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Rietveld structure refinement of the cation distribution in ferrite fine particles studied by X-ray powder diffraction

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Abstract

Samples of $ZnFe_2O_4$ and $CuFe_2O_4$ fine particles prepared by coprecipitation method have been studied by X-ray powder diffraction at room temperature. The oxygen position, the lattice parameter, the mean size of the nanoparticles and the cation distribution have been determined by means of Rietveld analysis, indicating the existence of mixed ferrites in both samples. These results are also evidenced through magnetic measurements in ferrofluid samples at room temperature.
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1. Introduction

Magnetic nanoparticles are a topic of great interest from both fundamental and technological point of view. Indeed, their magnetic properties result from a complex interplay between finite size effects, related to a low number of spins in a cooperative behavior, and interface effects, associated to a small coordination number of surface atoms [1]. When the nanoferrites are dispersed in a carrier liquid, the resulting colloidal suspension is called ferrofluid or magnetic fluid. These materials give rise to numerous technological applications due in part to the versatility of molecular carrier liquids such as polar and non-polar media. However, such applications are dependent on the structural and magnetic properties of the nanocrystals that generally differ from those of bulk materials [2].

The nanosized systems investigated herein are based on copper and zinc spinel ferrites. Spinels are isostructural with the mineral spinel $MgAl_2O_4$, and crystallize in a face-centered cubic lattice with eight formula units in the cubic unit cell, belonging to the space group Fd3m (O_h^7). Spinel ferrites have the general molecular formula $(M^{2+})[Fe_2^{3+}]O_4^{2-}$ where M^{2+} and Fe^{3+} are the divalent and trivalent cations occupying tetrahedral (A) and octahedral (B) interstitial positions of the FCC lattice formed by O^{2-} ions. A whole range of distribution of cations is possible in spinels which can be represented generally by the formula: $(M^{2+})_{(1-x)}(Fe^{3+})_x[(M^{2+})_x(Fe^{3+})_{(2-x)}]O_4$, where the ions inside the brackets are

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said to occupy B sites and the ions outside the bracket occupy A sites; x represents the so-called degree of inversion (defined as the fraction of A-site occupied by Fe^{3+} cations). In the above formula when $x = 0$, it is called normal spinel. When $x = 1$ it is called an inverse spinel. When $0 < x < 1$ it is called mixed spinel. Ideal zinc ferrite is a normal spinel, while ideal copper ferrite is an inverse spinel.

The magnetic properties of these oxides depend on the nature of the cations and their distribution between the two interstitial positions. Moreover, depending on the process utilized in the ferrite elaboration, partial inversion has been claimed to occur [3–6]. In this work, magnetic measurements suggest a cation redistribution of the nanostructures, which is confirmed by Rietveld structure refinement of X-ray powder diffraction data.

2. Experimental

Nanocrystalline spinels ferrites have been chemically synthesized, using hydrothermal coprecipitating of aqueous solutions of Fe^{3+} and M^{2+} ($M^{2+} = Cu^{2+}$ and Zn^{2+}) mixture in alkaline medium, in order to elaborate magnetic fluids [7]. The molar ratio $[Fe^{3+}]/[M^{2+}]$ and the composition of the nanoparticles are determined by atomic absorption spectroscopy. X-ray diffraction experiments were realized on powder samples after evaporation of the sol. Measurements were performed by means of an X-ray diffractometer installed in a conventional Rigaku/Geigerflex generator operating at 40 kV/30 mA and the Cu–$K\alpha$ radiation selected by a graphite monochromator. X-ray powder diffraction data were obtained in a 2θ scanning range from 25° to 80° with a step size of 0.05° (2θ) with 8 s counting time at each step.

The refinement of the structures was carried out with the GSAS program [8], developed by Larson and Von Dreele, from X-ray powder diffraction data. The structural model and initial structural parameters for both samples were taken as follows: space group Fd3m; metal and iron atoms were in the Wyckoff 8a and 16d special position and O atoms in the 32e special positions. Moreover, both octahedral and tetrahedral cation and oxygen sites are assumed to be fully occupied. Diffraction profiles were modeled by using a multiterm Simpson's rule integration of the pseudo-Voigt function. The fitting quality of the experimental data were checked by using the following parameters: the goodness of fit, χ^2, that must tend to 1 and two reliability factors, R_p and R_{wp} (weighted differences between measured and calculated values) that must be close to or less than 10% [9]. The refined crystallographic parameters were: the scale factor; the lattice parameter, a_0; the oxygen positional parameter, u; the mean particles size and the degree of inversion, x.

The magnetization properties of diluted samples of ferrofluid (non-interacting system) were investigated as a function of the applied magnetic field at room temperature by using a Squid device.

3. Results and discussion

A typical magnetization curve, normalized to the saturation value of the solution magnetization, M_s, is shown in Fig. 1. Here, $M_{max} = m_s\phi$, m_s being the saturation magnetization of the magnetic particle and ϕ the volume fraction of the magnetic material in solution. As for both samples the obtained curves reach the saturation, the high field extrapolation allows to evaluate the saturation magnetization of the magnetic particles by fitting the experimental data to the Langevin model [10].

Experimental saturation magnetizations of samples 1 and 2 are shown in Table 1. Such high values, compared to their respective saturation magnetizations of the ideal bulk ferrites suggest the existence of cation distribution in the crystalline structure.

Fig. 2 exhibits the experimental X-ray diffraction pattern for sample 2. Table 2 lists the final R factors, the structural parameters and their standard deviations. The nanoparticles diameters, D_{ref}, determined by Rietveld refinement, are in good agreement with those calculated

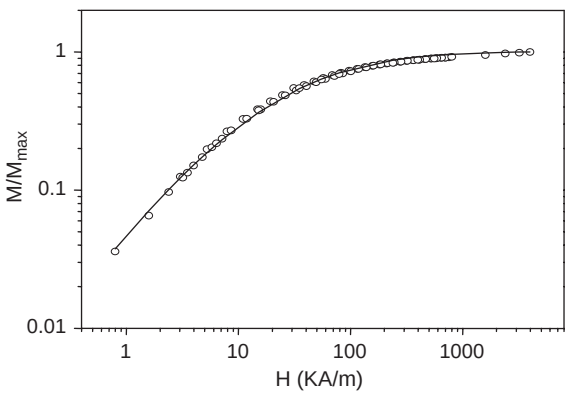

Fig. 1. Reduced magnetization of sample 2 as function of the applied magnetic filed. The solid line is the fit to the data using the Langevin formalism.

Table 1
Saturated nanoparticles magnetizations obtained from magnetization curves. The nanoparticles were subjected to an applied field $H = 4 \times 10^3$ kA/m

Sample	Ferrite	m_s (kA/m)	m_s bulk (kA/m)
1	$ZnFe_2O_4$	207	~ 0
2	$CuFe_2O_4$	177	126

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