Available online at www.sciencedirect.com

Journal of Magnetism and Magnetic Materials 295 (2005) 251–256

Journal of magnetism and magnetic materials

www.elsevier.com/locate/jmmm

Spinel cobalt ferrite by complexometric synthesis

Pham D. Thang*, Guus Rijnders, Dave H.A. Blank

Inorganic Materials Science, Faculty of Science and Technology, MESA⁺ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

Received 17 December 2004; received in revised form 11 January 2005
Available online 25 February 2005

Abstract

Magnetic fine particles of cobalt ferrite ($CoFe_2O_4$) have been synthesized using complexometric method in which ethylene diamine tetra acetic acid $C_{10}H_{16}N_2O_8$ (EDTA) acts as a complexing agent. The crystallographic structure, microstructure and magnetic properties of the synthesized powder were characterized by using X-ray diffraction (XRD), particle size analysis and vibrating sample magnetometry (VSM). The material crystallized in cubic spinel structure with lattice parameter of about 8.38 Å. Depending on the calcining temperature, the particle size of the powders varies in the range of hundreds of nanometers to tens of micrometers. A desired relative density above 95% of the theoretical value is obtained for the bulk sample after sintering. The calcined powders and sintered sample exhibit saturation magnetizations around 80 Am^2/kg which is expected for inverse $CoFe_2O_4$. With increasing calcining temperature the coercivity of these samples decreases. This simple synthesis route leads to a reproducible and stoichiometric material.

PACS: 74.25.Ha; 74.62.Bf; 75.50.Gg; 81.05.Je; 81.20.Ka

Keywords: Cobalt ferrite; Complexometric method; Crystallographic structure; Microstructure; Magnetic properties

1. Introduction

Recently, spinel ferrites have been intensively studied because of fundamental understanding as well as their applicability in a variety of areas such as high-density information storage system [1], ferrofluid technology [2–4], magnetocaloric refrigeration [5], medical diagnostics [6,7], magnetic resonance imaging enhancement [8] and gas sensors [9]. Among spinel ferrites, cobalt ferrite $CoFe_2O_4$ has attracted considerable attention due to their large magnetocrystalline anisotropy, high coercivity, moderate saturation magnetization, large magnetostrictive coefficient, chemical stability and mechanical hardness [10–19]. $CoFe_2O_4$ has an inverse spinel structure where oxygen atoms

---

*Corresponding author. Tel.: + 31 53 489 5419; fax: + 31 53 489 4683.
E-mail address: t.d.pham@tnw.utwente.nl (P.D. Thang).

0304-8853/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jmmm.2005.01.011

make up an FCC lattice and with one half of Fe^{3+} ions occupied the tetrahedral A sites and the other half, together with Co^{2+} ions located at the octahedral B sites.

For preparing $CoFe_2O_4$ powders, most frequently, aqueous solution of Fe^{3+} (or Fe^{2+}) and Co^{2+} is employed, followed by either oxidative co-precipitation at room temperature [20] or hydrothermal co-precipitation at high temperature [21,22]. In these techniques, the particle size of the powder is controlled through adjustment of the stirring speed. Co-precipitation methods are simple but typically result in loss of stoichiometry during filtering steps due to inevitable difference of solubility among the precipitates. Recently, the synthesis routes have became more involved with organic compounds. Oil-in-water [23] or water-in-oil micelle [24] and block copolymer as a template [25] have been used to prepare the nano-particles of Co-ferrite. Beside the advantage of producing nano-powders, those techniques have the disadvantage of low yield and complex synthesis route.

In this work we present a simple and reproducible method to synthesize $CoFe_2O_4$ powder by using complexometric method, in which an organic acid (ethylene diamine tetra acetic acid (EDTA)) is used to form soluble complexes with metal salts in aqueous solution. The clear solution is dehydrated to yield an amorphous solid precursor, which forms the desired compound after firing at elevated temperatures. This method provides homogeneous mixing on the atomic scale and good stoichiometric control since no filtering step is required. The microstructure and magnetic properties of the obtained powders and bulk sample will be discussed.

