The mean size of the nanoparticles decreases slightly with increasing cobalt amount x in $Co_xFe_{3-x}O_4$ and the smallest one is obtained for the highest quantity of cobalt ($x = 1.8$, $D = 4.3$ nm). For this latter composition, the shape of the particles is no more spherical (see Fig. 1d) and not well defined. HRTEM study performed on all the nanopowders shows that the produced particles exhibit high crystallinity with no significant number of defects such as dislocations or stacking faults (Fig. 1c and d). The $Co_xFe_{3-x}O_4$ pellets used for impedance spectroscopy were characterized by XRD and TEM coupled to EDS. During the electrical impedance spectroscopy measurements, the pellets were heated up to 900 °C, thus were liable to possible phase transitions and grain growth. Fig. 2 shows typical grains of the pellets heated up to 900 °C. For all the compositions, the grain sizes are submicronic, ranging between 200 and 600 nm, although it remains some smaller grains (Fig. 2). This shows that significant grain growth occurred during impedance spectroscopy measurements. For $CoFe_2O_4$ and $Co_{1.2}Fe_{1.8}O_4$ the chemical composition remains the same upon heating and the XRD diagram matches well