Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 36 (2010) 605–609
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Size and crystallinity-dependent magnetic properties of $CoFe_2O_4$ nanocrystals

C.H. Chia [a,*], S. Zakaria [a], M. Yusoff [a], S.C. Goh [a], C.Y. Haw [a], Sh. Ahmadi [a], N.M. Huang [b], H.N. Lim [c]

[a] School of Applied Physics, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia
[b] Solid State Physics Research Laboratory, Physics Department, University of Malaya, 50603 Kuala Lumpur, Malaysia
[c] Chemistry Department, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

Received 17 July 2009; received in revised form 3 August 2009; accepted 23 September 2009
Available online 29 October 2009

Abstract

$CoFe_2O_4$ nanocrystals were synthesized by a wet chemical coprecipitation approach. In order to investigate the effect of degree of crystallinity and mean crystallite size of $CoFe_2O_4$ nanocrystals on the magnetic properties, a series of $CoFe_2O_4$ samples with different degree of crystallinity and mean crystallite size were produced by varying the synthesis and subsequent calcination temperatures. The higher synthesis and subsequent calcination temperatures have resulted in greater degree of crystallinity and bigger mean crystallite size of $CoFe_2O_4$ nanocrystals. The VSM studies showed that the saturation magnetization (M_s) and coercivity (H_c) of the $CoFe_2O_4$ nanocrystals possessed a linear relationship with the mean crystallite size.

Keywords: A. Powders: chemical preparation; C. Magnetic properties; D. Ferrites; D. Spinels

1. Introduction

Nano-sized transition metal oxides with spinel structure have recently received wide attention in several scientific and technological fields [1,2]. Spinel ferrites with cubic unit cell have a formula of $M_XFe_{3-X}O_4$, where the divalent metallic ions (M^{2+}) can be either Fe, Mn, Co, Ni, Cu or Zn. Cobalt ferrite ($CoFe_2O_4$), one of the well known hard magnetic materials, has been widely used as high-density recording medium due to its strong magnetic anisotropy, moderate magnetization, and high coercivity at room temperature [3].

There are a number of methods which have been reported previously for the preparation of $CoFe_2O_4$ nanocrystals, including microemulsion [4–6], sol–gel techniques [7], hydrothermal synthesis [8,9], coprecipitation [10–14] and electrochemical synthesis [15]. The chemical coprecipitation is the most widely used method due to its high yield and simplicity in producing ultrafine magnetic nanocrystals. To date, there are two different chemical coprecipitation methods that have been used to produce $CoFe_2O_4$ nanocrystals, i.e., with and without oxidizing agent. Previous studies reported the precipitation of $CoFe_2O_4$ nanocrystals by mixing Fe^{2+}, Co^{2+} and NaOH in the presence of oxidizing agent such as H_2O_2 [16] and KNO_3 [3,17]. The oxidizing agent is required for the formation of Fe^{3+} from Fe^{2+} as precursor of the formation of $CoFe_2O_4$. However, the coexistence of Fe^{2+} and Fe^{3+} ions has resulted in the formation of magnetite (Fe_3O_4) and $CoFe_2O_4$ which will subsequently affect the purity of the products. In order to avoid this adverse effect, precipitation has been carried out without using oxidizing agent [18,19].

Previous studies have found that the synthesis temperature plays an important role in controlling the size of the $CoFe_2O_4$ which will significantly influence the magnetic properties of the products [11,18]. Besides, a number of attempts have also been made to improve the magnetic properties of the $CoFe_2O_4$ nanocrystals by subsequent calcination of the as-precipitated $CoFe_2O_4$ nanocrystals [16,20,21].

In the present study, $CoFe_2O_4$ nanocrystals are produced using a wet chemical method. The aim of this study is to investigate the effect of crystallite size and degree of crystallinity

* Corresponding author. Tel.: +60 3 8921 5473; fax: +60 3 8921 3777.
E-mail address: chia@ukm.my (C.H. Chia).

0272-8842/$36.00
doi:10.1016/j.ceramint.2009.10.001

of the $CoFe_2O_4$ nanocrystals on the magnetic properties. A series of $CoFe_2O_4$ nanocrystals with different crystallite size and degree of crystallinity were prepared by varying the synthesis temperature and further calcinations. To the best of our knowledge, these aspects, however, have never been reported altogether in previous studies which are of favorable in controlling the crystallinity and magnetic properties of the $CoFe_2O_4$ nanocrystals.

2. Experimental procedures

2.1. Materials

Analytical grade of cobalt chloride hexahydrate ($CoCl_2{\cdot}6H_2O$), ferric chloride ($FeCl_3$) and sodium hydroxide (NaOH) were used without further purification. The solutions of Co(II) and Fe(III) were prepared by dissolving required weights of $CoCl_2{\cdot}6H_2O$ and $FeCl_3$ in 0.01 M HCl separately. This is to avoid any precipitation of iron oxy-hydroxides prior to the synthesis process.

