Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 38 (2012) 2563–2568

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Magnetite syntheses from room temperature to 150 °C with and without microwaves

Sridhar Komarneni [a,*], Weiwei Hu [b], Young Dong Noh [a], Amanda Van Orden [a], Shouhua Feng [b], Chengzhen Wei [c], Huan Pang [c], Feng Gao [c], Qingyi Lu [d], Hiroaki Katsuki [e]

[a] *Materials Research Institute, The Pennsylvania State University, University Park, PA 16802, USA*
[b] *The State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130012, PR China*
[c] *State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, Nanjing University, Nanjing 210093, PR China*
[d] *Department of Materials Science and Engineering, Nanjing University, Nanjing 210093, PR China*
[e] *Saga Ceramics Research Laboratory, 3037-7, Arita-machi, Saga 844-0024, Japan*

Received 16 October 2011; received in revised form 8 November 2011; accepted 9 November 2011
Available online 18 November 2011

Abstract

Parameters such as temperature, time and presence or absence of microwaves affected the particle size and magnetic properties of synthetic magnetite. The presence of microwaves during crystallization significantly increased the particle size of magnetite in a short time with improved magnetic properties. Magnetite samples were characterized by X-ray diffraction, transmission electron microscopy (TEM) and saturation magnetization measurements. The TEM crystal sizes varied from about 40 to 50 nm at room temperature to greater than 50 nm with wider crystal size distribution at higher temperatures. The saturation magnetization values of synthetic magnetites ranged from 57.4 to 89.0 emu/g.

Keywords: Magnetite; Microwave-assisted synthesis; Conventional-hydrothermal synthesis; Saturation magnetization

1. Introduction

It is well known that magnetite is a naturally occurring ferrite mineral with magnetic properties and has an inverse spinel structure. Ferrites are an extremely important group of materials with a wide variety of applications in many fields. Among the spinel ferrites, magnetite has been utilized in many fields [1] such as in biosensors [2], drug delivery [3], ferrofluids [4], magnetic refrigeration [5], magnetic resonance imaging [6], magnetic storage media [7], printing inks [8] etc. Spinel ferrites were previously prepared by the traditional solid-state process [9], mechanochemical process [9], Pichini process [10], combustion process [11], coprecipitation [12] hydrothermal process [13], microwave-hydrothermal process [14], sol–gel process [15] and ball milling [16], the latter led to ferrite preparation with controlled nanosize and properties. Among these methods, only solution-based and hydrothermal methods are capable of precisely controlling the particle sizes. The particle sizes of magnetite required for different applications are different and hence there are numerous studies dealing with controlled particle sizes. Si et al. [1] prepared ferrite nanoparticles of 5–15 nm at room temperature by precipitating ferrous sulfate in the presence of polyacrylic acid or the sodium salt of carboxymethyl cellulose at a pH of about 13. Magnetite nanoparticles of 4–43 nm were synthesized at room temperature by precipitating ferric and ferrous chlorides with ammonia solution but without surfactants [17]. Zhou et al. [18] prepared magnetite nanoparticles from emulsions using ferrous sulfate and ferric nitrate as precursors and precipitating them using NaOH or NH_4OH. A recent method [19] utilized air oxidation of $Fe(OH)_2$ under visible light irradiation in the presence of trace concentration of ethylenediaminetetraacetic acid (EDTA) to synthesize magnetite nanocrystals of 11.5 to 30 nm at room temperature. Kang et al. [20] reported well-defined magnetite nanoparticles of about 8.5 nm by titrating ferrous and ferric salt solution into 1.5 M NaOH at room temperature without any surfactants. Magnetite particles of less than 6 nm were precipitated at 80 °C by forced mixing of ferrous and ferric

---

[*] Corresponding author.
E-mail address: komarneni@psu.edu (S. Komarneni).

0272-8842/$36.00 © 2011 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2011.11.027

