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Reference:

Ciocarlan Radu-George, Pui Aurel, Gherca Daniel, Cool Pegie, et al.- Quaternary $M_{0.25}Cu_{0.25}Mg_{0.5}Fe_2O_4$ (M = Ni, Zn, Co, Mn) ferrite oxides : synthesis, characterization and magnetic properties
Materials research bulletin - ISSN 0025-5408 - 81(2016), p. 63-70
Full text (Publishers DOI): <http://dx.doi.org/doi:10.1016/j.materresbull.2016.05.001>

Innovative Superparamagnetic Quaternary $M_{0.25}Cu_{0.25}Mg_{0.5}Fe_2O_4$ (M=Ni, Zn, Co, Mn) Ferrite Oxides: synthesis, characterization and magnetic properties

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Keywords: A. nanostructures; B. magnetic properties; B. chemical synthesis; C. infrared spectroscopy; C. X-ray diffraction.

Abstract

This paper reports the synthesis using the coprecipitation method of $M_{0.25}Cu_{0.25}Mg_{0.5}Fe_2O_4$ (where M = Mn, Zn, Co, Ni) nanoparticles in presence of carboxymethyl cellulose (CMC) as in-situ surfactant. The crystalline structure and surface morphology were examined by means of X-ray diffraction (XRD), and surface electron microscopy SEM. These show that the average diameter of the magnetic nanoparticles (MNPs) is in the range of 3 to 10 nm. X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) show that the MNPs are activated with hydrophilic

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groups belonging to the surfactant which coat them and enhance the stability. The vibrating sample magnetometry measurements show the superparamagnetic behavior of the nanoparticles. Due to their small crystallite size, which implies large surface area, and their functionalization with organic groups the obtained nanoparticles can be used in medical and catalytic applications.

1. Introduction

Superparamagnetic nanoparticles (SPN) of ferrites represent a class of materials intensely studied in the last decade due to the large number of applications they can be employed in biomedicine, waste water treatment or industry. The need for a good control over the structure and morphology imposed the development of a large number of synthesis methods in between hydrothermal method [1], co-precipitation [2], sol-gel [3], microemulsions and reversed micelles [4], organic precursor decomposition, laser ablation [5] are the most used. These methods in specific conditions allow a fine tuning of size, structure and morphology of the SPNs obtained and thus a fine control of their properties and behavior.

Selecting the appropriate parameters of the synthesis method is crucial for the most of their medical application. The most important characteristics of the nanoferrites that influence drastically the magnetic properties are the size and the shape of the NPs. For this reason most synthesis methods employ the use of various surfactants and capping agents so that the size of the nanoparticles remains under the critical value [6]. Another reason for using surfactants is that it may modify the surface of the nanoparticles, preparing them for further functionalization with different organic groups. The cations' distribution among tetrahedral (A) and octahedral (B) sites is an important factor in tuning the magnetic and catalytic properties [7].

Ferrite nanoparticles have been successfully used in medicine as contrast agents for MRI [8] and in cancer treatment through hyperthermia [9] some ferrite nanoparticles being already commercially available and approved by the US Food and Drug Administration. Magnetic nanoferrites have also been used in the adsorption and removal of toxic species such as heavy metals (Pb, Cd, Cr, Co, etc.) and arsenic [10], organic dyes [11], and also in the catalytic and photocatalytic degradation under visible light of organic pollutants such as dyes [12, 13], nitrophenols and their derivatives [14], polychlorinated biphenyls [15].

A study conducted by Zhou et al. [16] of a series of ferrite with chemical formula $\text{Li}_x\text{Cu}_{0.6}\text{Mg}_{0.4-x}\text{Fe}_2\text{O}_4$ shown that the magnetic properties, in particular the specific magnetizations (Ms) and coercivity (Hc), can be precisely tailored by controlling the composition and calcination temperature of the precursor oxalates.

