Journal of Magnetism and Magnetic Materials 343 (2013) 86–91

Contents lists available at SciVerse ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Effect of different doping on the structural, morphological and magnetic properties for Cu doped nanoscale spinel type ferrites

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ARTICLE INFO

Article history:
Received 18 December 2012
Received in revised form
23 April 2013
Available online 7 May 2013

Keywords:
Nanoparticle
Spinel ferrite
Magnetic behavior
Spin-valve

ABSTRACT

$Cu_xM_{1-x}Fe_2O_4$ (M=Co, Mn and Ni; x=0.0, 0.6 and 1.0) spinel type ferrite nanoparticles have been synthesized by cetyltrimethylammonium bromide (CTAB) assisted hydrothermal route using NaOH solution. The purity, structural characterization and magnetic properties have been investigated using the scanning electron microscopy, x-ray diffraction analysis and a quantum design vibrating sample magnetometer depending on the temperature. The scanning electron microscopy imaging exhibits very powerful aspect. The average size of composite nanoparticles for all samples was determined. Diameter of the samples is synthesized in nanoscale. The x-ray diffraction results have indicated that these samples are high phase purity, crystalline and inverse spinel ferrites. The temperature evolution of the magnetic properties and different doping effects for the samples have been observed. The pseudo spin-valve behavior has been showed for $Cu_{0.6}Co_{0.4}Fe_2O_4$ and $CoFe_2O_4$ samples. These samples can be considered as promising materials for magnetic recording media and electromagnetic absorbing technologies applications.

1. Introduction

In recent years, the synthesis and characterization of nanoscale magnetic materials have attracted much attention as the materials in this size range would allow investigating the fundamental aspects of magnetic ordering phenomena in magnetic materials with reduced dimensions and could also lead to potential applications [1–3]. Nano scale ferrites are likely to become an integral part of the future nanotechnology primarily as their electrical, permittivity and magnetic elements. This type of structures belong to a large class of compound that have a spinel type structures. These materials may be complex composite structures or polymeric compound. Especially, nanocomposites and nanoparticles have an important place in nanoscience and nanotechnology. These structures are usually a reinforced polymer matrix in which the inorganic particles (nano-sized fillers) are formed. The potential applications of spinel type ferrite nanoparticles (NPs) are very attractive for magneto-sensor, thermal medicine, micro-electro mechanical systems, bio-sensor, magneto-electronics, data storage media, computer hard disks, microwave electronic devices and nano-transistors. The NPs have relevance to thin films devices in the breed of magneto-electronics, spin-valve, spin-transistors, spin-dependence tunneling devices etc. Polymer nano-metallic composites are excellent materials due to thermal, mechanical, chemical, magnetic, electrical, electronic and optical properties with a very high commercial pot ential and in many application areas [4,5]. The spinel type ferrite NPs serve as better electromagnetic interference (EMI) suppressors compared to their dielectric counterparts on account of their excellent magnetic properties. The ferrite materials exhibit various electrical and magnetic properties of which complex permeability and permittivity, in particular, are important in determining their high frequency characteristics [6,7]. With fast advancement of wireless communications, the absorbers of electromagnetic (EM) waves are becoming increasingly important for applications outside special fields such s silent rooms, radar systems and military application. The composite materials were very significant for the development of absorbers [8–10].

The physical properties of ferrites are related to the structure of solids. They belong to a large class of compounds which have a spinel structure. The spinel unit cell consists of a cubic array of 32 oxygen anions, 16 Fe^{3+} ions and 8 Fe^{2+} ions. A total of 24 metal cations are distributed among eight tetrahedral interstices and 16 octahedral interstices [11,12]. Therefore, the physical properties of the spinel type nanoparticles such as magnetic, microwave and doping effects are determined by many factors, the particle size and shape, the type and the degree of defectiveness of the crystal lattice, the key of these including the chemical composition, and the interaction between the