salts with NaOH [21]. Octahedral nanoparticles of 60–80 nm were synthesized [22] using ferrous sulfate, sodium nitrate and sodium hydroxide in a nitrogen atmosphere in the temperature range of 60–100 °C. Khollam et al. [23] prepared magnetite powders by reaction of ferrous sulfate and sodium hydroxide in the temperature range of 90–200 °C under microwave hydrothermal (MH) conditions. Monodisperse ferrite nanoparticles were synthesized by microwave-assisted heating at 220 °C for 5 min and 250 °C for another 5 min [24]. Caillot et al. [25] used microwave-hydrothermal flash treatment of alcoholic solutions of ferrous chloride and sodium ethoxide solutions to prepare nanocomposite powders of hematite, spinel phase (maghemite) and magnetite at about 160 °C. Magnetite was also synthesized using ferric chloride, polyethylene glycol (PEG-20000) and hydrazine under microwave-assisted conditions at 100 °C for 10 min [26]. Hong et al. [27] prepared magnetite nanoparticles by the co-precipitation of ferrous and ferric salts using ammonia and microwave (MW) irradiation apparently using a domestic oven without any temperature control. Although all of the above synthesis techniques yielded magnetite, there is still a need to further explore the synthesis of magnetite at different temperatures with and without microwaves to achieve different sizes and crystallinities or to show faster crystallization. Therefore, the objectives of the present research were (a) to develop a simplified synthesis method for magnetite at room temperature without microwaves (b) to develop a faster method under microwave-assisted conditions at higher temperatures and (c) to measure the magnetic properties of the synthesized magnetites.

2. Materials and methods

2.1. Synthesis of magnetite

(1) Room temperature synthesis

The following chemical precursors were used for different syntheses: $FeCl_2$ (Aldrich, 98%), NaOH (Alfa aesar, 97%), and ammonia solution (EMD chemical, 28–30%, w/w), and Na_2CO_3 (JT Baker, 100.1%). In a typical synthesis, 0.008 mole of $FeCl_2$ was dissolved in 25 ml of ethanol in a beaker. Then 0.032 moles of NaOH or Na_2CO_3 was dissolved in 10 ml of deionized water. Under stirring, the above NaOH or Na_2CO_3 alkaline solution or 0.032 mole of ammonia solution was added to the $FeCl_2$ solution in the beaker. A blackish precipitate formed immediately. The resultant solid was washed with deionized water three times and then finally with ethanol. After washing, it was dried at room temperature.

(2) Microwave-assisted method

$FeCl_2$, NaOH, ammonia solution and Na_2CO_3 were used as above for various microwave-assisted syntheses. After mixing of the precursors in Teflon vessels as described above for room temperature syntheses, the vessels were heated by microwave-assisted conditions using a multi-mode MARS-5 microwave digestion system (CEM Corp., Matthews, NC) at 80–150 °C for 1–16 min. The microwaves operated at a frequency of 2.45 GHz with a power of 300 W. The experiments were carried out in double-walled digestion vessels having an inner non-reactive Teflon PFA liner and an outer Ultem polyetherimide shell of high mechanical strength. Temperature and pressure probes allowed the reaction to be controlled by monitoring the temperature or pressure within a control vessel. Temperature of solution was measured by using an established technique with phosphor sensor in a sapphire thermowell. The maximum operating temperature and pressure for the system are 240 °C and 350 psi, respectively. For comparison with microwave-assisted conditions of magnetite syntheses at 150 °C, conventional-hydrothermal experiments were also conducted in Parr reactors (Moline, Illinois, USA) at 150 °C for 1–16 h. The resultant solids were washed with deionized water and ethanol, and then dried at 60 °C prior to characterization by different techniques.

2.2. Characterization

2.2.1. Powder X-ray diffraction analyses

All synthetic magnetites were characterized by powder X-ray diffraction (XRD) analyses using a Scintag X-ray diffractometer with CuKα radiation and particle sizes were estimated by using the well-known Scherrer's equation. Each synthetic magnetite sample was loaded in to the same cavity of a zero background slide to have about the same weight for comparison with each other.

2.2.2. Transmission electron microscopy (TEM) analyses

For TEM analyses, the magnetite powders were dispersed in alcohol or deionized water, dropped on to copper grids and then dried in air. The TEM images were obtained from JEM-2010 or JEM-2100 instrument at an acceleration voltage of 200 KV.

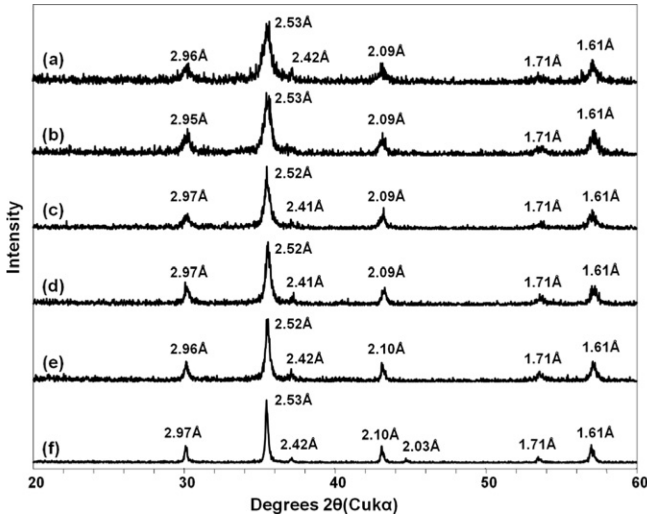

Fig. 1. X-ray diffraction patterns of magnetite synthesized (a) using $FeCl_2 + NH_4OH$ at room temperature (YN398), (b) using $FeCl_2 + Na_2CO_3$ at room temperature (YN389) and using $FeCl_2$ and NaOH at different temperatures for 15 min under microwave-assisted conditions: (c) 80 °C, (d) 100 °C, (e) 120 °C, and (f) 150 °C (the 2.03 Å peak corresponds to Fe metal).