Magnesia doped nickel ferrite nanopowders $\text{Ni}_{1-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ with x ranging from 0 to 0.7 have been synthesized by Moradmard [17] using co-precipitation method. To achieve the spinel phase synthesis the samples were annealed at 900 °C. The increase in magnesia concentration caused variation in the average crystallite size and lattice constant with a maximum for x=0.5. Doping magnesia in nickel ferrite gave rise to a decrease in the specific saturation magnetization (13emu/g for x=0.5) whereas doping led to increase in coercivity field (183 Oe for x=0.5).

A recent study published by Reddy et al. [18] report data on nanocrystalline magnesium-copper-zinc ($\text{Mg}_{0.30}\text{Cu}_{0.20}\text{Zn}_{0.50}\text{Fe}_2\text{O}_4$) ferrites prepared by microwave sintering technique. The effect of the sintering temperature on particle size and magnetic properties were investigated and demonstrate the increase of the grain size, initial permeability and saturation magnetization by increasing the sintering temperature.

Nano-crystalline ferrite powders with chemical formula $Mg_{0.5}Zn_{0.5-x}Cu_xFe_2O_4$ with x in between 0 and 0.5 powders were synthesized using co-precipitation method by Zaki et al. [19] Magnetic data showed that the saturation magnetization increases with Cu^{2+} concentration up to $x = 0.2$ when the specific saturation magnetization had the maximum value of 55emu/g and the coercive field was 22 Oe.

A comparative study between nickel zinc ferrite and magnesium copper zinc ferrite prepared by water-in-oil microemulsion was done by Hee et al. [20]. The $Mg_{0.5}Zn_{0.2}Cu_{0.3}Fe_2O_4$ nanoparticles showed a crystalline structure with an average crystallite size of 13.5 nm and exhibited soft ferromagnetic behavior with values of 28 emu/g and 126 Oe for specific saturation magnetization and coercive field respectively.

Abdullah Dar et al. studied Mg doped Ni-Cu-Zn nano-ferrites system for power applications [21]. Magnesium substituted nickel copper zinc nano-ferrite having the general formulae $Ni_{0.5-x}Cu_{0.2}Zn_{0.3}Mg_xFe_2O_4$ with $x= 0.0 \dots 0.4$ were prepared at relatively lower temperature (900°C) by sol-gel technique. An improvement in magnetic properties has observed in the magnesium substituted nickel copper zinc nano-ferrite. The coercive field decreased with Mg concentration with a minimum value for $x=0.4$ while the specific saturation magnetization remained around 45 emu/g for particles with grain size greater of 50nm.

To the best of our knowledge is the first time when a series of quaternary spinel ferrites nanoparticles with chemical formula $M_{0.25}Cu_{0.25}Mg_{0.5}Fe_2O_4$ ($M=Ni, Zn, Co, Mn$) were synthesized in co-precipitation methods by using as surfactant a natural product, cheap and environmentally friendly, carboxymethyl cellulose (CMC). The structural and magnetic characteristics of the nanoparticles were deeply investigated in order to determine the influence of the synthesis process on properties and to identify possible applications in medicine and industry.

2. Materials and Methods

FeCl₃·6H₂O (Min. 98%, VWR BDH Prolabo), CoCl₂·6H₂O (Min. 98%, VWR BDH Prolabo), MgCl₂·6H₂O (ACS reagent, 99% Sigma-Aldrich), MgCl₂·6H₂O (Reagent Plus >99% Sigma-Aldrich), NiCl₂·6H₂O, CuCl₂·2H₂O (99% Sigma-Aldrich), ZnCl₂ (≥98% Sigma-Aldrich), MnCl₂·4H₂O (99% Sigma-Aldrich), CMC and Sodium hydroxide were used for synthesis. All the solutions were made in distilled water and all the chemicals were used as received without any purification.

