Journal of Alloys and Compounds 716 (2017) 171–183

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

The effect of calcination temperature on the structural and magnetic properties of co-precipitated $CoFe_2O_4$ nanoparticles

T. Prabhakaran [a, *], R.V. Mangalaraja [a, **], Juliano C. Denardin [b], J.A. Jiménez [c]

[a] Advanced Ceramics and Nanotechnology Laboratory, Department of Materials Engineering, Faculty of Engineering, University of Concepcion, Concepcion, 4070409, Chile
[b] Department of Physics, University of Santiago and CEDENNA, Santiago, Chile
[c] Department of Physical Metallurgy, CENIM-CSIC, Madrid, Spain

ARTICLE INFO

Article history:
Received 23 November 2016
Received in revised form
27 April 2017
Accepted 5 May 2017
Available online 6 May 2017

Keywords:
Spinel cobalt ferrites
Co-precipitation
Calcination temperature
Magnetic properties

ABSTRACT

Cobalt ferrite ($CoFe_2O_4$) nanoparticles were co-precipitated from metal nitrates at the reaction temperatures of 40 and 85 °C for 1 h and were further calcinated at 500 and 800 °C for 2 h. The effect of calcination temperature on the structural, morphological, compositional and magnetic properties was investigated. Both, the reaction and calcination temperatures were significantly influenced the crystallite size and magnetic properties of cobalt ferrite nanoparticles and the crystallite size was increased with the calcination temperature. The synthesized nanoferrites were roughly in spherical morphology with the stoichiometric ratio of 1:2 Co:Fe. Co-precipitated and calcinated cobalt ferrites showed the ferromagnetism at room temperature and 5 K (−268 °C) and the saturation magnetization was increased with the calcination temperature. At low temperature, $CoFe_2O_4$ nanoparticles calcinated at 800 °C showed the saturation magnetization of 84.36 and 92.70 emu/g for the reaction temperatures of 40 and 85 °C, respectively and the values were in accordance with the magnetization of bulk cobalt ferrites.

1. Introduction

Spinel cobalt ferrite ($CoFe_2O_4$) nanoparticles are important and potential candidate for many possible applications. These nanoferrites are used in various fields, from the small scale toys manufacturing companies to the large scale such as, ferrofluids, sensors, catalysis, biomedical, refrigerants and high density recording media fabrication industries [1–4]. Cobalt ferrite nanoparticles exhibit the significant room temperature saturation magnetization and moderate coercivity values when compared to the other spinel ferrites. In addition, it has large magnetocrystalline anisotropy constant. Spinel ferrites have a general formula $(Co_\delta Fe_{1-\delta})[Co_{1-\delta}Fe_{1+\delta}]O_4$, where parentheses and square bracket represent (A) tetrahedral and [B] octahedral sites, respectively [5]. The notation δ denotes the degree of inversion that defines the fraction of divalent Co^{2+} ions and trivalent Fe^{3+} ions in (A) and [B] sites and it will vary based on the experimental method. In inverse spinel cobalt ferrites, the available Fe^{3+} ions are equally distributed between (A) and [B] sites, where the entire Co^{2+} ions occupy [B] site. Due to the antiparallel alignment, the magnetic moments of Fe^{3+} ions at (A) and [B] sites cancel each other. Hence, the net magnetization of cobalt ferrite is comes out from Co^{2+} ions in [B] site [6].

So far various efforts have been taken to fine-tune and enhance the magnetic properties of spinel ferrite nanoparticles where the particle size, shape, composition and core shell structure are the key factors [1,7]. The particle size and shape of cobalt ferrites can be modified by the proper selection of pH, concentration of alkaline solution, reaction temperature, nucleation rate, the steps involved in the synthesis procedure and diverse synthesis methods. The composition can be altered by changing the molar ratio of Fe^{3+} and Co^{2+} salts solution and also by the substitution of various elements [8,9]. In addition to that, the most important way to achieve single phase nanoparticles with desired size is by processing the synthesized nanoparticles at elevated temperatures. The possible advantages of the calcination process are, the elimination of impure phases, increase of crystallite size, enhancement on the density of nanoparticles, and the influence on the cation redistribution between (A) and [B] sites in spinel ferrites [10].

* Corresponding author.
** Corresponding author.
E-mail addresses: prabhakarant85@gmail.com (T. Prabhakaran), mangal@udec.cl (R.V. Mangalaraja).

http://dx.doi.org/10.1016/j.jallcom.2017.05.048
0925-8388/

There are several reports that discussed the effect of calcination temperature and duration on the particles size and magnetic properties of nanoparticles. El-Okr et al. reported the synthesis of cobalt ferrites by co-precipitation method and the particle size dependent magnetic properties of calcinated (at 500–900 °C for 2 h) nanoparticles were reported [11]. Cobalt ferrite nanoparticles co-precipitated from metal chlorides were calcinated at 400 to 800 °C for 3 h and their magnetic properties were discussed by Veverka et al. [12]. Kumar et al. discussed the effect of calcination temperature, 100–900 °C for 1 h on the magnetic properties of co-precipitated cobalt ferrite nanoparticles [13]. Cobalt ferrite nanoparticles were also synthesized through citrate and co-precipitation methods and the temperature effects on the anisotropy constant were discussed by Kumar et al. [14]. Maaz et al. adopted wet chemical route for the synthesis of cobalt ferrite nanoparticles using oleic acid as a surfactant. And the magnetic properties of the samples calcinated at 800–1000 °C for 10 h were reported [15]. Similarly, few other reports discussed the effect of calcination temperature on the magnetic properties of cobalt ferrite nanoparticles derived from sol-gel or auto-combustion methods [4,16–18]. In addition to the chemical routes, solid state process followed by the calcination at 1000 °C for 6 h and 3 h were reported by Moayyer et al. [19] and Abbas et al., respectively [6]. Moreover, we can also see the reports that deal only with the structural and electrical properties of the calcinated cobalt ferrites [20,21].

