Journal of Alloys and Compounds 506 (2010) 201–204

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Synthesis and characterization of nano-sized cobalt ferrite prepared via polyol method using conventional and microwave heating techniques

Amal M. Ibrahim[a,*], M.M. Abd El-Latif[b], Morsi M. Mahmoud[b]

[a] Surface Chemistry and Catalysis Laboratory, Physical Chemistry Department, National Research Center, Al Buhouth St., Cairo, Egypt
[b] Fabrication Technology Department, Advanced Technology and New Materials Research Institute, Mubarak City for Scientific Research and Technology Applications, Alexandria, Egypt

ARTICLE INFO

Article history:
Received 13 February 2010
Received in revised form 23 June 2010
Accepted 30 June 2010
Available online 7 July 2010

Keywords:
Nano-sized cobalt ferrite
Polyol method
Microwave technique
Magnetic properties

ABSTRACT

Nano-sized single-phase cobalt ferrite samples were prepared via polyol method using ethylene glycol as a high boiling point solvent as well as a reducing agent. These samples were prepared by two different heating techniques; conventional heating technique and microwave assisting technique using a 2.45 GHz multimode microwave synthesis unit. The crystallite size of the obtained samples was found to be in the range from 10 nm to 12 nm. The obtained samples were characterized using transmission electron microscope (TEM) and X-ray diffraction (XRD). Quantum design SQUID magnetometer was used to study the magnetic measurement.

1. Introduction

Spinel ferrite nano-particles have shown a growing interest in recent years due to their specific magnetic and electrical properties. They have potential applications in high-density magnetic recording devices specially those with high coercivity [1,2], electronic devices [3] and medicine [4]. One of the most recent applications studied is to be used in the complete decomposition of CO_2 [5]. This decomposition has significantly improved by developing ultra fine ferrite particles with high surface area as a catalyst [6]. Among spinel ferrites, $CoFe_2O_4$ has cubic spinel structure. $CoFe_2O_4$ has been extensively studied because of its interesting magnetic properties. It has remarkable chemical stability and mechanical hardness as well as its high coercivity (5400 Oe) and moderate saturation magnetization (≈80 emu/g) [7]. The physical and chemical properties of spinel nano-particles are greatly affected by the synthesis route. Therefore a large number of research have been reported in the literature concerning with the preparation methods for such materials such as mechanochemical [8], post-laser deposition [9], combustion [10], hydrothermal [11], co-precipitation [12], sol–gel [13], and many other methods [14]. Nanocrystalline cobalt ferrite dispersed in silica has been prepared by mechanical alloying and subsequent heat-treatment [15]. Also magnetic nanocomposites of Co-ferrite nano-particles dispersed in silica matrix ($CoFe_2O_4/SiO_2$) have been prepared by the sol–gel technique using tetraethylorthosilicate (TEOS) as precursor of silica, and metallic nitrates as precursors of ferrite [16]. Preparation of cobalt ferrites at ambient temperature by a controlled aerial oxidation of starting ferrous and cobalt ions solution was achieved [17]. Polyol method is one of the preparation methods that have been used for many oxides and nanocomposite materials [18], in this method a high boiling point solvent is used as a solvent as well as a reducing agent of the metallic ions under reflux conditions. This method produces soft and hard magnetic nanoparticles [19,20]. Microwave processing of materials is a technology that can provide a new, powerful, and significantly different tool to process materials or to improve the performance characteristics of existing materials. In many cases, materials processing using microwave technology have numerous advantages when compared with traditional materials processing techniques [21]. These anticipated benefits include more precise and controlled volumetric heating, faster ramp-up to temperature, lower energy consumption, and enhanced quality and properties of the processed materials. Microwave synthesis technique was reported that it enhances the rate of chemical reactions and also gives better yields in some cases [22]. Some researches have studied the preparation of monometallic nano-particles coated with polyvinylprollidine (PVP) using domestic microwave oven [23]. Furthermore microwave has been used to prepare iron oxide nano-particles [24]. On the other hand microwave hydrothermal method has been used to synthesize cobalt nanopowder [25]. In this study, preparation of the $CoFe_2O_4$ particles will be investigated using both the conven-

* Corresponding author. Tel.: +202 33371718; fax: +202 33370931.
E-mail address: amozarei@yahoo.com (A.M. Ibrahim).

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doi:10.1016/j.jallcom.2010.06.177

tional polyol heating method and also the combination between the polyol method and microwave heating. The products from both methods have been characterized using TEM to compare the homogeneity and the particle size distribution of produced ferrite. XRD has been used to evaluate the crystalline structure and purity of the prepared phases. Finally, the magnetic properties of the prepared samples have been studied.