2.1 Preparation of nanocrystalline M_{0.25}Cu_{0.25}Mg_{0.5}Fe₂O₄

Nanocrystalline samples with chemical composition M_{0.25}Cu_{0.25}Mg_{0.5}Fe₂O₄ were prepared by coprecipitation method using CMC as surfactant, following the protocol described in previous works [22, 23]. The stoichiometric amounts of analytical reagent (0.2 mol/L MCl₂·xH₂O, 0.2 mol/L CuCl₂·2H₂O, 0.2 mol/L MgCl₂·6H₂O and 0.4 mol/L FeCl₃·6H₂O) were mixed under constant magnetic stirring. Then, 40 mL of CMC 1% solution were added into the above solution, to restrict the particles growth and as capping agent, followed by the dropwise addition of an aqueous solution of 3M NaOH. During the synthesis the pH of the mixture was maintained in the range of 11-12 by using of NaOH solution. To convert the coprecipitate of hydroxides into spinel ferrite, the mixture was heated and maintained for an hour at 80°C under constant stirring. The mixture was then cooled to room temperature. The precipitate was separated using a magnet and several times washed with water and ethanol. All the resulting powders were calcined in air at 500 °C for 6 hours.

2.2 Structural characterization

The structural analysis of the annealed samples was performed by powder X-ray Diffraction (XRD) using an X-ray diffractometer (Bruker D8 ADVANCE) with CuK α radiation ($\lambda = 0.15406$ nm). The average crystallite size and lattice constant were estimated using FullProf 2000 program [24], by profile matching, with a peak shape modelled by a pseudo Voigt function [25]. **Polycrystalline** LaB₆ was used as a standard for instrumental profile corrections. Infrared spectra of the samples were measured with Jasco 660 plus FT-IR spectrometer, between 4000 and 350 cm⁻¹, using the KBr pellet method. The particle morphology and the particle size of the fine annealed powders were studied by scanning electron microscope (SEM) using a TESCAN device. The differential scanning calorimetry measurements (DSC) have been carried out with a Netzsch DSC 204 F1 System. Measurements were performed on heating and cooling with a rate of 5–10 K/min using 20–30 mg samples encapsulated in standard Al crucibles. An argon stream was used during the whole experiment as a protective gas.

The surface elemental composition of the samples and the chemical states of oxygen, and carbon were derived from X-ray Photoelectron Spectroscopy (XPS) measurements. They were performed on a PHI 5000 VersaProbe, ULVAC-PHI spectrometer, equipped with a monochromatic AlK α X-ray source ($h\nu=1486.6$ eV) under a take-off angle of the photoelectrons of 45°. The surface quantification has been carried-out following the standard procedure [26] by using the high resolution XPS spectra of O 1s and C1s. The calibration of binding energy (BE) scale was performed by considering the BE of the C1s peak (284.6eV). Peak deconvolution has been done using PHI-MultiPak software. In addition, valence band X-ray photoelectron spectroscopy data were used for the identification of materials [27].

2.3. Magnetic Properties

The magnetic properties of fine particles were investigated using a vibrating sample magnetometer (VSM) Princeton Measurements system. The magnetization versus magnetic field loop were plotted at room temperature and DC applied magnetic field was varied in the range of ± 10 kOe. Because the maximum value of the magnetic fields used in the experiment was not sufficient to produce saturation the values of the saturation magnetization were calculated by the interception of the magnetization curve in the closure region versus the inverse of the applied magnetic field.

3. Results and discussions

3.1. Crystal structure of nanoparticles

Powder XRD profiles of the powders of $M_{0.25}Cu_{0.25}Mg_{0.5}Fe_2O_4$ (M=Ni, Zn, Co, Mn) synthesized in CMC and annealed at 500°C under air are presented in Fig. 1.

Fig. 1.

For all patterns the diffraction peaks exhibit Bragg reflections perfectly indexed to the cubic spinel structure (space group $Fd-3m$) indicating the formation of the single-phase spinel ferrite after annealing. The observed broadening of the diffraction peaks due the small size of the crystalline domains, confirms that the coprecipitation of stoichiometric mixtures of transition metal chlorides in CMC, leads to the stabilization of nanoparticles in cubic spinel phase. Refinement of the lattice parameters and crystallite size was employed with FullProff

program. The difference, between observed / simulated and experimental powder XRD patterns of nanoparticles are given in Fig. 2.

Fig. 2.

