Materials Research Bulletin 48 (2013) 2060–2065

Contents lists available at SciVerse ScienceDirect

Materials Research Bulletin

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

Nanocrystalline spinel ferrite (MFe_2O_4, M = Ni, Co, Mn, Mg, Zn) powders prepared by a simple aloe vera plant-extracted solution hydrothermal route

Santi Phumying [a,b], Sarawuth Labuayai [a,b], Ekaphan Swatsitang [a,b], Vittaya Amornkitbamrung [a,b], Santi Maensiri [c,*]

[a] Department of Physics, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand
[b] Integrated Nanotechnology Research Center (INRC), Khon Kaen University, Khon Kaen 40002, Thailand
[c] School of Physics, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand

ARTICLE INFO

Article history:
Received 18 July 2012
Received in revised form 8 February 2013
Accepted 12 February 2013
Available online 28 February 2013

Keywords:
A. Magnetic materials
B. Chemical synthesis
C. Electron microscopy
C. X-ray diffraction
D. Magnetic properties

ABSTRACT

Nanocrystalline spinel ferrite MFe_2O_4 (M = Ni, Co, Mn, Mg, Zn) powders were synthesized by a novel hydrothermal method using $Fe(acac)_3$, $M(acac)_3$ (M = Ni, Co, Mn, Mg, Zn) and aloe vera plant extracted solution. The X-ray diffraction and selected-area electron diffraction results indicate that the synthesized nanocrystalline have only spinel structure without the presence of other phase impurities. The crystal structure and morphology of the spinel ferrite powders, as revealed by TEM, show that the $NiFe_2O_4$ and $CoFe_2O_4$ samples contain nanoparticles, whereas the $MnFe_2O_4$ and $MgFe_2O_4$ samples consist of many nanoplatelets and nanoparticles. Interestingly, the $ZnFe_2O_4$ sample contains plate-like structure of networked nanocrystalline particles. Room temperature magnetization results show a ferromagnetic behavior of the $CoFe_2O_4$, $MnFe_2O_4$ and $MgFe_2O_4$ samples, whereas the samples of $NiFe_2O_4$ and $ZnFe_2O_4$ exhibit a superparamagnetic behavior.

1. Introduction

The synthesis of nanocrystalline spinel ferrite (with the general formula MFe_2O_4 (e.g. M = Mn, Co, Ni, Cu, Zn, Mg)) has become an important part of modern ceramic research. The study of nanocrystalline spinel ferrite particles has great relevance to modern technological applications in several industrial and biological fields, including magnetic recording media and magnetic fluids for the storage and/or retrieval of information, magnetic resonance imaging (MRI) enhancement, catalysis, magnetically guided drug delivery, sensors, and pigments [1,2]. It is well known that the chemical, structural, and magnetic properties of spinel ferrite particles are strongly influenced by their composition and microstructures, which are sensitive to the preparation methodologies [3,4]. Many synthesis routes have been used to prepared particles of spinel ferrite [5–15]. Among the other methods, hydrothermal route has been recently received much attention. Recently, many conditions have been applied to the preparation via hydrothermal process of spinel ferrite. Baykal et al. [13] reported hydrothermal synthesized $NiFe_2O_4$ nanocrystals from ferric chloride hexahidride ($FeCl_3{\cdot}6H_2O$) and nikel chloride ($NiCl_2$), using cetyltrimethylammonium bromide (CTAB) as the surfactant and NH3 and NaOH as hydrolyzing agents. Yu et al. [14] hydrothermally synthesized $ZnFe_2O_4$ using metal Zn sheet and $FeCl_2$ as reactants in ammonia solutions. Recently, Liu et al. [15] successfully prepared $CoFe_2O_4$ nanoplateletes and nanoparticles by hydrothermal reaction from ferric chloride ($FeCl_3$), cobalt dodecyl sulfate ($Co(DS)_2$) and NaOH aqueous solution. However, most of these conditions involve a strictly controlled synthesis environment, expensive reagent and complicated procedures. Therefore, simple and cost effective conditions via hydrothermal process to synthesize spinel ferrite particles by utilization of cheap, nontoxic and environmentally benign precursors are still the key issues.