2. Experimental

2.1. Materials and methods

Chemicals used in this study were of analytical grade. Cobalt nitrate ($Co(NO_3)_2{\cdot}6H_2O$, 98%) was supplied from Belami Fine Chemicals, while ferric nitrate ($Fe(NO_3)_3{\cdot}9H_2O$, 98%), was supplied from Hinedia Chemicals and ethylene glycol ($C_2H_4(OH)_2$ was supplied from Universal Fine Chemicals Pvt. Ltd.

Preparation of the cobalt ferrite particles achieved by using polyol method, 2.9 g of cobalt nitrate ($Co(NO_3)_2{\cdot}6H_2O$) and 8.08 g of ferric nitrate ($Fe(NO_3)_3{\cdot}9H_2O$) were added in ethylene glycol in a solid to liquid ratio 1:10. The mixture was mixed and refluxed for 2 h. After completion of the reaction the produced powder was filtered, washed with ethanol and dried at 200 °C for 6 h. The produced solid was then calcined at 600 °C and 800 °C for 3 h. In case of preparation of cobalt ferrite using the microwave technique the precursor's mixture in ethylene glycol, mentioned before, was placed in a closed Teflon tube prior to the exposure to the microwave energy in a 2.45 GHz multimode cavity at 900 W for 2 min. The reaction in the microwave cavity was designed due to the fact that ethylene glycol has a high dielectric loss value which will be heated very fast in the microwave heating system. After completion of the reaction, the solid produced was filtered, washed with ethanol and dried. The products from both convenient polyol method and microwave technique were characterized by using X-ray diffraction analysis (XRD), transmission electron microscope (TEM) and quantum design SQUID magnetometer.

2.2. Techniques

X-ray diffraction analysis was carried out using X-ray diffractometer (Schimadzu-7000, USA) to evaluate the phase composition, XRD spectra were obtained with a 30 kW rotating anode diffractometer fitted with a copper target. XRD spectra were obtained between 20° and 80° (2θ) in continuous scan with 4°/min using the standard θ–2θ geometry.

The morphology of the synthesized powders was studied by Jeol JEM transmission electron microscope (TEM) with Max. Mag. 600k× and resolution 0.2 nm. The samples were prepared by sonication for 30 min.

A quantum design SQUID magnetometer was used to obtain hysteresis loops of products at 25 °C and in fields up to 15 kOe.

3. Results and discussion

3.1. X-ray analysis and microstructure

X-ray diffraction pattern of $CoFe_2O_4$ samples prepared using both conventional and microwave methods is shown in Fig. 1. The crystallite size was calculated from peak at $2\theta = 35.5°$ with miller indices (3 1 1) according to shcerrer Eq. (1):

$$L = \frac{0.89\lambda}{\beta \cos\theta} \quad (1)$$

where β is the FWHM of diffraction peak, λ is the wavelength of X-ray employed to do this measurement (0.154 nm), L is the crystallite size, and θ is the peak position of Bragg peak.

As shown from the figure, only the single spinel phase structure of $CoFe_2O_4$ was obtained (JCPDS No. 22-1086). The pattern in Fig. 1(a) represents the cobalt ferrite synthesized by microwave heating system. It shows a typical pattern of $CoFe_2O_4$ with two significant peaks centred at $2\theta = 35.45°$ and 57.28° [26]. The broadening of the peaks is indicating small crystallite size, where $CoFe_2O_4$ particles produced are amorphous with low crystallite size 10 nm. Fig. 1(b) represents the conventionally calcined ferrite sample at 600 °C for 3 h. It shows the significant pattern of $CoFe_2O_4$ with peaks centred at $2\theta = 35.54°$, 43.1°, 57.3° and 62.7° [27]. The crystallite size of the produced particles is 11 nm. Finally Fig. 1(c) represents the calcined product at 800 °C for 3 h. It shows the same pattern of the sample calcined at 600 °C but with increased crystallinity.