The refinements plots of observed and calculated patterns indicate a good agreement between experimental and simulated XRD data. Refinement of the structural (lattice cell constants) and microstructural parameters (crystallite size) were performed in space group $Fd-3m$ and the corresponding refined values are listed in Table 1.

Table 1.

The crystallite size from XRD, for all the samples obtained in CMC, are smaller than the simple nano-particles prepared in the same conditions in mineral oils [28, 29, 30]. The variation of lattice parameters is not well correlated with the cation radius values Cu^{2+} (0.73 Å), Mn^{2+} (0.80), Co^{2+} (0.745 Å), Zn^{2+} (0.74Å), Ni^{2+} (0.69 Å).[30, 31]. For such nanosized particles is very difficult to calculate the four cation distribution along A and B sites.

The density value from the XRD data, $d_{X\text{-ray}}$, (Table 1) was determined for each of the series' components, taking into consideration that each primitive cell belonging to the cubic spinel structure contains 8 molecules [32].

$$d_{X\text{-ray}} = \frac{8M}{Na^3}$$

Where M is the molecular mass of each component of the series, N is Avogadro's number ($6.023 \cdot 10^{23}$ particles/mol) and a is the experimental lattice parameter. This values change can be assigned to the varying molecular masses but also the components' ionic radii. [33, 34].

3.2. SEM analysis

The surface morphology and the microstructure of the MNPs ferrites prepared by co-precipitation method and annealed at 500 °C studied with SEM technique are presented in Fig.3. The micrographs suggest nanoparticles in the range of nanometers with strong tendency to agglomerate.

Fig. 3.

3.3. DSC analysis

Fig. 4 presents the heating and cooling DSC curves up to 500 °C of the $Zn_{0.25}Cu_{0.25}Mg_{0.5}Fe_2O_4$ nanoparticles. In DSC the endothermic peak with maximum at 118°C was attributed to loss of water.

Fig. 4.

The small exothermic peak at around 330°C can be attributed to the loss of carbon chains belonging to the surfactant, followed by a major endothermic peak at 400°C attributed to the metallic ions (Fe, Mg, Cu and Mn) interdiffusion and formation of the spinel phase [35]. A large exothermic effect is observed on the cooling curves attributed to the cooling of the samples without any changes, proving that the obtain MNP's are stable.

3.4. FTIR spectra

The FTIR spectra for the $M_{0.25}Cu_{0.25}Mg_{0.25}Fe_2O_4$ nanoparticles is represented in transmittance (T) versus wavenumber (ν) in Fig. 5, in the 4000-350 cm^{-1} region. The FTIR spectra of all compounds indicate the formation of the spinel phase, suggested by an intense peak at around 570 cm^{-1} , which can be assigned to tetrahedral compounds, and two peaks at 390 cm^{-1} assigned to octahedral compounds.

Fig. 5.

The wide peak found at 3402 – 1625 cm^{-1} corresponds to the valence vibrations characteristic to the hydroxyl group from water. Two other characteristic vibrations can be found at 1625 – 1619 cm^{-1} and 1401 – 1391 cm^{-1} which can be assigned to the carboxyl group ($-COO^-$) belonging to the surfactant. The adsorption maxima (ν_1, ν_2) corresponding to the spinel structure are presented in Table 2. The lower intensity adsorption bands that can be observed in the 390 – 383 cm^{-1} can be associated to the stretching of the metal ions and oxygen bonds in the octahedral sites [36]. The strong adsorption bands observed at 580 – 569 cm^{-1} can be assigned to the stretching vibrations of the bonds between oxygen and the metals

in tetrahedral sites. The maxima at 390 and 570 cm^{-1} therefore confirm the formation of spinel type structure for the magnesium ferrite nanoparticles, according to Waldron's study [37].

Table 2.

The valence vibrations for M-O (M=Ni, Zn, Co, Mn) can be found as weak bands in the 500-350 cm^{-1} region.

