Journal of Magnetism and Magnetic Materials ∎ (∎∎∎∎) ∎∎∎–∎∎∎

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

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

Phase formation, morphology and magnetic properties of $MgFe_2O_4$ nanoparticles synthesized by hydrothermal technique

Jeeranan Nonkumwong [a], Supon Ananta [b], Pongsakorn Jantaratana [c], Santi Phumying [d], Santi Maensiri [d], Laongnuan Srisombat [a,*]

[a] Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand
[b] Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand
[c] Department of Physics, Faculty of Science, Kasetsart University, Bangkok 11900, Thailand
[d] Advanced Materials Physics Laboratory (Amp.), School of Physics, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand

ARTICLE INFO

Article history:
Received 8 October 2014
Received in revised form
22 December 2014
Accepted 2 January 2015

Keywords:
Hydrothermal technique
Magnesium ferrite nanoparticles
Magnetic property
Morphology
Phase formation

ABSTRACT

In the present work, the processing conditions for obtaining monodispersed magnesium ferrite ($MgFe_2O_4$) nanoparticles with the desired morphology and relatively high saturation magnetization via hydrothermal technique were developed. For the first time, the effects of base type and reaction conditions (i.e. temperature and time) on phase formation, morphology and magnetic properties of the obtained products were determined by using a combination of XRD, TEM/EDX and VSM techniques. It is seen that the saturation magnetization of the particles can be increased by employing lower reaction temperature and/or shorter reaction time, while narrow size distribution of the particles can be maintained. In addition, it was found that pure phase of superparamagnetic $MgFe_2O_4$ nanoparticles with the smallest size of about 65 nm was obtained by using CH_3COONa as a base at 180 °C for 14 h.

1. Introduction

Due to magnetic responsiveness for external magnetic field induced separation and delivery, magnetic nanoparticles (MNPs) are of great interest for biomedical applications [1,2]. For example, conventional hyperthermia instruments for cancerous tissue therapy require inserting antennas into patient body (i.e. cause some wound) to target area and heating up by using microwave or radio frequency [3]. Hence, filling cancer cell with the MNPs in order to generate heat, by using alternating current (AC) magnetic field from external coils (i.e. without patient injure), is one of the great challenge. In connection with this, spinel ferrites such as $CoFe_2O_4$, $NiFe_2O_4$ and $MgFe_2O_4$ have been widely explored owing to their tunable cation ordering which are the key parameters for such heat treatment [4,5]. To apply these materials for hyperthermia treatment, superparamagnetism of synthesized particles is required. Furthermore, in order to align the spin arrangement for superparamagnetic materials with the applied AC magnetic field, the particle size of such materials should be small enough (i.e. <150 nm) to give single-domain structure [2,6].

Among several processing techniques introduced for the preparation of highly monodispersed nanoparticles with a control over size and morphology, a hydrothermal method has been established as one of the suitable method [7,8]. For example, Wang [9] and Mansour et al. [10] reported that the nanoparticles synthesized from this method exhibit high crystallinity without further high temperature annealing process, resulting in high magnetization. Verma et al. [11] successfully synthesized superparamagnetic $MgFe_2O_4$ powders with particle size ~3 nm by hydrothermal technique. However, the synthetic route has to be assisted by microwave which is require optional set up to primary instrument of hydrothermal method. Later, Sasaki et al. [12] reported that superparamagnetic $MgFe_2O_4$ with particle size of ~20 nm can be successfully prepared by using supercritical water conditions. Also, more complicated system and instruments such as flow-type apparatus, high-pressure pump and high temperature reactor are required. In 2007, low-temperature solvothermal method was introduced for the production of $MgFe_2O_4$ by Deng et al. [13], but the obtained products do not show superparamagnetism because of large particle size (~300–800 nm). Recently, Rafique et al. [14] demonstrated that $CoFe_2O_4$ nanoparticles with smaller size exhibit better superparamagnetism. On the other hand, Mohapatra et al. [15] reported that the particles size of $CoFe_2O_4$ nanoparticles derived from of base i.e. the stronger the base, the larger the particle size. In recent year, it has been

* Corresponding author.
E-mail address: slaongnuan@yahoo.com (L. Srisombat).

http://dx.doi.org/10.1016/j.jmmm.2015.01.001
0304-8853/

Table 1
Physical and magnetic properties of samples prepared under various conditions.

Preparation condition			Particle size		Lattice strain	M_s (emu/g)	H_c (Oe)	M_r (emu/g)	M_r/M_s	Remarks
Base	Temp. (°C)	Time (h)	Crystallite size (nm)[a]	Cluster size (nm)						
CH_3COONa	180	12	13.98	70 ± 11[b]	0.0076	59.77	2.94	0.58	9.7×10^{-3}	Effect of base
NH_4OH			–	93 ± 22[b]	–	–	–	–	–	
KOH			–	Incomplete conversion	–	–	–	–	–	
NaOH			–	Incomplete conversion	–	–	–	–	–	
CH_3COONa	160	12	–	40 ± 7[b]	–	–	–	–	–	Effect of temperature
	180		13.98	70 ± 11[b]	0.0076	59.77	2.94	0.58	9.7×10^{-3}	
	200		12.50	138 ± 14[b]	0.0090	50.16	2.12	0.35	7.0×10^{-3}	
	220		12.70	63 ± 10[b]	0.0088	51.03	0.21	0.05	9.8×10^{-4}	
CH_3COONa	180	8	13.53	81 ± 13[c]	0.0083	65.40	0.57	0.19	2.9×10^{-3}	Effect of time
		10	13.98	80 ± 11[c]	0.0080	64.64	1.32	0.45	7.0×10^{-3}	
		12	13.98	84 ± 16[c]	0.0076	59.77	2.94	0.58	9.7×10^{-3}	
		14	11.15	65 ± 8.5[c]	0.0101	53.92	0.07	0.03	5.6×10^{-4}	
		16	14.23	73 ± 9[c]	0.0079	57.12	4.59	0.96	1.7×10^{-2}	

[a] The crystallite size of the particle was calculated by the Debye–Scherrer equation.
[b] The cluster size of the particle was measured from TEM images of JEOL JEM-2010 TEM.
[c] The cluster size of the particle was measured from TEM images of FEI TECNAI TEM.