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http://dx.doi.org/10.1016/j.jmmm.2013.04.079

particles [13]. Ferrites have vast applications, from microwave to radio frequencies. They exhibit relatively high resistivity at carrier frequency, sufficiently low losses for microwave applications and a wide range of other electric properties [14,15]. The frequency evolutions of the real and imaginary parts of the permittivity for nanoscale ferrite particles have been calculated at room temperature [6]. The technological importance of YFe_2O_4 (Y=Ni, Co, Zn, Mn, etc.) has motivated several studies on the synthesis as well as the physical properties of this material. In addition, the magnetic and catalytic properties of cubic copper ferrite nano-powders synthesized from secondary resources are also investigated [16]. Shortly, ferrite nanoparticles have been prepared by mechanical-milling [17], hydro thermal method [18–22], microwave route [23–26], sol–gel method [27,28], surfactant-assisted route [29–31], ball-milling technique [32], micro-emulsion method [31–33], co-precipitation method [34,35], electrochemical [36,37], organic acid precursor method [38] citrate precursor method [39], mill scale fines via conventional oxide ceramic process [40], solid state method [41], and hydrothermal processing [42]. Desired size of the particles can be obtained from these methods. But, these methods are difficult to employ on a large scale.

In the scope of this work, the CTAB-assisted hydrothermal method was used to synthesize $Cu_xM_{1-x}Fe_2O_4$ (M=Co, Mn and Ni; $x=0.0$, 0.6 and 1.0) spiel type nanoparticles and the effect of NaOH hydrolyzing agents was investigated. The effects of CTAB as a transferring agent, and concentrated NaOH as hydrolyzing agents on particle size and morphology were investigated. The synthesized nanocrystalline samples were characterized by x-ray diffraction (XRD) and scanning electron microscopy (SEM). The magnetic properties of spinel type samples were investigated using a quantum design vibrating sample magnetometer (VSM) depending on the temperature. The magnetic characterization of spinel composites nanostructures has been examined in detail. Also, magnetic properties were investigated according to the decreasing temperature and the amount of additives. According to the obtained results, the most appropriate electromagnetic radiation absorbing materials (EMRAM), electronic devices, electromagnetic interference/noise, and anti-materials (electromagnetic interferences, EMI) were characterized.

2. Experimental

Cetyltrimethylammonium bromide (CTAB) with a uniform and ordered chain structure is easily absorbed at the surface of metal oxide colloid. When the surface of the colloid absorbs this type of cationic surfactant, the activities of colloid greatly decrease and the growth rate of the colloids in some certain facet will be confined. The linear CTAB has been widely used in the synthesis of a series of nanoparticles in solution. The surfactant CTAB plays a key role in controlling the nucleation and growth of the samples. The surface tension of solution is reduced to the existence of surfactant, which lowers the energy needed for the formation of a new phase of samples. The $Cu_xM_{1-x}Fe_2O_4$ (M=Co, Mn and Ni; $x=0.0$, 0.6 and 1.0) spinel type composite nanoparticles have been prepared using the surfactant-assisted hydrothermal process by using CTAB. This CTAB-assisted hydrothermal method is very useful for the solid state powder technology. Because, this method for preparation of nanoparticles is cheap and does not require extreme high processing temperature (for example the hydrothermal method at a temperature of about 150 °C). In addition, this method is used to synthesize good crystalline and homogeneous nanoparticles [43,44]. With this method, 0.003 mol surfactant CTAB was dissolved in 35 ml deionized water to form a transparent solution. The $Cu_xCo_{1-x}Fe_2O_4$ spinel type ferrite nanoparticles have been synthesized by the CTAB-assisted hydrothermal route using NaOH solution. Then ferric chloride hexahydrate ($FeCl_3 \cdot 6\,H_2O$) of 0.004 mol is added to solution and mixed for 10 min. After 10 min, stoichiomeric amount of $CuCl_2 \cdot 6\,H_2O$ and $CoCl_2 \cdot 6\,H_2O$ was introduced into mixed solution under vigorous stirring. Deionised water is added to make the solution for a total volume of 40 ml and pH of the solution mixture was adjusted to 11 by the addition of 2 M NaOH. Before being transferred to a teflon lined autoclave of 50 ml capacity, the solution mixture was pre-treated under an ultrasonic water bath for 40 min; hydrothermal synthesis was carried out at 130 °C for 15 h in an electric oven without shaking or stirring. Afterwards, the autoclave was allowed to cool to room temperature gradually. The black precipitate collected was washed with distilled water several times in an ultrasonic bath to remove any possible impurities. The solid was then heated at 500 °C and dried under vacuum for 5 h. Other synthesis procedures were performed in the same way. For details of the synthesis processes of samples in this work see Refs. [30,45,46,7].