Aloe vera (*Aloe barbadensis Mill.*) is a perennial succulent belonging to the Liliaceal family, and it is a cactus-like plant that grows in hot, dry climates [16]. For many years, aloe vera has been reported to possess immunomodulatory, anti-inflammatory, UV protective, antiprotozoal, and wound- and burn-healing promoting properties [17–20]. Recently, the extract of aloe vera plant has been successfully used to synthesize single crystalline triangular gold nanoparticles (~50–350 nm in size) and spherical silver nanoparticles (~15 nm in size) in high yield by the reaction of aqueous metal source ions (chloroaurate ions for Au and silver ions for Ag) with the extract of the aloe vera plant [21]. Recently our group has reported the use of aloe vera plant for the synthesis of

* Corresponding author. Tel.: +66 44 224957; fax: +66 44 224651.
E-mail address: santimaensiri@gmail.com (S. Maensiri).

0025-5408/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.materresbull.2013.02.042

indium oxide (In_2O_3) nanoparticles with particle size of 5-50 nm [22]. Most recently, our group has also reported the use of aloe vera plant for the synthesis of various complex oxide nanoparticles, including hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAp) [23], (Ni–Cu–Zn)Fe_2O_4 [24], MFe_2O_4 (M = Cu, Ni, Zn) [25]. This biosynthetic route is very simple and provides high-yield nanosized oxide materials with well crystalline structure and acceptable properties. However, high calcination temperature is needed to convert the precursor to form crystalline materials.

In this paper, we report a novel hydrothermal synthesis of MFe_2O_4 (M = Ni, Co, Mn, Mg, Zn) using metals acetylacetonate and aloe vera plant-extracted solution.

2. Experimental

In this study, $Fe(acac)_3$ and $M(acac)_2$ (M = Ni, Co, Mn, Mg, Zn) were purchased from Aldrich Chemical Co as the starting chemical material. Aloe vera-extracted solution was prepared from a 35 g portion of thoroughly washed aloe vera leaves which were finely cut and boiled in 100 ml of de-ionized water. The resulting extract was used as an aloe vera-extracted solution. In the preparation of MFe_2O_4 (M = Ni, Co, Mn, Mg, Zn) samples, $Fe(acac)_3$ (10 mmol) and $M(acac)_2$ (5 mmol) were first dissolved in 50 ml aloe vera extract solution under vigorous stir at room temperature for 1 h. The mixtures were added to a sealed Teflon-lined autoclaved of 100 mL capacity, which was heated and maintained at 200 °C for 2 h, and then gradually cooled to room temperature. The precipitation were collected by filtration and washed with de-ionized water and ethanol for several times, and finally dried in air at 85 °C.

The crystal phase identification was conducted by powder X-ray diffraction (XRD) using Cu*K*a radiation with $\lambda = 0.15418$ nm (PW3040 mpd control, The Netherlands). The particle size and morphology of the prepared powders were characterized by scanning electron microscopy (SEM) (LEO VP1450VP, U.K.), transmission electron microscopy (TEM) (JEOL 2010, 200 kV, Japan). The magnetic properties of the calcined powders were examined at room temperature (293 K) using a vibrating sample magnetometer (VSM 7403, Lake Shore, USA).

3. Results and discussion

The XRD patterns of the MFe_2O_4 (M = Ni, Co, Mn, Mg, Zn) powders are shown in Fig. 1. The patterns of the as-prepared samples can be indexed to $NiFe_2O_4$ (JCPDS 86-2267), $CoFe_2O_4$ (JCPDS 22-1086), $MnFe_2O_4$ (JCPDS 74-2403), $MgFe_2O_4$ (JCPDS 73-2410) and $ZnFe_2O_4$ (JCPDS 22-1012). No diffraction peaks of other impurities were observed, which indicates the high purity of the final products was successfully synthesized under the current experimental condition. The average crystallite sizes of MFe_2O_4 nanoparticles were calculated from X-ray line broadening of the reflections of (2 2 0), (3 1 1), (4 0 0), (5 1 1) and (4 4 0) using Scherrer's equation (i.e. $D = 0.89\lambda/(\beta \cos\theta)$, where λ is the wavelength of the X-ray radiation, θ is the diffraction angle and β is the full width at half maximum (*FWHM*) [26]), and were found to be 8.2 ± 0.7 nm, 8.5 ± 1.9 nm, 15.9 ± 5.1 nm, 45.3 ± 15.1 nm and 17.9 ± 3.1 nm for the samples of $NiFe_2O_4$, $CoFe_2O_4$, $MnFe_2O_4$, $MgFe_2O_4$ and $ZnFe_2O_4$, respectively. The crystallite sizes and lattice parameters are also summarized in Table 1.