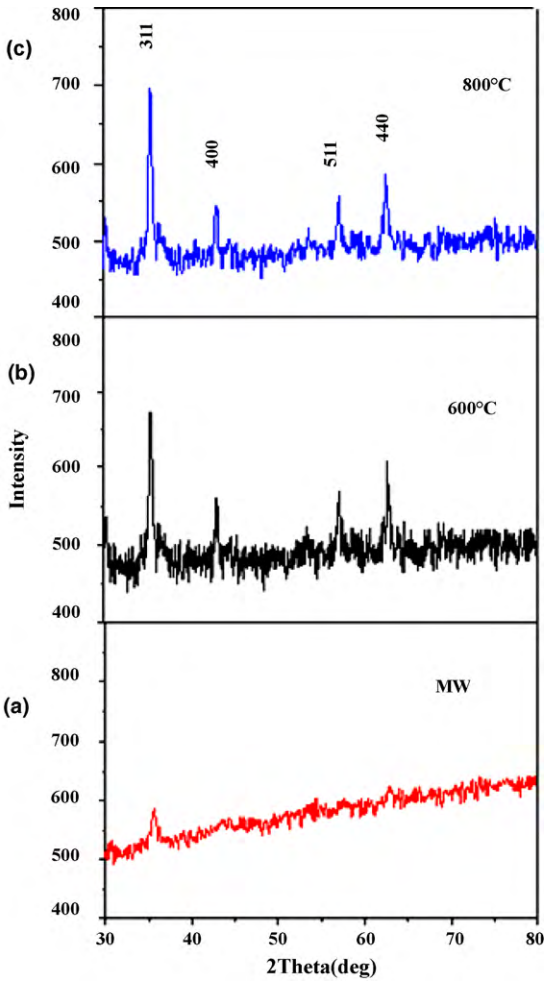

Fig. 1. X-ray diffraction pattern of $CoFe_2O_4$.

From Fig. 1, it is clear that the XRD patterns of the prepared samples matches and agrees with the fact that both the crystallinity and the crystallite size increase with temperature as well as the dwell time. The crystallite size of the sample calcined at 800 °C is 12 nm.

3.2. Transmission electron microscope studies

Fig. 2 shows the TEM micrograph of samples prepared by both the microwave and the conventional polyol techniques. These TEM images show small agglomerates of cobalt ferrite nano-particles. In case of microwave prepared sample (Fig. 2(a)) the average particle size is 19 nm. On the other hand the average particle size of the samples calcined at 600 °C and 800 °C are 20 nm and 23 nm, Fig. 2(b) and (c), respectively. The homogeneity of the sample treated at 600 °C is appeared to be the highest among all the prepared samples. This could be devoted to the fact that the densification increase as the calcination temperature increases. Also as the calcination temperature increases the density of the material increases due to the sintering [28], in addition, the heat gradient in case of using microwave heating system may be affecting the homogeneity of the prepared samples.

3.3. Magnetic properties

Magnetic properties of the prepared samples were investigated at room temperature with a peak field 5 kOe. The hysteresis loops for samples prepared using microwave technique as well as con-