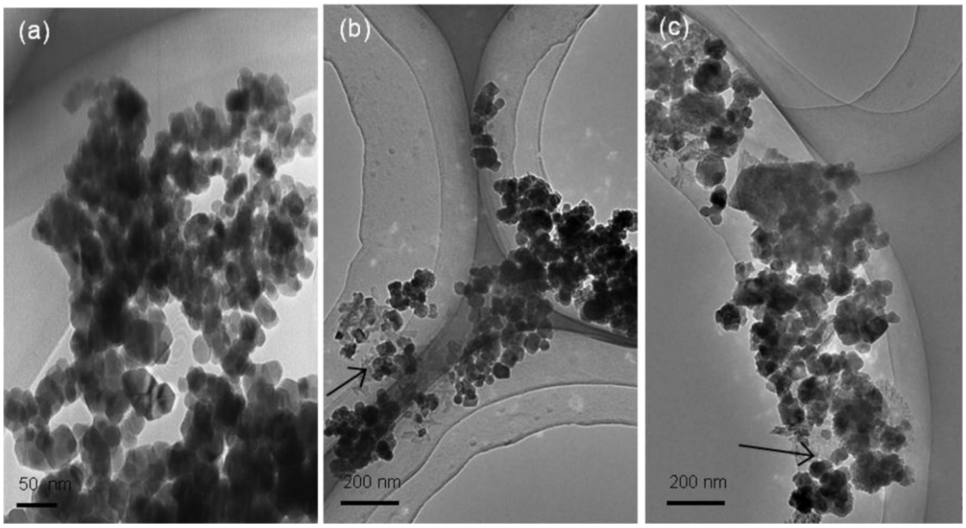

Fig. 2. Transmission electron micrographs of magnetite particles prepared at room temperature with $FeCl_2$ and NaOH (YN414) but no microwaves (a) and of magnetite particles prepared at different temperatures with $FeCl_2$ and NaOH using microwave-assisted conditions: (b) 80 °C and (c) 150 °C.

Table 1
Microwave-hydrothermal and room temperature synthesis conditions, phases formed, magnetic properties and particle sizes of synthetic products.

Sample number	Precursors	T (°C)	Duration	Phase	Saturation magnetization		Particle size[a] (Å)
					μ_B/f.u.	emu/g	
YN383	$FeCl_2 + NaOH$	150	15 min	Magnetite; trace Fe^0	3.69	89.0	>1000
YN384	$FeCl_2 + NaOH$	120	15 min	Magnetite	2.90	70.0	381(29)[b]
YN385	$FeCl_2 + NaOH$	100	15 min	Magnetite	2.87	69.2	300(20)
YN386	$FeCl_2 + NaOH$	80	15 min	Magnetite	2.94	70.9	241(18)
YN387	$FeCl_2 + NH_4OH$	80	15 min	Magnetite	2.46	59.3	234(21)
YN388	$FeCl_2 + Na_2CO_3$	80	15 min	Magnetite	ND	ND	ND
YN389	$FeCl_2 + Na_2CO_3$	RT		Magnetite	2.53	61.0	186(12)
YN398	$FeCl_2 + NH_4OH$	RT		Magnetite	2.38	57.4	154(9)

[a] Calculated using $d_{(3\ 1\ 1)}$ peak at 2.52–2.53 Å based on Scherrer's equation.
[b] Standard deviations are shown in the parentheses.ND, not determined; RT, room temperature and no microwaves.

2.2.3. Magnetic properties measurement

The magnetic properties were measured on a Superconducting Quantum Interference Design (SQUID) magnetometer (Quantum Design). The magnetic hystereses were measured at room temperature in a field of ±3 T.