2. Experimental

2.1. Synthesis process

The solutions of 129.40 ml of 0.966 M $Co(NO_3)_2$ (99%, Merck) and 289.35 ml of 0.864 M $Fe(NO_3)_3$ (99.5%, Merck) were used as starting materials. They were firstly mixed before adding 109.6 g EDTA (99.4%, Merck). During mixing, the pH of the solution was kept between 8.5 and 9 by adding ammonium hydroxide $NH_4OH \cdot H_2O$ 25% to prevent any kind of precipitation. The temperature of the solution was maintained at around 250 °C under a continuous stirring speed of 300 rpm for 2 h. The solution mixture was then thermolysed at 230 °C for 18 h to produce the desired precursor. A very voluminous and dry powder was obtained, which was ground by hand before calcination at 700–1050 °C for 10 h in a Pt boat. The heating and cooling rates used in calcining were 2 °C/min. The calcined powder was milled in acetone by using ZrO_2 balls for 5 h.

Green compacts of the powder were prepared by uniaxially pressing at a pressure of 16 MPa for 5 min, followed by isostatically pressing at 4000 MPa for 5 min. These compacts were finally

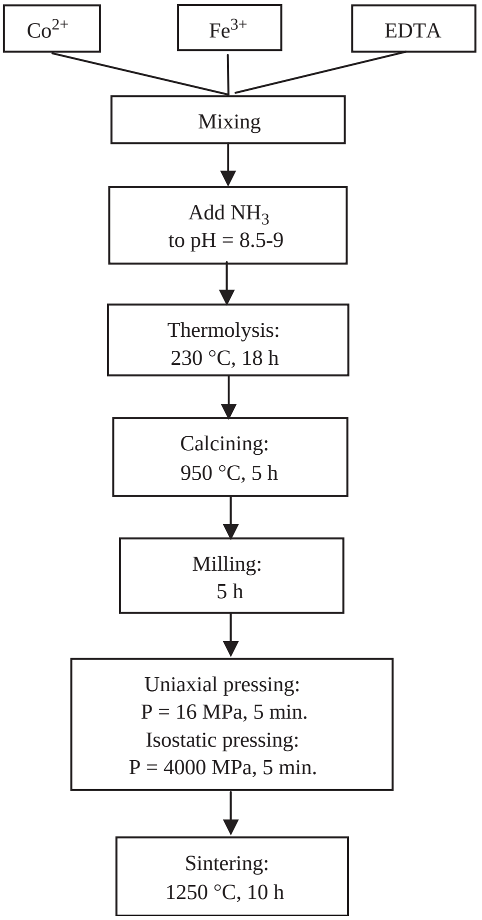

Fig. 1. The synthesis route.

sintered in air at 1250 °C for 10 h using the heating and cooling rates of 1 °C/min. The flow chart of the synthesis route is represented in Fig. 1.

2.2. Characterization

The crystallographic structure of both calcined powder and sintered sample were investigated by a Philips PNA-analytical diffractometer using CuK_α wavelength. The particle size of calcined powder was measured by a micro-meter Mastersizer 2000 (Malvern instrument) based on the light scattering technique. The sintering behaviour of the green compact was analysed using a home-made dilatometer. Magnetic hysteresis measurements were carried out on a VSM Oxford at room temperature in the magnetic field range from +2400 kA/m (+3 T) to −2400 kA/m (−3 T).

3. Results and discussion

In Fig. 2 we show the X-ray diffraction (XRD) patterns of the powders prepared at various calcining temperatures. For the temperature range between 850 and 1050 °C, the obtained patterns correspond to the standard structure of $CoFe_2O_4$, which has a cubic spinel type (Fd3m). At lower calcining temperature, for example, 700 °C, small reflections of a second phase appeared which possibly belongs to α-Fe_2O_3 structure (marked by star symbols in this figure). The XRD diagrams were analysed by means of the Rietveld refinement procedure [26] from which the crystallographic lattice parameter of the samples was determined and listed in Table 1.

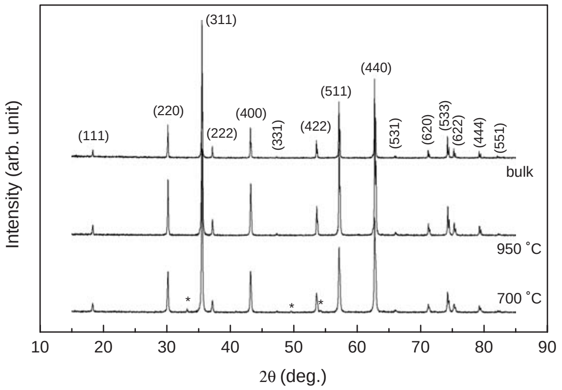

Fig. 2. XRD patterns of powders calcined at 700 °C (bottom), 950 °C (middle) and sintered bulk sample (top).