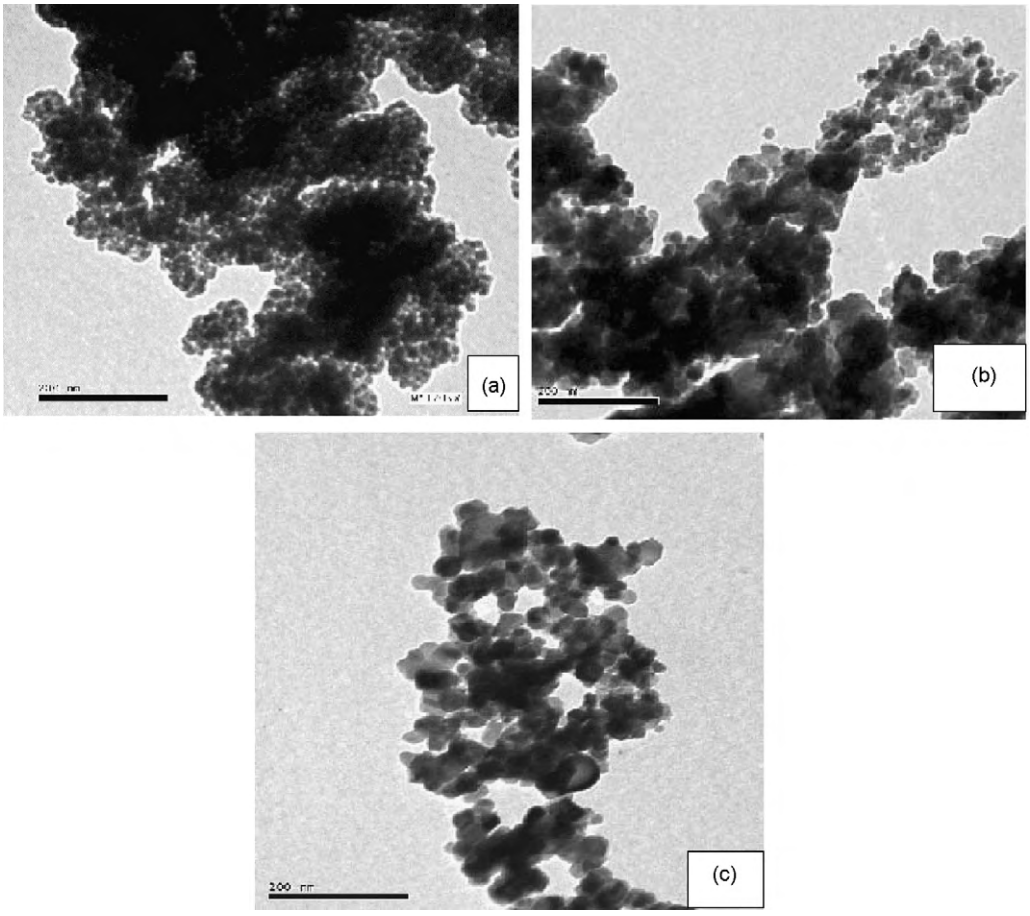

Fig. 2. Transmission electron microscope image of $CoFe_2O_4$. (a) Sample by microwave. (b and c) Samples at 600 °C and 800 °C.

ventional polyol method at different calcination temperatures are shown in Fig. 3 and summarized in Table 1.

The saturation magnetization Bs values are 27.76 emu/g and 51.46 emu/g for samples prepared by the conventional method at different calcination temperatures (600 °C and 800 °C). These values are in accordance with previous studies. The magnetic properties of the nano-sized materials depend on the preparation method as well as the crystallite size [29,30]. It was found in previous studies that the coercivity (Hc) increases as the particle size decreases [31] but in this case the crystallite size of the prepared samples is much smaller than the single domain size of cobalt ferrite which is reported to be 70 nm. In this study it is observed that the coercivity increases as the crystallite size increases. The magnitudes of the coercivity of the prepared samples in all cases are much smaller than that reported for cobalt ferrite. As it is known that as the Hc increases the material becomes closer to be hard or permanent magnetic material and as Hc decreases the material will be soft magnetic material. The saturation magnetization (Bs) decreased as the particle size decreases. Bs values for the samples prepared by convenient heating technique are less than that reported for the bulk $CoFe_2O_4$ and this is devoted to the particle size which is less than the critical size which is estimated to be 70 nm [32], meanwhile the saturation magnetization of the sample prepared using microwave heating technique is 94.8 emu/g. This value is close to the reported for $CoFe_2O_4$ (≈90 emu/g) [20,33]. This behaviour could be attributed to the presence of undetectable very small clusters of metallic Co(0) and/or Fe(0) [22]. This explanation agrees with the logic probability of the reduction of few metallic ions by the polyol solvent during the reaction.

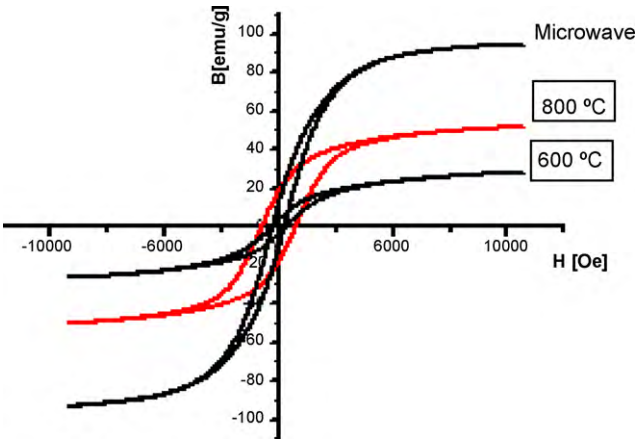

Fig. 3. Hysteresis loops of $CoFe_2O_4$ prepared at different conditions measured at 25 °C.

Table 1
Magnetic properties with particle size of the ferrite samples.

	MW	600 °C	800 °C
Br/Bs	0.127	0.148	0.36
Bs (emu/g)	94.8	27.76	51.46
Hc (Oe)	282	251.8	763.1
Average particle size (nm)	19	20	23

4. Conclusions

Cobalt ferrite nano-particles were successfully prepared by polyol method using both conventional and microwave heating techniques. Conventionally prepared samples that were calcined at 600 °C and 800 °C developed a nano-particle in the range from 11 nm and 12 nm. On the other hand, microwave heating technique in combination with polyol method produced cobalt ferrite nano-particles in the range of 10 nm. The XRD spectra showed that single-phase ferrite was obtained. For all produced samples the coercivity showed unexpected values much lower than the reported values for both bulk and powder cobalt ferrite. The saturation magnetization value of the microwave produced sample was larger than that of the samples produced by convenient heating technique. The sample obtained by using microwave heating technique exhibits significant characteristics with the smallest particle size, the highest saturation magnetization value and also low coercivity.

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