3. Results and discussion

3.1. Crystallization of magnetite under different conditions

Poorly crystallized magnetite as determined by XRD (Fig. 1a and b) was obtained at room temperature with all the three alkaline sources, Na_2CO_3, NH_4OH and NaOH in the absence of microwaves. Increasing the concentration of NaOH from 0.032 M to 1 M also yielded poorly crystallized magnetite as determined by the breadth of XRD peaks (Figure, not shown). Transmission electron micrographs revealed that the magnetite particles prepared at room temperature with $FeCl_2$ and NaOH are about 40–50 nm (Fig. 2a) leading to broad X-ray peaks (Fig. 1a and b). Table 1 shows the results of magnetite syntheses from 80 to 150 °C with different alkaline sources such as NH_4OH, NaOH and Na_2CO_3 and using microwaves during synthesis. Crystallinity of magnetite increased with increasing temperature under microwave-assisted conditions as can be seen from XRD patterns which showed sharper and

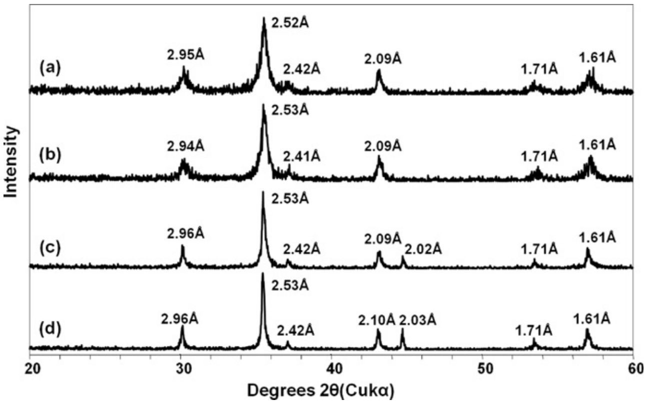

Fig. 3. X-ray diffraction patterns of magnetite synthesized using $FeCl_2$ + NaOH at 150 °C as a function of time under microwave-assisted conditions (a) 0 min (YN422); (b) 4 min (YN425); (c) 8 min (YN426); and (d) 16 min (YN427).

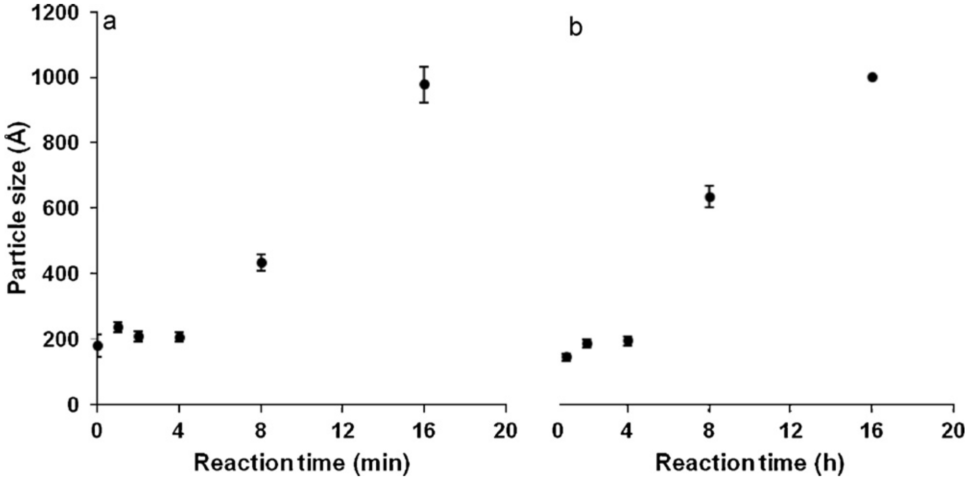

Fig. 4. Particle size of magnetite as determined by XRD based on Scherrer's equation as a function of synthesis time under microwave-hydrothermal conditions at 150 °C (a) and under conventional-hydrothermal conditions at 150 °C (b).