The nanoparticles in this work were measured by a Size Malvern Instruments Zeta Sizer Nano-ZS [6,7]. SEM imaging was performed using a Philips XL30 SFEG. x-Ray diffraction analysis was performed using a Bruker D8 advance Diffractometer with Cu Kα radiation. Magnetic hysteresis loops measurements were carried out with a Quantum Design Vibrating Sample Magnetometer (VSM) model 6000.

3. Result and discussion

Table 1 indicates the diameter (d) and quantity of doping for $Cu_xCo_{1-x}Fe_2O_4$, $Cu_xMn_{1-x}Fe_2O_4$, and $Cu_xNi_{1-x}Fe_2O_4$, spinel-ferrite type composite nanoparticles. The samples correspond to $CoFe_2O_4$, $MnFe_2O_4$, and $NiFe_2O_4$, at pure or no doping (or $x=0.0$). These diameters of particles were measured by a Size Malvern Instruments Zeta Sizer Nano-ZS [6,7]. In addition, diameters of the particles were checked by XRD and SEM. The diameter of $MnFe_2O_4$ sample is rather similar to the atomic diameter of elements. The density of nickel is greater than the density of cobalt. Thus, the diameter of nickel (Ni) is greater than the size of cobalt in general.

The cross-sectional SEM imaging for some selected $Cu_xCo_{1-x}Fe_2O_4$ ($x=0.0$, $d=41$ nm), $Cu_xMn_{1-x}Fe_2O_4$ ($x=0.6$, $d=50$ nm), and $Cu_xNi_{1-x}Fe_2O_4$ ($x=0.6$, $d=62$ nm) are shown in Fig. 1a, b, and c respectively. The SEM imaging exhibits very powerful aspect in the micrometer scale. The average size of composite nanoparticles for all samples was determined by analyzing these SEM figures and the Debye–Scherrer equation (see Fig. 2 for details).

Fig. 2 shows typical XRD results of $Cu_xCo_{1-x}Fe_2O_4$ ($x=1.0$, 0.6 and 0.0) composite nanoparticles. The $CuFe_2O_4$, $Cu_{0.6}Co_{0.4}Fe_2O_4$ and $CoFe_2O_4$ nanoparticles were analyzed by XRD in order to investigate the crystalline phases. The patterns show the reflection planes (111), (220), (311), (222), (400), (422), (511), and (440). The XRD patterns have indicated that these samples are of the spinel cubic structure (JCPS Card no. 25-283) [34,16]. The XRD results in this work agree with the XRD result of $CuFe_2O_4$ nanoparticles [16]. The most intense peak for this type of spinel nanostructure appears in (311).

The largest peak for all samples is observable at $2\theta=$~35 °C. The x-ray diffraction planes are (111), (220), (311), (222), (400), (422), (511), and (440) [34]. The average particle sizes of the ferrite type particle were determined from the full width at half maximum (FWHM) of the most intense peak (311) using the Debye–Scherrer

Table 1
The diameter (d) values of doping for spinel-ferrite type composite nanoparticles.

Size Table	$x=0.0$ (d, nm)	$x=0.6$ (d, nm)	$x=1$ (d, nm)
$Cu_xCo_{1-x}Fe_2O_4$	41	55	48
$Cu_xMn_{1-x}Fe_2O_4$	57	50	42
$Cu_xNi_{1-x}Fe_2O_4$	54	62	64