We analysed particles size of $CoFe_2O_4$ powders after calcining at different temperatures. The fine powder was firstly dispersed in water and stabilized by 15 wt% Darvan C (ammonium polymethacrylic acid, R.T Vanderbilt Co., Norwalk, USA) to prevent their agglomeration. Then few drops of this sol were mixed into water inside the analysis box. In Fig. 3 the distributions of particle size of calcined powders are represented. The results indicate that the particle sizes can be varied in the range of 0.6–10.6 µm depending on the calcining temperature (see Table 1). With increasing temperature, the grain growth leads to the increase of average particle size, from around 2 µm for sample calcined at 850 °C up to above 5 µm for

Table 1
Crystallographic lattice parameter and particle size of calcined $CoFe_2O_4$ powders

Calcined sample °C	a (Å)	Particle size range (µm)	Average particle size (µm)	Volume of particles at average size (%)
850	8.372±0.004	0.6–7.0	2.1	11.7
950	8.376±0.003	1.0–10.1	3.7	12.4
1050	8.374±0.005	1.6–10.6	5.2	13.1

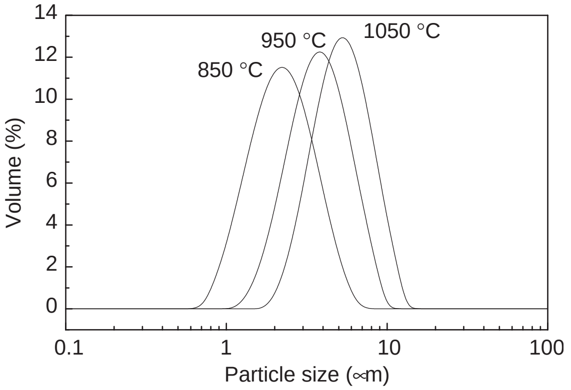

Fig. 3. Particle size distribution of $CoFe_2O_4$ powders calcined at different temperatures with calcining time of 5 h.

sample calcined at 1050 °C. Meanwhile, the relative volume of particles with the average sizes also increases as presented in Table 1.

In order to optimize the sintering process, we employed dilatometry to measure the thermal expansion behaviour of a green compact sample. The measurement was carried out in air with heating and cooling rates of 1 °C/min. The shrinkage behaviour of a sample during heating and subsequent isothermal at 1250 °C is demonstrated in Fig. 4. From the measurement one can calculate the change in relative density, ρ_S, of the sample as a function of annealing temperature and annealing time using the following formula:

$$\rho_S(\%) = \frac{\rho_g}{1-(dL/L_0)^3}100\%, \tag{1}$$

where ρ_g is the relative density of the green compact determined using the Archimedes method by immersion in mercury. In the calculation, the theoretical densities of $CoFe_2O_4$ and Hg were taken as 5.29 and 13.53 g/cm^3, respectively. The terms L_0 and dL represent the length at room temperature and the change in length of the sample during sintering, respectively.

From Fig. 4 one can see that the solid-state densification of $CoFe_2O_4$ initiated at around 1000 °C. The sintering rate is slow and the material still continues to densify during the isothermal heat treatment at 1250 °C. After 10 h annealing at this temperature, the relative density is 97% of the theoretical density. This calculated result is in agreement with the value of 96% measured by the Archimedes method.

The relative density of bulk samples as a function of the sintering temperature is shown in Fig. 5. The high values above 95% of the relative density were achieved only after sintering at 1250 °C for 10 h. This sintering condition is used to make bulk samples as in the following. The XRD pattern of a typical bulk sample obtained after being calcined at 950 °C and then sintered at 1250 °C for 10 h is similar to that of the calcined powder (see Fig. 2). The lattice parameter of this sample, 8.381 ± 0.002 Å, is larger than those of the calcined powders.

The magnetic properties of the calcined powders and sintered sample were characterized by

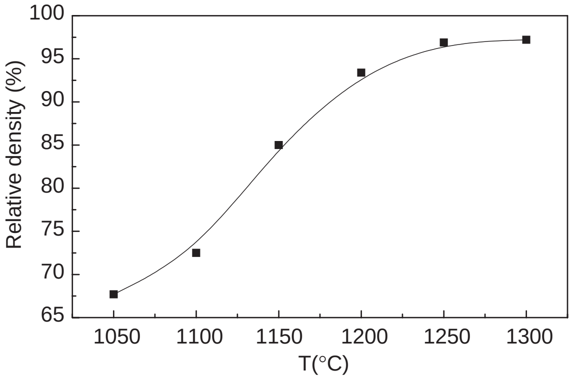

Fig. 5. Relative density of $CoFe_2O_4$ as a function of sintering temperature with sintering time of 10 h.