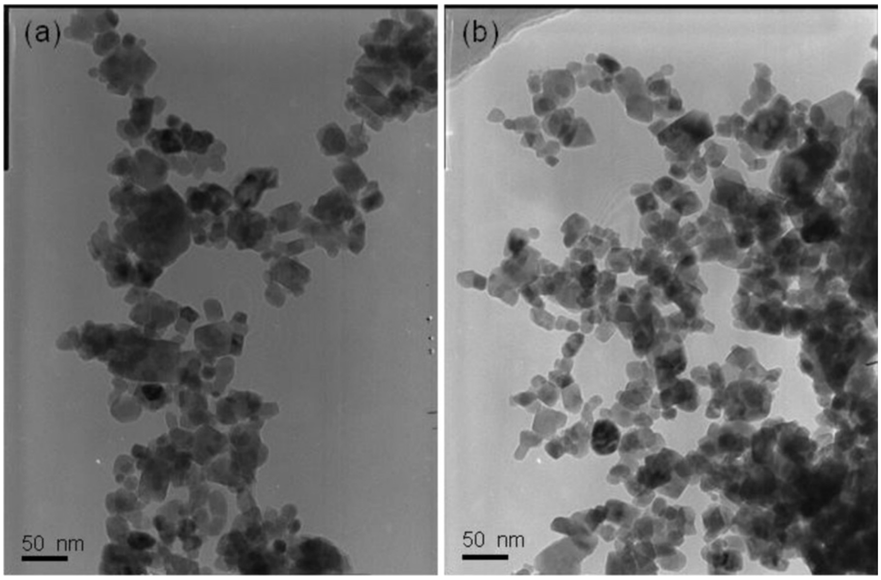

Fig. 5. Transmission electron micrograph of magnetite particles prepared at 150 °C for different durations with $FeCl_2$ and NaOH using microwave-assisted hydrothermal conditions: (a) 8 min (YN426) and (b) 16 min (YN427).

narrower peaks with increased temperature (Fig. 1c to f). Microwave-assisted conditions led to magnetite in all cases after treatment for 15 min (Table 1; Fig. 1). Transmission electron microscopy revealed that the particle size obtained at 150 °C is larger than the particle size obtained at 80 °C (Fig. 2b and c), as expected. The particle size and morphology are not uniform in the magnetites synthesized at temperatures of ≥80 °C (Fig. 2b–c) but appear to be more or less uniform at room temperature (Fig. 2a). The non-uniformity of magnetite crystals at higher temperatures could be attributed to a lack of equilibrium because of short treatment time. In addition, the magnetite particles appear to have crystallized well at temperatures of 80 °C and 150 °C but not at lower temperatures as indicated by faceted crystals at the highest temperature (Fig. 2c), as expected. The particles crystallized at temperatures of 80 °C and 150 °C showed some small aggregated crystals

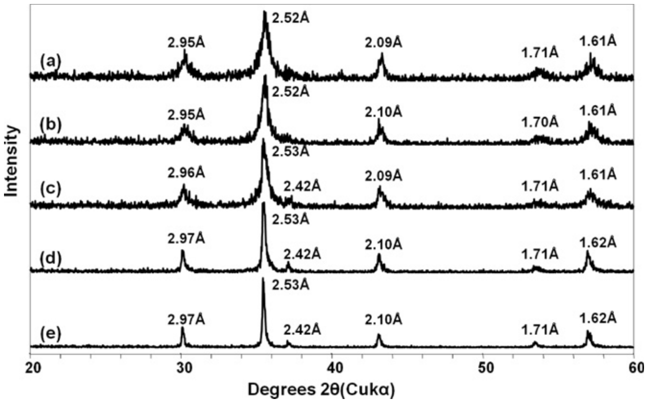

Fig. 6. X-ray diffraction patterns of magnetite synthesized using $FeCl_2$ + -NaOH at 150 °C as a function of time under conventional-hydrothermal conditions: (a)1 h, (b) 2 h, (c) 4 h, (d) 8 h and (e) 16 h.

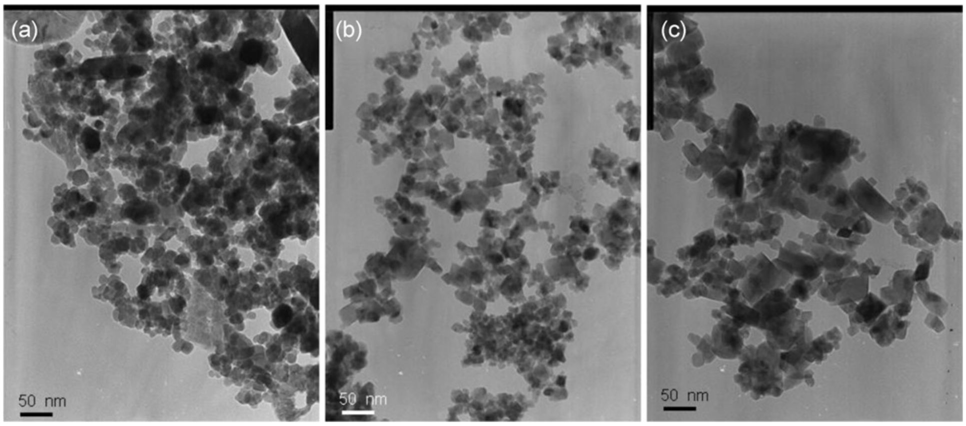

Fig. 7. Transmission electron micrographs of magnetite particles synthesized for different durations with $FeCl_2$ and NaOH using conventional-hydrothermal conditions: (a) 1 h, (b) 4 h and (c) 16 h.

