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The role of copper ions on the structural and magnetic characteristics of MgZn ferrite nanoparticles and thin films

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ABSTRACT

In this study $Cu_xMg_{0.5-x}Zn_{0.5}Fe_2O_4$ ($x=0$–0.5) nanoparticles and thin films were prepared by sol–gel processing. The morphologies of nanoparticles were observed by transmission electron microscope (TEM). The Mössbauer spectroscopy (MS) was employed to determine the site preference of the constitutive elements. Magnetic dynamics of the nanoparticles was studied by the measurement of AC magnetic susceptibility versus temperature at different frequencies. The phenomenological Néel–Brown and Vogel–Fulcher models were employed to distinguish between interacting or non-interacting system. Results exhibited that there is strong interaction between fine particles. X-ray diffraction (XRD) patterns of the thin films indicate the formation of single-phase cubic spinel structure. Atomic force microscope (AFM) was employed to evaluate the surface morphologies of the prepared thin films. Vibrating sample magnetometer (VSM) was employed to probe magnetic properties of samples. It was found that with an increase in the amount of copper, the saturation of magnetization and initial permeability increase.

1. Introduction

Soft magnetic materials have great potential application in electronic industry. The most common type is cubic spinel ferrites with formula AB_2O_4, which contains tetrahedral (A site) and octahedral (B site) crystalline sites. The magnetic and electrical properties of soft ferrite could be easily tuned by incorporation and suitable distribution of additional cations (divalent or trivalent) in the spinel structure. Nanocrystalline ferrite thin films have potential applications in high-density magneto-optic recording devices, color imaging, bioprocessing, ferrofluids, magnetic refrigeration and monolithic microwave integrated circuits (MMICs) [1–7].

MgZn ferrite in thin film configuration and powder forms has cubic spinel structure and is widely used in many electronic devices because of high electrical resistivity, hard mechanical properties, high Curie temperature and environmental stability. Several investigators have studied the magnetic and electrical properties of MgZn ferrites in powder and bulk forms by partially substituting Mg with Cu ions [8–14].

In the recent years, we have focused our studies on the preparation and magnetic characteristics of ferrite nanoparticles [15–19]. We felt that there are still some lags in magnetic characteristics of this type of ferrite, particularly magnetic susceptibility of MgCuZn ferrite is not widely studied. With this view in mind the present paper premise deals with the fabrication of MgCuZn ferrite in nanoparticles and thin films configuration by a sol–gel method. The site preference and magnetic susceptibility characteristics of nanoparticles were investigated. The nanoparticles were dispersed in the ferrite solution (sol) in order to fabricate thin films. Magnetic properties and structural features of the prepared films were characterized by X-ray diffractometer, atomic force microscopy and vibrating sample magnetometer.

2. Materials and methods

2.1. Preparation of nanoparticles and thin films

The MgCuZn ferrite nanoparticles were prepared by a sol–gel method. The aqueous sol was produced by dissolving iron nitrate, copper nitrate, magnesium nitrate and zinc nitrate, according to desired stoichiometric proportion, in deionized water and then mixed together by constant stirring. Citric acid was added to the sol for the enhancement of nitrates dissolution. The pH value of

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solution was adjusted to 7 using ammonia. All the solutions were dark brown indicating the presence of Fe^{3+} ions. The gels were obtained by slow evaporation at 70 °C until the gel dried. Then, dried gels were sintered at 800 °C for 1 h. The synthesized ferrites with average particle size of 10 nm were dispersed in the subsequent solution in order to fabricate thin films with dip coating. The wet films were deposited by a dip coating method on the substrate of Si/SiO_2 and the wet films were dried at 100 °C for 10 min to remove the mixed solvents. Finally, the dried films were annealed at 800 °C for 30 min in air and cooled slowly in the furnace. The thickness of the nanocrystalline ferrite thin films was in the range 600–650 nm. The thickness of the films was measured by the Surface Profiler, Talystep (Taylor-Hobson, UK).

2.2. Characterization of ferrite nanoparticles

The morphology and size distribution of nanoparticles were investigated by transmission electron microscopy (TEM) model JEOL 2010. Energy-dispersive X-ray spectroscopy microanalysis (EDAX) was used to probe the constitutive elements into the samples. The MS characterizations were performed in the transmission geometry, using a conventional spectrometer, operated in the constant acceleration mode. The γ-rays were provided by a 57Co(Rh) source, with a nominal starting activity of 25 mCi. The Mössbauer spectra were analyzed using a non-linear least-square routine, with Lorentzian line shapes. Eventually, a hyperfine magnetic field distribution, B_{hf} Dist., was used as histograms in the spectral analysis. All isomer shift (δ) data are given relative to α-Fe throughout this paper. The AC magnetic susceptibility of nanoparticles has been measured versus temperature at different frequencies in the selected range of 40–1000 Hz and 130–220 K, respectively, using a Lake Shore AC susceptometer model 7000.