Though several reports available on the effect of calcination temperature on the magnetic properties of the cobalt ferrite nanoparticles they fail to study both reaction and calcination temperatures and particle size effect on the magnetic properties. They either discuss the temperature effect or particle size effect on cobalt ferrites. Hence, the present article is framed to study the both effects on the magnetic properties of cobalt ferrites. Co-precipitation method is preferred for the synthesis, owing to its simplicity and environmental friendly process compared to other chemical and solid-state routes. In addition, it does not require any organic or toxic acids for the synthesis. For the investigation, cobalt ferrite nanoparticles are co-precipitated at two different reaction temperatures of 40 and 85 °C and are subsequently calcinated at 500 and 800 °C for 2 h. The present article covers the detailed study on the effect of calcination temperature and particle size on the structural and magnetic properties at room temperature (RT) and low temperature of 5 K (−268 °C). Further, the comparison of the present results with earlier reports is discussed in the last section of the manuscript recommends the suitable experimental conditions and calcination temperature to achieve considerable magnetic properties of cobalt ferrite nanoparticles.

2. Experimental methods

2.1. Synthesis

The chemicals, cobalt nitrate hexahydrate (Co $(NO_3)_2 \cdot 6H_2O$) 98% + A.C, iron nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$) 98% and sodium hydroxide (NaOH) pellets ≥ 98% ACS grade were purchased from Sigma-Aldrich and were used without further purification. Double-distilled water was used as a solvent for the synthesis. $CoFe_2O_4$ nanoparticles were co-precipitated as follows: 400 ml of aqueous cobalt nitrate (0.1 M) and iron nitrate (0.2 M) were prepared separately and then mixed together while stirring. The reaction temperature of the solution was fixed at 40 and 85 °C individually and the solution was continuously stirred. Once the desired reaction temperature of the solution was reached, 400 ml of aqueous (0.84 M) NaOH solution was added drop wise at the constant rate while stirring. The precipitation was started and the solution was fixed at the reaction temperature of 1 h. After cooled down to room temperature the precipitates were washed several times with distilled water to remove unwanted ions. The final black precipitates were dried at 100 °C for 18 h in an oven and grounded into fine powder. In order to study the effect of calcination temperature on the properties of cobalt ferrite nanoparticles, the samples synthesized at reaction temperatures of 40 and 85 °C were calcinated at 500 and 800 °C for 2 h in air. The temperature was raised from room temperature to 500 °C in 2 h and maintained at the same temperature for 2 h soaking and then slowly cooled down to room temperature in 5 h. Similar procedure was followed for the calcination of the samples at 800 °C. The sample codes F0, F500, F800, E0, E500, and E800 were assigned with respect to the reaction temperature and calcination temperature, and are listed in Table 1.

2.2. Characterizations

The as-prepared and calcinated cobalt ferrite nanoparticles were characterized as follows. The crystal structure, average crystallite size, and phase purity of cobalt ferrite nanoparticles were identified from X-ray diffraction (XRD) patterns obtained using Cu-K_α radiation for 2θ value range from 10 to 80° with the step of 0.02° using Model Bruker-axs 104025-0. Besides, the Rietveld method was applied for the calculation of structural parameters from XRD patterns. We have used the version 4.2 of the Rietveld analysis program TOPAS (Bruker AXS) and crystallographic information of the different phases obtained from Pearson's crystal structure database for inorganic compounds release 2015/2016 Materials Park: ASM International, 2015. The morphology and compositional details of the ferrites were recorded by using a scanning electron microscopy (SEM) model ZEISS EVO MA10. The particle size distribution of cobalt ferrite nanoparticles calcinated at 800 °C was obtained by using a transmission electron microscopy (TEM) HITACHI HT7700. The magnetic properties of the samples were measured by using a vibrating sample magnetometer (5TminiVSM from Cryogenic Ltd.) with a maximum applied field of 6 kOe for room temperature and 50 kOe for 5 K (−268 °C) measurements.

3. Results and discussion

3.1. Structural studies

X-ray diffraction patterns of co-precipitated and calcinated cobalt ferrite nanoparticles are shown in Figs. 1 and 2. XRD patterns are well matched with the standard diffraction data JCPDS No: 03-0864 to confirm the face centered cubic spinel structure of synthesized cobalt ferrite with space group $Fd\bar{3}m(227)$. Furthermore, the Rietveld refinement has been performed on the XRD data to calculate the structural parameters, composition, and possible site occupancy in cobalt ferrite nanoparticles. From the refinement profile it is understood that the intensity of X-ray reflections increases and the full width half maximum becoming narrower with the increase of calcination temperature indicates the improved crystallite size of cobalt ferrites. The sample (F0) synthesized at the reaction temperature of 40 °C has secondary phase corresponding to 4.6% of α-Fe_2O_3. This impure phase is completely eliminated and single phase cobalt ferrites are obtained when the samples (F500 and F800) are calcinated at elevated temperatures. Fig. 2 shows the XRD patterns of cobalt ferrite nanoparticles co-precipitated at high reaction temperature of 85 °C. The as-prepared (E0) and the sample (E500) calcinated at 500 °C have α-Fe_2O_3 and Co_3O_4 phases which are finally disappeared at 800 °C. The 14.5 and 11.54% of α-Fe_2O_3 phase are estimated for the sample E0 and E500, respectively, and 10.78% of Co_3O_4 phase is found for the sample E500. The negligible amount of Co_3O_4 phase is not shown in the fitting analysis of the