(see arrows) along with faceted crystals (Fig. 2b and c). The presence of these small aggregated particles suggests that the process of 'Ostwald ripening' was not complete with the short treatment time of 15 min. Small aggregated masses could also be seen at 80 °C along with nanocrystals of magnetite (see arrow in Fig. 2b). Crystallinity as a function of time was investigated at 150 °C under microwave-assisted hydrothermal conditions and the results of XRD are presented in Fig. 3. Ramping up the temperature to 150 °C in 5 minutes and stopping the treatment immediately after reaching 150 °C led to magnetite with broad peaks (Fig. 3a) and further treatment for 4 min did not affect the breadth of the peak significantly (Fig. 3b). However, increasing the treatment time to 8 and 16 min led to higher crystallinity of magnetite as indicated by sharper and narrower X-ray diffraction peaks (Fig. 3c and d) and larger particle sizes as calculated from XRD data using Scherrer's equation (Fig. 4a). At longer treatment times, a part of the Fe^{2+} was reduced to Fe^0 metal as can be seen from peaks at 2.02 to 2.03 Å peaks in the XRD patterns (Fig. 3c and d) along with highly crystallized magnetite as indicated by sharp peaks. Transmission electron micrographs clearly showed well-faceted crystals with 8 to 16 min of treatment time at 150 °C (Fig. 5). The effect of treatment time on crystallinity of magnetite under microwave-hydrothermal conditions (Fig. 3) was compared to that under conventional hydrothermal conditions (Fig. 6). To get the same crystallinity as determined by the sharpness of XRD peaks, conventional hydrothermal conditions required 8–16 h (Fig. 6d and e) of treatment time while microwave–hydrothermal (M–H) conditions needed only 8 to 16 min (Fig. 3c and d). Particle sizes determined by Scherrer's equation using $d_{(311)}$ peak at 2.52–2.53 Å (Fig. 4b) and transmission electron micrographs of conventional-hydrothermally prepared magnetite (Fig. 7) also support this observation. For example, only 8–16 min were needed to get a particle size in the range of 435 to 977 nm by M–H process (Fig. 4a) while 8–16 h were needed to get the particle size in the range of 635 to >1000 nm by C–H process (Fig. 4b). In addition, metallic iron crystallized at 150 °C under M–H condition (Fig. 3; Table 1) but not under C–H condition (Fig. 6). These results clearly suggest that M–H process led to better crystallinity of magnetite as has been previously observed in many other syntheses of materials by us [28–30].

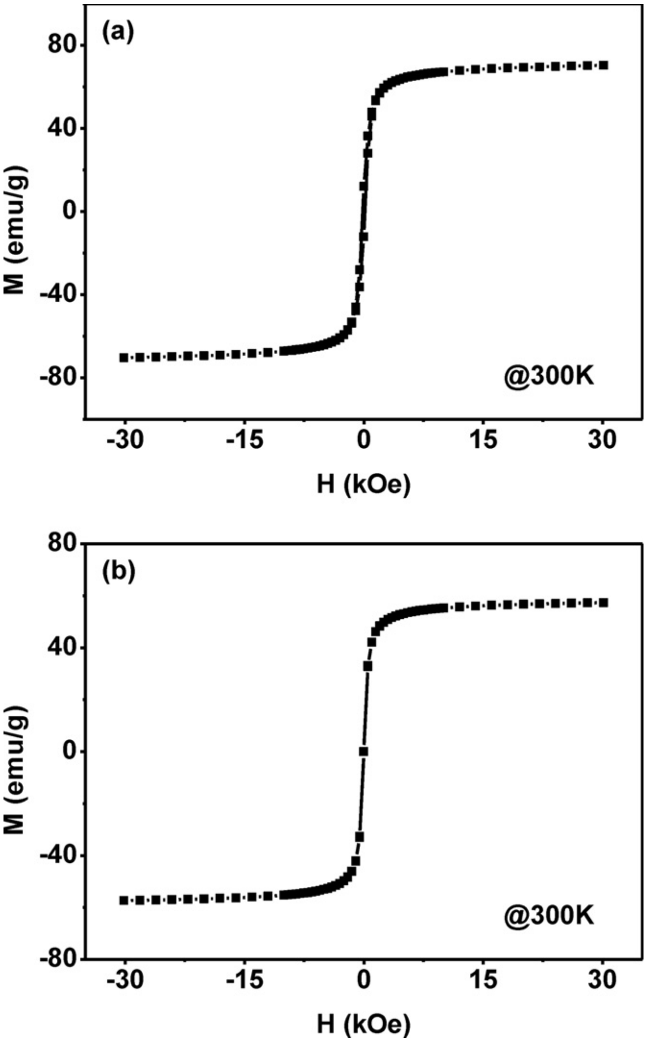

Fig. 8. Hysteresis loops of field dependence of magnetization at 300 K for a sample prepared at 120 °C, YN384 (a) and for another sample prepared at 25 °C, YN398 (b).