2.3. Characterization of ferrite thin films

The phase identification of thin films was performed by X-ray diffraction (XRD) using CuKα radiation. Atomic force microscopy was employed to evaluate the surface morphology of thin films. Room temperature magnetization and hysteresis loops of the films were measured using a VSM.

3. Results and discussion

3.1. Structural properties of nanoparticles

The particle size distribution was estimated based on analyzing the bright field images of randomly selected nanoparticles. Table 1 reflects the range of particle size of prepared samples. It reveals from Fig. 1(a) that the particle size of $Cu_{0.3}Mg_{0.2}Zn_{0.5}Fe_2O_4$ is in the range of 7–14 nm. The value of mean particle size is in close agreement with the XRD results. The EDAX microanalyzer of the mentioned sample proved the existence of the constitutive elements. The heating thermograms of samples (not shown here) exhibited that nearly 35% of sample evaporated while heating to 500 °C. The heating analysis of ferrite nanoparticles exhibit one exothermic peak at temperature of 210 °C. The mentioned peak is attributed to the amorphous-to-crystalline phase transition.

Table 1
The particles size range according to the TEM observation.

x	0	0.1	0.2	0.3	0.4	0.5
Particle size range (nm)	2–5	4–9	7–11	9–14	13–25	20–35

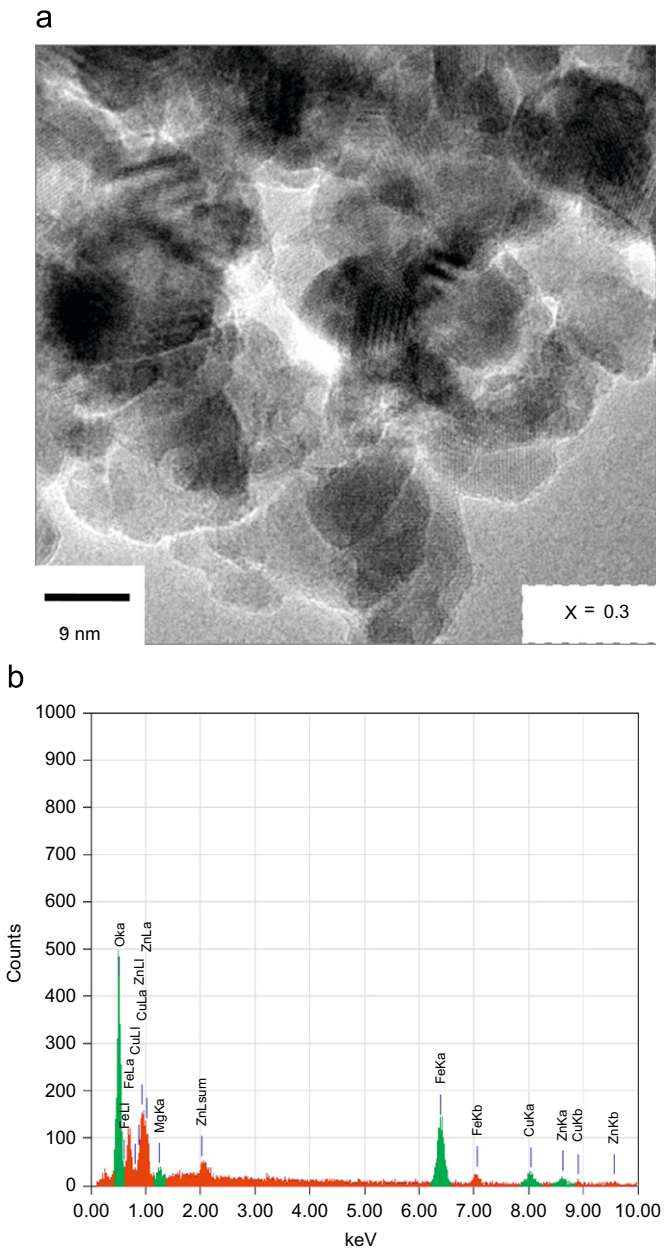

Fig. 1. (a) TEM micrograph and (b) EDAX result of sample $x=0.3$.

Fig. 2 shows the room temperature (RT) Mössbauer results for some representative samples. The spectra revealed ferrites not completely magnetically ordered and were fitted considering hyperfine magnetic field distributions (see insets, in the figures). Table 2 presents the obtained hyperfine parameters, for the whole series of the samples. According to this data, all the iron cations are in the ferric state (Fe^{3+}). Substitution of magnesium by copper from $X=0.5$ down to $X=0.2$ does not significantly change the average magnetic hyperfine field. However, a clear decrease occurs from $X=0.1$, including the appearing of a paramagnetic fraction for the $X=0$ sample. Since the size of nanoparticles of sample $x=0$ is in the range of 2–5 nm, the influence of superparamagnetic on doublet is obvious. The doublet arises from both A- and B-site ferric ions. The doublet is gradually disappeared by lowering the temperature [20]. The doublet could also be attributed to the presence of a small amount of a secondary phase, paramagnetic at RT. Earlier results on the