The presence of organic fragments resulting from the CMC decomposition can be identified in the FT-IR spectra through the adsorption bands in the range of 3550 -3240, 2950-2850, 1630 - 1618, 1378 cm^{-1} and also some small bands between 1632 and 600 cm^{-1} . The bands observed between 2950-2850 cm^{-1} and in the range 1630 cm^{-1} can be assigned to $\nu_{\text{C-H}}$ and respectively $\nu_{\text{C=O}}$, $\nu_{\text{C=C}}$ and $\delta_{\text{H}_2\text{O}}$ from the surfactant [22, 23, 38]. In addition the bands observed at 3500 and 1382 cm^{-1} can be assigned to OH stretch and to plan and out of plane stretch, and the broad band around of 3424 cm^{-1} is assigned to the stretching mode of H_2O molecule and OH groups.

The presence of organic fragments on the ferrite's surface can also be confirmed through XPS analysis.

3.5. XPS analysis

Figs. 6 (a, b, c and d) show the XPS survey spectrum for the samples. As it can be seen, the chemical elements present at the surface's samples are C, O, Mg, Fe, Cu, Ni (Fig.6.a); C, O, Mg, Fe, Cu, Zn (Fig.6. b); C, O, Mg, Fe, Cu, Co (Fig.6.c); C, O, Mg, Fe, Cu, Mn (Fig.6.d).

Fig. 6.

The O *1s* spectra of the samples (Fig. 7) were deconvoluted into a main component at 530.0 eV binding energy (BE), corresponding to oxide, O²⁻, [39], a secondary one at 531.5 eV usually associated with OH⁻ groups [40] and the third one located at 532.4 eV corresponding to C-O and O-C=O bonds [39].

Fig. 7.

Fig. 8 presents the deconvolution of the C *1s* signal, which was resolved into three peaks with the following BE values: 284.6 (ascribed to C-C/C-H bonds), 285.9 eV and 288.2 eV corresponding to C-O, and O-C=O bonds, respectively [41]. The latter two are consistent with the interpretation of the oxygen spectra.

Fig. 8.

By analyzing the VB-XPS data, (Fig. 9) the shape of acquired spectra, especially in the (10 ÷ 18) eV indicate that the iron is presented in the samples in the Fe³⁺ species [26].

Fig. 9.

3.6. Magnetic properties of the MFe_2O_4 nanoparticles

Magnetic hysteresis curves of $M_{0.25}Cu_{0.25}Mg_{0.5}Fe_2O_4$ nanoparticles with $M = Ni, Zn, Co, Mn$ recorded at room temperature in the applied field range -10 to 10 kOe are shown in Fig. 10.

Fig. 10.

Low field hysteresis curves in the inset of Fig. 5 show that Co and Ni ferrite nanoparticles with smaller crystallite and grain size are superparamagnetic while Zn and Mn ferrite nanoparticles are weak ferrimagnetic with coercive field of 2 and 25 Oe. It is known that below the single domain limit, the coercive field decreases with decrease in the particle size and approaches 0 Oe at the superparamagnetic limit. The specific saturation magnetization calculate by the the interception of magnetization versus $1/H$ was found to vary in between 8 and 21 emu/g. The calculated values of are much lower than that of the bulk counterpart (80 emu/g for CuMgZn or other stoichiometric Mn, Ni or Zn ferrites. The values of saturation magnetization are dependent on particles size. The pronounced reduction in saturation magnetization can be attributed to the presence of randomized surface spins in the nanoparticles where the number of atoms on the surface is high compared to that in the volume [42]. The size dependence of saturation magnetization can be explained by the noncollinear spin arrangement on the nanoparticle's surface [43].

4. Conclusion

It was obtained a new series of ferrite nanoparticle with four metals ($M_{0.25}Cu_{0.25}Mg_{0.5}Fe_2O_4$, where $M = Mn, Zn, Co, Ni$). The XRD diffraction patterns for

samples confirm the purity phase and they were used for determination of crystallite size (3-10 nm). The activated surface of nanoparticle with OH and C-O groups was observed by FTIR spectroscopy and confirmed by XPS analysis. The magnetic properties show that Co and Ni ferrite nanoparticles are superparamagnetic while Zn and Mn ferrite nanoparticles are ferromagnetic.

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