3.2. Magnetic properties of magnetite crystallized under different conditions

Saturation magnetization data collected by using a Superconducting Quantum Interference Design (SQUID) magnetometer are shown in Table 1 for various magnetites synthesized at different temperatures. The saturation magnetization of the sample prepared at 150 °C is the highest with added contribution from Fe^0 metal (Table 1) in this sample. The saturation magnetization values of the magnetite samples synthesized here are consistent with those reported previously [23,24] for nanophase magnetites. The magnetic hystereses measured at room temperature in a field of ±3 T for a few samples are shown in Fig. 8. These hysteresis loops of field dependence of magnetization at 300 K for a sample prepared at 120 °C, YN384 and for another sample prepared at 25 °C, YN398 (Table 1) are typical for nanophase magnetites [24]. In addition, the magnetic hystereses shown in Fig. 8 suggested superparamagnetic behavior, as expected in nanosized ferromagnets.

4. Conclusions

Magnetite nanoparticles of different particle sizes were synthesized from room temperature to 150 °C with and without microwaves. The use of microwaves significantly increased particle size of magnetites as determined by XRD and particle size calculations by Scherrer's equation. The saturation magnetization values of the magnetite samples synthesized here varied from 57.4 to 89.0 emu/g, which are typical for magnetites.

References

[1] S. Si, A. Kotal, T.K. Mandal, S. Giri, H. Nakamura, T. Kohara, Size-controlled synthesis of magnetite nanoparticles in the presence of polyelectrolytes, Chem. Mater. 16 (2004) 3489–3496.

[2] J.M. Perez, F.J. Simeone, Y. Saeki, L. Josephson, R. Weissleder, Viral-induced self-assembly of magnetic nanoparticles allows the detection of viral particles in biological media, J. Am. Chem. Soc. 125 (2003) 10192–10193.

[3] V.G. Roullin, J.R. Deverre, L. Lemaire, F. Hindre, M.C.V. Julienne, R. Vienet, J.P. Benoit, Anti-cancer drug diffusion within living rat brain tissue: an experimental study using [3H] (6)-5-fluorouracil loaded PLGA microspheres, Eur. J. Pharm. Biopharm. 53 (2002) 293–299.

[4] A.I. Anton, Measurements of turbulence suppression due to a transverse magnetic field applied on a ferrofluid motion, J. Magn. Magn. Mater. 85 (1990) 137–140.

[5] R.D. McMichael, R.D. Shull, L.J. Swartzendruber, L.H. Bennett, R.E. Walson, Magnetocaloric effect in superparamagnets, J. Magn. Magn. Mater. 111 (1992) 29–33.

[6] P. Oswald, O. Clement, C. Chambon, E. Schouman-Claeys, G. Frija, Liver positive enhancement after injection of superparamagnetic nanoparticles: respective role of circulating and uptaken particles, Magn. Reson. Imaging 15 (1997) 1025–1031.

[7] K. Yamaguchi, K. Matsumoto, T. Fujii, Magnetic anisotropy by ferromagnetic particles alignment in a magnetic field, J. Appl. Phys. 67 (1990) 4493–4495.

[8] V.T. Peikove, K.S. Jeon, A.M.J. Lane, Characterization of magnetic inks by measurements of frequency dependence of AC susceptibility, J. Magn. Magn. Mater. 193 (1999) 307–310.

[9] V. Sepelak, U. Steinike, D.-Chr. Uecker, R. Trettin, S. Wi(mann, K.D. Becker, High-temperature reactivity of mechanosynthesized zinc ferrite, Solid State Ionics 101 (1997) 1343–1349.

[10] F. Cheng, Z. Peng, C. Liao, Z. Xu, S. Gao, C. Yan, D. Wang, J. Wang, Chemical synthesis and magnetic study of nanocrystalline thin films of cobalt spinel ferrites, Solid State Commun. 107 (1998) 471–476.

[11] K.C. Patil, M.M.A. Sekar, Synthesis, structure and reactivity of mete1 hydrazine carboxylates: combustible precursors to fine particle oxide materials, Int. J. Self-Propag. High-Temp Synth. 3 (1994) 181–196.