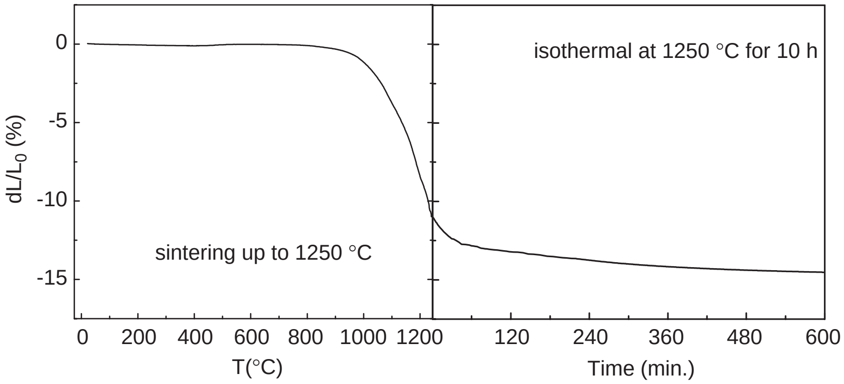

Fig. 4. Shrinkage of a green compact (calcined at 950 °C) during sintering at constant heating rate of 1 °C/min (a) and isothermal conditions at 1250 °C for 10 h (b).

measuring the magnetic hysteresis loop at room temperature. The powdered samples were immobilized to prevent torque due to increasing magnetic field. The obtained results are presented in Fig. 6. From these measurements the magnetic moment and the coercivity are derived and listed in Table 2.

Some important observations can be made from these experiments:

(a) The saturation magnetization gets a maximum of 81.2 Am^2/kg after calcining at 850 °C. For the samples calcined at other temperatures, the saturation magnetizations slightly fluctuate around 80 Am^2/kg.
(b) The highest coercivity of about 120 kA/m (0.15 T) is obtained for the sample calcined at 950 °C. Samples calcined at 1050 °C and sintered at 1250 °C exhibit lower coercivities of about 75 kA/m (0.09 T) and 25 kA/m (0.03 T), respectively.

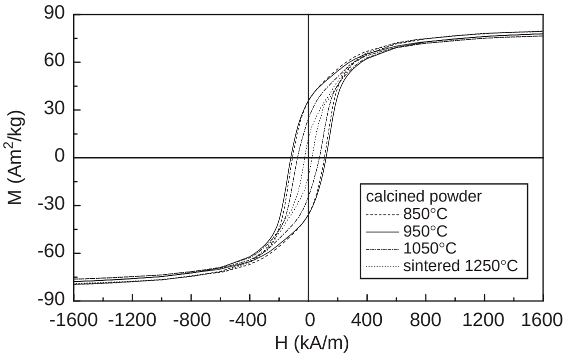

Fig. 6. Room temperature magnetic properties of powders after calcining at different temperatures.

Table 2
Magnetic properties of the powders calcined at different temperatures and sintered sample. M_s is the saturation magnetisation and H_c is the coercivity

Sample	M_s (Am^2/kg)	H_c (kA/m)
850 °C	81.2	109.4
950 °C	79.3	120.5
1050 °C	77.7	75.2
Sintered	80.4	25.0

The saturation magnetization observed for the calcined and sintered samples are well in agreement with the reported value of 80 Am^2/kg for the pure inverse $CoFe_2O_4$ phase [27,28]. The variation of the saturation magnetization with different heat treatments is possibly due to the rearrangement of the cation distribution, i.e. the degree of inversion, in $CoFe_2O_4$ [29,30] in which there is the exchange of Co^{2+} and Fe^{3+} ions from octahedral to tetrahedral sites and vice versa. The decrease of the coercivity with increasing calcining temperature is attributed to the grain growth as can be seen in Table 1.

4. Conclusion

The $CoFe_2O_4$ powder and bulk sample have been prepared by complexometric method using EDTA as a complexing agent. The powders calcined at above 850 °C show desired crystallographic structure and good magnetic properties. The bulk sample obtained by sintering at 1250 °C has high relative density of above 95% compared to the theoretical one. This good quality sample can be used for further work such as a target for fabrication of spinel ferrite thin films.