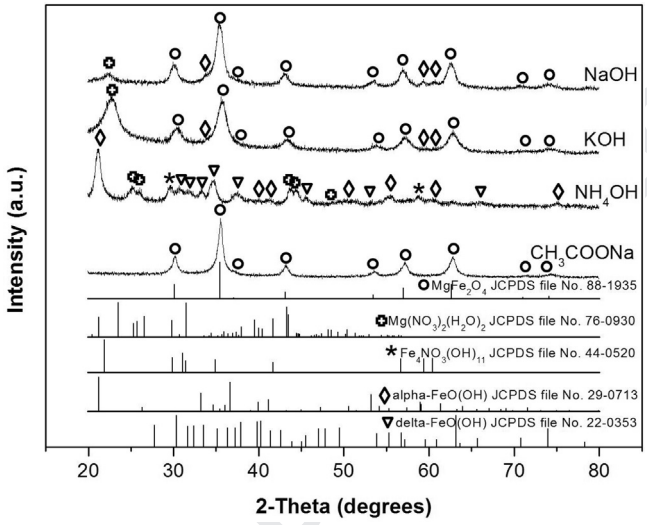

Fig. 1. Powder XRD patterns of particles synthesized at 180 °C for 12 h by using different bases.

reported that the particle size of $CoFe_2O_4$ nanoparticles can be tailored via the employed reaction temperature [16]. Moreover, Wang et al. [17] also reported that $NiFe_2O_4$ nanoparticles with smaller size can be achieved by using shorter reaction time.

Hence, The aim of the present work was to explore a hydrothermal technique without using addional complicated instrument for the production of $MgFe_2O_4$ nanoparticles and to perform a systematic study of the type of bases, reaction temperature and reaction time. The obtained $MgFe_2O_4$ was characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), energy-dispersive X-ray (EDX) spectroscopy and vibrating sample magnetometry (VSM) techniques in order to investigate the phase formation, morphology and magnetic properties, respectively.

2. Experimental details

As received $Mg(NO_3)_2 \cdot 6H_2O$ (Loba Chemie, 99% purity), $Fe(NO_3)_3 \cdot 9H_2O$ (Carlo Erba, 98% purity), ethylene glycol (Fisher Scientific, 99.5% purity), CH_3COONa (Loba Chemie, 99.5% purity), NaOH (Ajax, 97.0% purity), KOH (Carlo Erba, 85% purity) and ammonia solution 25% (NH_4OH) (Merck) were used as the starting chemicals, without further purification.

The $MgFe_2O_4$ nanoparticles were synthesized by using the salt of magnesium (instead of zinc) via a hydrothermal method which is slightly modified from a procedure advocated by Li et al. for the synthesis of $ZnFe_2O_4$ [18]. In a typical synthesis, 2 mmol of $Mg(NO_3)_2 \cdot 6H_2O$ and 1 mmol of $Fe(NO_3)_3 \cdot 9H_2O$ were dissolved in 30 mL ethylene glycol. In general, the amount of base affects the precipitation of the metal salts. The preliminary study showed that no precipitation was formed by using 1.5 mmol of CH_3COONa. In order to investigate the effects of base types on the formation of $MgFe_2O_4$ nanoparticles, the suitable amount of base forming precipitates was chosen here. The 15 mmol of CH_3COONa or NaOH or KOH or NH_4OH base was added into the mixture solution and then transferred to a Teflon-lined stainless steel autoclave (series 5500 HP compact reactor). The autoclave was heated to 180 °C, maintained for 12 h and cooled down to room temperature naturally [18]. The precipitates were collected by magnetic separator, washed three times with deionized water, another three times with ethyl alcohol and dried at 70 °C for 12 h [9]. In order to investigate the effects of reaction temperature and time on phase formation, morphology and magnetic properties of the $MgFe_2O_4$ nanoparticles, the reaction temperatures ranging from 160 to 220 °C [16] and the reaction time ranging from 8 to 16 h [17] (detailed in Table 1) were applied for a given base. The advantage of this technique over other is that the required reaction temperature for this technique is not extremely high (~150 °C for ferrite) while other method such as solid-state method require much higher temperature (~800 °C) [19].

X-ray diffraction (XRD; Bruker D2 phaser diffractometer) using CuK_α radiation was employed for phase identification, crystallite size and strain analysis [20]. Crystallite size was calculated by using Debye–Sherrer's equation (i.e., $D = 0.89\lambda/(\beta \cos \theta)$ where D is crystallite size, 0.89 is the Sherrer constant, λ is wavelength of X-ray radiation, β is full width at half maximum of the most intense peak (311) and θ is Bragg angle). By applying Debye–Sherrer's equation, the estimated crystallite size of the samples can be calculated from the most intense peak (311) of XRD data as shown in Table 1. A combination of the transmission electron microscopy