[12] Q. Chen, A.J. Rondinone, B.C. Chakoumakos, Z.J. Zhang, Synthesis of superparamagnetic $MgFe_2O_4$ nanoparticles by coprecipitation, J. Magn. Magn. Mater. 194 (1999) 1–7.

[13] S. Komarneni, E. Fregeau, E. Breval, R. Roy, Hydrothermal preparation of ultrafine ferrites and their sintering, J. Am. Ceram. Soc. 71 (1988) C-26–C-28.

[14] S. Komarneni, M.C. D'Arrigo, C. Leonelli, G.C. Pellacani, H. Katsuki, Microwave-hydrothermal synthesis of nanophase ferrites, J. Am. Ceram. Soc. 81 (1998) 3041–3043.

[15] D.H. Chen, X.R. He, Synthesis of nickel ferrite nanoparticles by sol–gel method, Mater. Res. Bull. 36 (2001) 1369–1377.

[16] Z. Cvejic, S. Rakic, A. Kremenovic, B. Antic, C. Jovalekic, P. Colomban, Nanosize ferrites obtained by ball milling: crystal structure cation distribution, size-strain analysis and Raman investigations, Solid State Sci. 8 (2006) 908–915.

[17] I. Martínez-Mera, M.E. Espinosa-Pesqueira, R. Pérez-Hernández, J. Arenas-Alatorre, Synthesis of magnetite (Fe_3O_4) nanoparticles without surfactants at room temperature, Mater. Lett. 61 (2007) 4447–4451.

[18] Z.H. Zhou, J. Wang, X. Liua, H.S.O. Chan, Synthesis of Fe_3O_4 nanoparticles from emulsions, J. Mater. Chem. 11 (2001) 1704–1709.

[19] R.F. Chen, G.Q. Song, Y. Wei, Synthesis of variable-sized Fe_3O_4 nanocrystals by visible light irradiation at room temperature, J. Phys. Chem. C 114 (2010) 13409–13413.

[20] Y.S. Kang, S. Risbud, J.F. Rabolt, P. Stroeve, Synthesis and characterization of nanometer-size Fe_3O_4 and γ-Fe_2O_3 particles, Chem. Mater. 8 (1996) 2209–2211.

[21] Y.H. Zhu, Q.F. Wu, Synthesis of magnetite nanoparticles by precipitation with forced mixing, J. Nanopart. Res. 1 (1999) 393–396.

[22] W. Yu, T.L. Zhang, J.G. Zhang, X.J. Qiao, L. Yang, Y.H. Liu, The synthesis of octahedral nanoparticles of magnetite, Mater. Lett. 60 (2006) 2998–3001.

[23] Y.B. Khollam, S.R. Dhage, H.S. Potdar, S.B. Deshpande, P.P. Bakare, S.D. Kulkarni, S.K. Date, Microwave hydrothermal preparation of submicron-sized spherical magnetite (Fe_3O_4) powders, Mater. Lett. 56 (2002) 571–577.

[24] H.Y. Hu, H. Yang, P. Huang, D.X. Cui, Y.Q. Peng, J.C. Zhang, F.Y. Lu, J. Lian, D.L. Shi, Unique role of ionic liquid in microwave-assisted synthesis of monodisperse magnetite nanoparticles, Chem. Commun. 46 (2010) 3866–3868.

[25] T. Caillot, D. Aymes, D. Stuerga, N. Viart, G. Pourroy, Microwave flash synthesis of iron and magnetite particles by disproportionation of ferrous alcoholic solutions, J. Mater. Sci. 37 (2002) 5153–5158.

[26] W.W. Wang, Y.J. Zhul, M.L. Ruan, Microwave-assisted synthesis and magnetic property of magnetite and hematite nanoparticles, J. Nanopart. Res. 9 (2007) 419–426.

[27] R.Y. Hong, T.T. Pan, H.Z. Li, Microwave synthesis of magnetic Fe_3O_4 nanoparticles used as a precursor of nanocomposites and ferrofluids, J. Magn. Magn. Mater. 303 (2006) 60–68.

[28] S. Komarneni, R. Roy, Q.H. Li, Microwave-hydrothermal synthesis of ceramic powders, Mater. Res. Bull. 27 (1992) 1393–1405.

[29] S. Komarneni, Q.H. Li, R. Roy, Microwave-hydrothermal processing of layered anion exchangers, J. Mater. Res. 11 (1996) 1866–1869.

[30] S. Komarneni, Nanophase materials by hydrothermal microwave-hydrothermal and microwave solvothermal methods, Curr. Sci. 85 (2003) 1730–1734.