Acknowledgements

The authors would like to thank H. Kruidhof for the useful discussions, K.W. Wiratha and S. Ran for their help during the sample preparation and dilatometry measurement. This work is supported by the VICI grant from the Netherlands Organisation for Scientific Research (NWO), the Dutch Technology Foundation (STW) and the Foundation for Fundamental Research on Matter (FOM).

References

[1] R.F. Zolio, US Patent, 4,474,866, 1984.
[2] J. Popplewell, L. Sakhnini, J. Magn. Magn. Mater. 149 (1995) 72.
[3] K. Raj, B. Moskowitz, R. Casciari, J. Magn. Magn. Mater. 149 (1995) 174.

[4] I. Anton, I. de Sabata, L. Vékás, J. Magn. Magn. Mater. 85 (1990) 219.
[5] L. Gunther, Phys. World 3 (1990) 28.
[6] R.S. Molday, D. Mackenzie, J. Immunol. Methods 52 (1982) 353.
[7] J.W.M. Bulte, et al., J. Magn. Reson. Imaging 4 (1994) 497.
[8] C.W. Jung, P. Jacobs, Magn. Reson. Imaging 13 (1995) 661.
[9] C.V. Gopal Reddy, S.V. Manorama, V.J. Rao, J. Mater. Sci. Lett. 19 (2000) 775.
[10] K.C. Patil, S. Sundar Manoharan, D. Gajapathy, in: N.P. Cheremisino (Ed.), Handbook of Ceramics and Composites, Synthesis and Properties, vol. 1, Marcel Dekker Inc., New York, 1990, p. 469.
[11] N.N. Evtihiev, N.A. Economov, A.R. Krebs, N.A. Zamjatina, IEEE Trans. Magn. 12 (1976) 773.
[12] J. Martens, A. Voermans, IEEE Trans. Magn. 20 (1984) 1007.
[13] Y. Tamara, M. Kojima, N. Hasegawa, M. Tsuji, K. Ehrensberger, A. Steinfeld, J. Phys. IV France 7 (1997) C1–673.
[14] M. Abe, T. Itoh, Y. Tamaura, Thin Solid Films 216 (1992) 155.
[15] R.K. Ahrenkiel, T.J. Coburn, IEEE Trans. Magn. 11 (1975) 1103.
[16] J.W.D. Martens, W.L. Peeters, H.M. Van Noort, M. Errnan, J. Phys. Chem. Solids 46 (1985) 411.
[17] K. Suzuki, T. Namikawa, T. Yamazaki, Jpn. J. Appl. Phys. 27 (1988) 361.
[18] S.N. Okuno, S. Hashimoto, K. Inomata, J. Appl. Phys. 71 (1992) 5926.
[19] R. Valenzuela, Magnetic Ceramics, Cambridge University Press, Cambridge, 1994.
[20] M. Rajendran, R.C. Pullar, A.K. Bhattacharya, D. Das, S.N. Chintalapudi, C.K. Majumdar, J. Magn. Magn. Mater. 232 (2001) 71.
[21] T. Pannaparayil, S. Komarneni, IEEE Trans. Magn. 25 (1989) 4233.
[22] P.C. Morais, V.K. Garg, A.C. Oliveira, L.P. Silva, R.B. Azevedo, A.M.L. Silva, E.C.D. Lima, J. Magn. Magn. Mater. 225 (2001) 37.
[23] N. Moumen, P. Veillet, M.P. Pileni, J. Magn. Magn. Mater. 149 (1995) 67.
[24] Y. Ahn, E.J. Choi, S. Kim, H.N. Ok, Mater. Lett. 50 (2001) 47.
[25] S.R. Ahmed, P. Kofinas, Mater. Res. Soc. Symp. Proc. 661 (2001) KK 10.10.1.
[26] H.M. Rietveld, J. Appl. Crystallogr. 2 (1969) 65.
[27] J. Smith, H.P.J. Wijn, Ferrites, Philips Technical Library, Eindhoven, The Netherlands, 1959.
[28] M.M. Schieber, in: E.P. Wohlfarth (Ed.), Selected Topics in Solid State Physics, vol. VIII, North-Holland, Amsterdam, 1967.
[29] G.D. Rieck, J.J.M. Thijssen, Acta Crystallogr. B 24 (1968) 982.
[30] G.A. Sawatzky, F. van der Woude, A.H. Morrish, J. Appl. Phys. 39 (1968) 1204.