2.2. Preparation of $CoFe_2O_4$ nanocrystals

In a typical experimental procedure, stoichiometric volume of Co^{2+} and Fe^{3+} solutions (molar ratio of 1:2) are added into a round bottom flask containing an aqueous solution of NaOH at desired temperature. The mixture immediately turned into a dark brown color, indicating the ferrite formation. The mixture is vigorously stirred at a constant stirring rate (~200 rpm) with a turbine mixer and heated at constant temperature for 60 min. The final pH of the suspension is approximately 12. The precipitates are washed with deionized water by the centrifugation at 8000 rpm. The washing and centrifugation are performed 5 times for each precipitate. The obtained precipitate is then dried in an oven at 50 °C for 24 h. The precipitate is then ground into powder for characterization tests. Four samples were produced at different temperatures (40, 60, 80 and 100 °C). In order to produce $CoFe_2O_4$ nanocrystals with greater crystallinity and bigger crystallite size, the as-prepared $CoFe_2O_4$ nanocrystals (precipitated at 100 °C) are calcined at different temperatures, i.e., 300, 450, 600, 750, 900 and 1200 °C for 12 h.

2.3. Characterizations

All samples are analyzed using a X-ray diffractometry (Siemens diffractometer D5000) with Cu K_α radiation (λ = 1.5418 Å). The sample is continuously scanned at a scanning rate of 0.02° s^{-1} in the 2θ range of 25–80°. The mean crystallite size of the crystals is determined by Scherrer's equation [22]

$$D_{hkl} = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where $D_{h\,k\,l}$ is the average crystallite size, β is the broadening of full width at half maximum intensity (FWHM) of the main intense peak (3 1 1) in radian, θ is the Bragg angle and λ is the radiation wavelength. A transmission electron microscope (Philips CM12) is employed to examine the microstructure and the size of the crystals. The samples are firstly dispersed into the acetone solution (90%) and subjected to an ultrasonic treatment for about 10 min. A drop of the suspension of the crystals is placed on a carbon coated copper grid and then left to dry at the ambient temperature for at least 30 min. The grid is then stored in a desiccator for further tests. The morphology of the crystals and the energy dispersion X-ray analysis (EDX) are studied using a scanning electron microscope (Leo 1450 VP). The magnetic properties are measured at 25 °C using a computerized vibrating sample magnetometer (LDJ 9500).

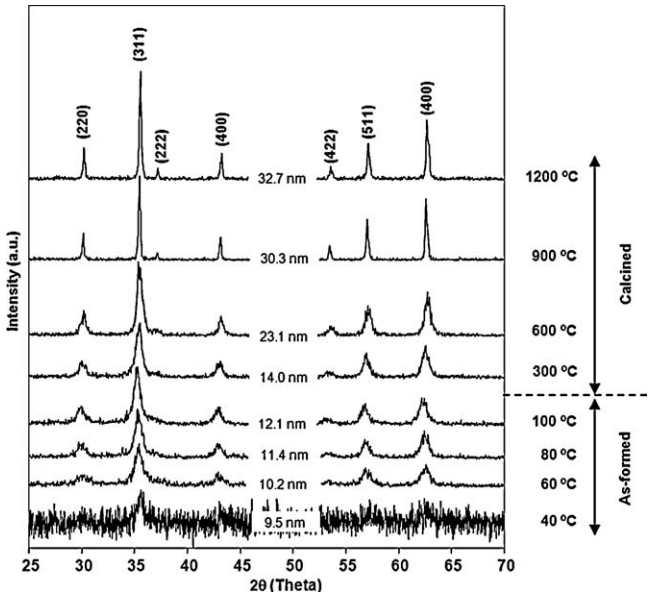

Fig. 1. Size-dependent powder-XRD patterns of as-prepared and calcined $CoFe_2O_4$ nanocrystals produced at different temperatures. The mean crystallite size ($D_{3\,1\,1}$) is estimated by the Scherrer's formula.

Table 1
X-ray diffraction studies and magnetic properties of the produced $CoFe_2O_4$ nanocrystals.

Synthesis temperature (°C)	Calcination temperature (°C)	$I_{(3\,1\,1)}$ (CPS)	$D_{3\,1\,1}$ (nm)	M_s (emu/g)	H_c (Oe)	M_r/M_s
40	–	72	9.5	6.3	53	0.13
60	–	79	10.2	18.7	132	0.14
80	–	89	11.4	32.2	164	0.16
100	–	108	12.1	35.8	249	0.18
100	300	116	14.0	43.2	376	0.25
100	600	148	23.1	54.9	751	0.42
100	900	174	30.3	56.3	1067	0.49
100	1200	228	32.7	60.7	1201	0.39