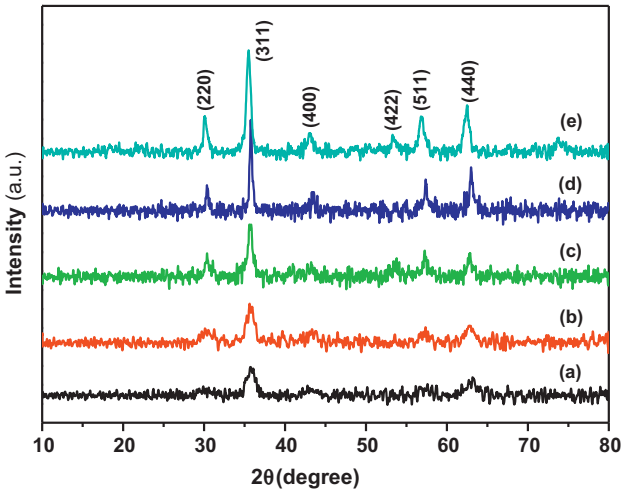

Fig. 1. XRD patterns of the prepared ferrite samples: (a) $NiFe_2O_4$, (b) $CoFe_2O_4$, (c) $MnFe_2O_4$, (d) $MgFe_2O_4$ and (e) $ZnFe_2O_4$.

Table 1
Average crystal sizes from XRD, spinel lattice parameter *a* calculated from XRD spectra, the specific magnetization (M_s), and coercive fields (H_c) of the MFe_2O_4 (M = Ni, Co, Mn, Mg, Zn) samples prepared at 200 °C for 2 h.

Samples	Average crystallite size from XRD (nm)	Spinel lattice parameter *a* (nm)	M_s (emu/g) at 10 kOe	H_c (Oe)
$NiFe_2O_4$	8.2 ± 0.7	0.8358 ± 0.0002	31.9	7.5
$CoFe_2O_4$	8.5 ± 1.9	0.8390 ± 0.0004	55.3	74.3
$MnFe_2O_4$	15.9 ± 5.1	0.8393 ± 0.0004	52.4	43.9
$MgFe_2O_4$	45.3 ± 15.1	0.8364 ± 0.0003	68.9	98.2
$ZnFe_2O_4$	17.9 ± 3.1	0.8431 ± 0.0003	7.06	9.8

The XRD results show that nanocrystalline MFe_2O_4 powders can be synthesized at relatively low temperature by hydrothermal synthesis using the aloe vera plant-extracted solution. The formation of MFe_2O_4 in the present work could be the result of various mechanisms. However, it is believed that aloe vera extract here functions as a complexing agent in a solution like in a modified sol–gel process where the complexing agent chelates metal cations in solution and homogeneously mixes them in atomic scale. For the aloe vare plant-extracted solution synthesis of MFe_2O_4 (M = Cu, Ni, Zn) [25] followed by conventional calcination, the synthesis temperature and time is consequently much lower than solid state reaction where high temperature is required for diffusion of solid reactants. Interestingly, for the present study, when a mixed solution of aloe vera plant extract and metal cations is subjected to hydrothermal process, MFe_2O_4 can be easily formed at low temperature with short reaction time. Although more studies are needed to explain the mechanism in detail, it is established that aloe vera-extracted solution can be used with hydrothermal route to prepare the MFe_2O_4 or other complex oxides.

The morphology of the MFe_2O_4 (M = Ni, Co, Mn, Mg, Zn) samples were further investigated by SEM. Fig. 2 shows the morphology of the MFe_2O_4 (M = Ni, Co, Mn, Mg, Zn) powders. The estimated clusters of particles are 50-100 nm. Detailed morphology and structure of the MFe_2O_4 (M = Ni, Co, Mn, Mg, Zn) samples were further investigated by TEM. It is clearly seen from the TEM bright-field images (Fig. 3a–e) that the $NiFe_2O_4$ and $CoFe_2O_4$ samples contain nanoparticles with particle sizes of ~6–10 nm, whereas the $MnFe_2O_4$ and $MgFe_2O_4$ samples consist of many nanoplatelets and nanoparticles with particle sizes of ~6–40 and ~10–50 nm for the samples of $MnFe_2O_4$ and $MgFe_2O_4$, respectively. Interestingly, The $ZnFe_2O_4$ sample contains plate-like structure of networked nanocrystalline particles with sizes of ~5–15 nm. The corresponding selected-area electron diffraction (SAED) patterns (inset of Fig. 3) of all MFe_2O_4 samples show spotty ring patterns of crystalline spinel