

# Structural and magnetic properties of cobalt ferrites synthesized using sol-gel techniques

A. HUNYEK\*, C. SIRISATHITKUL, P. HARDING AND D. J. HARDING

Molecular Technology Research Unit, School of Science, Walailak University, Nakhon Si Thammarat 80161, Thailand

Cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ ) was synthesized using sol-gel techniques from cobalt nitrate: iron nitrate: polyvinyl alcohol (PVA) gel in a ratio of 1:2:12. Variations in the amount of PVA in water (5 %, 10 % and 15 %) influenced the crystallite size and phases of the ferrite products, which in turn controlled their magnetic properties. X-ray diffraction studies indicated single phase  $\text{CoFe}_2\text{O}_4$  with larger crystallite size and with the hysteresis loops displaying an increase in both coercive field and squareness as the PVA content was increased. Differential scanning calorimetry (DSC) showed that desorption of water and combustion of excess gel were clearly observed in  $\text{CoFe}_2\text{O}_4$  prepared from 10 % and 15 % PVA in water. In the case of 5 % PVA in water, two other ratios of cobalt nitrate: iron nitrate: PVA solution were also tested and it was found that the 1:2:10 ratio led to the smallest coercive field and squareness.

Keywords: *cobalt ferrites, sol-gel method, XRD, DSC, hysteresis loops*

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## 1. Introduction

Soft ferrites are an important class of ceramic materials and have been widely studied for electromagnetic applications. When used in high frequency inductors or transformers, the core loss of ferrites is minimal because of their high electrical resistivity and magnetic softness [1]. Ferrites of the general formula,  $\text{AFe}_2\text{O}_4$ , where  $\text{A}^{2+}$  is a divalent cation, usually  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$ , have a spinel structure and involve a cubic close packed (fcc) arrangement of oxide anions,  $\text{O}^{2-}$ . The tetrahedral and octahedral interstitial sites in the lattice are partially occupied by the  $\text{A}^{2+}$  and  $\text{Fe}^{3+}$  cations, respectively, and this property results in magnetic behavior of these ferrites. In the case of magnetite ( $\text{Fe}_3\text{O}_4$ ), cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ ) and nickel ferrite ( $\text{NiFe}_2\text{O}_4$ ), their structures are inverse spinels while zinc ferrite ( $\text{ZnFe}_2\text{O}_4$ ) has a normal spinel structure [2]. The exact properties and thus the ultimate use of ferrites depend upon the sample preparation and processing. Moreover, the size, morphology and porosity of the crystalline ferrite can significantly

influence its magnetic properties. Therefore, there has recently been a considerable interest in preparing spinel ferrite nanoparticles in which the individual nanoparticles may behave as single magnets owing to their wide range of applications from magnetic storage devices to catalysts and biomedical functions [3].

Of particular relevance to the current work is  $\text{CoFe}_2\text{O}_4$ , which exhibits considerable magnetostriction effects [4] and microwave absorbing properties [5]. Like other spinel ferrites,  $\text{CoFe}_2\text{O}_4$  can be synthesized by various wet chemical methods such as chemical co-precipitation [6], solvothermal methods [7], microemulsion [8], microwave synthesis [9] and sol-gel routes [10, 11]. The sol-gel method is also efficient for preparing ferrite thin films [12], nanocomposites [13, 14] as well as doping materials with magnetic nanoparticles [15]. The advantage of the gel reaction is that it permits controlled decomposition of precursors to cobalt ferrites producing nanoparticles in-situ while the chelating gel is dried during the heat treatment phase. Since it can be consistently controlled, homogeneity on a molecular level can be obtained [16].

\*E-mail: ahunyek@hotmail.com

In this work we report the synthesis of  $\text{CoFe}_2\text{O}_4$  nanocomposites by a sol-gel technique using polyvinyl alcohol (PVA) as a chelating agent. In the characterization stage, the structural and magnetic properties of the ferrites are analyzed as functions of the sol-gel compositions in order to find the optimum synthetic conditions for the preparation of  $\text{CoFe}_2\text{O}_4$ .

## 2. Experimental

The PVA powder was slowly dissolved in distilled water (5 %, 10 % and 15 % w/v) under constant stirring in order to avoid clumping of the material. The PVA solution was kept at temperatures between 70 and 80 °C for 5–7 hours or until the solution became clear. Cobalt nitrate,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and iron nitrate,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  powders were then mixed with the PVA solution in a ratio of 1:2:12. The reaction mixture was stirred for 3 hours and the temperature was then increased to 80 °C for 10–12 hours or until the gel was dry. In the case of 5 % PVA in water, samples with two other ratios of cobalt nitrate (weight): iron nitrate (weight): PVA solution (volume), i.e. 1:2:6 and 1:2:10 were also prepared. All the samples were sintered at 800 °C for 4 hours.

The morphology of the ferrite products was examined by scanning electron microscopy (SEM) and their structures were characterized by powder X-ray diffraction (XRD). A copper target was used as an X-ray source ( $K_\alpha$ , wavelength = 1.54058 Å) with 40 kV between the cathode and the copper target. The measurement was performed in the range of  $2\theta$  angles from 10 to 80 degrees with a rotating step of 0.02 degrees. Crystallite size was calculated from the peak width using Scherrer's formula [17].

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

where  $\beta$  is the broadening of the diffraction line measured at half maximum intensity and  $\lambda$  is the wavelength of  $K_\alpha$ . To study the effect of the composition of the precursors on the magnetic and thermal properties, the samples were characterized

by vibrating sample magnetometry (VSM) and differential scanning calorimetry (DSC).

## 3. Results and discussion

From the XRD patterns in Fig. 1, the cubic spinel  $\text{CoFe}_2\text{O}_4$  phase [JCPDS 22-1086] can be identified in each sample by reflections from the (220), (311), (400), (511) and (440) planes at 30.0°, 35.4°, 43.0°, 56.9°, 62.6° respectively. In addition, all the samples prepared from 5 % PVA powder in water (A, B, C) also contain  $\alpha\text{-Fe}_2\text{O}_3$  [JCPDS 33-0664] as evidenced by the peak at 33.1° corresponding to the (014) reflection plane. In the samples prepared from 10 % PVA (D) and 15 % PVA (E), the  $\text{Fe}_2\text{O}_3$  peaks are absent and the  $\text{CoFe}_2\text{O}_4$  peaks are particularly sharp, which is consistent with a high degree of crystallinity in the samples. This result is consistent with recent work where ethylene glycol was used in the sol-gel [11]. We have also obtained the single phase  $\text{CoFe}_2\text{O}_4$  in the case of a larger crystallite size. The crystallite size, calculated from the line broadening of the (311) diffraction peak is 40–50 nm but due to agglomeration of particles into clusters an approximate value of hundreds of nanometers in size must be assumed, as it is evident in Fig. 2. The morphology, as can be seen in this SEM micrograph, still reflects the cubic structure of the ferrites.

The effect of the PVA content is also shown in the DSC curves in Fig. 3. The major endothermic peak, corresponding to the desorption of water [18], is shifted from 90 °C to lower temperatures with larger heat absorption as the PVA content increases. Moreover, the samples synthesized from highly-concentrated PVA gel (D and E) possess less prominent endothermic peaks around 200 °C which are attributed to the combustion of the excess PVA [19]. Otherwise, these ferrite products have rather flat curves indicating good thermal stability between 100 and 300 °C.

Hysteresis loops of the ferrite products are shown in Fig. 4 and magnetic parameters from these loops are compared in Table 1. All synthetic

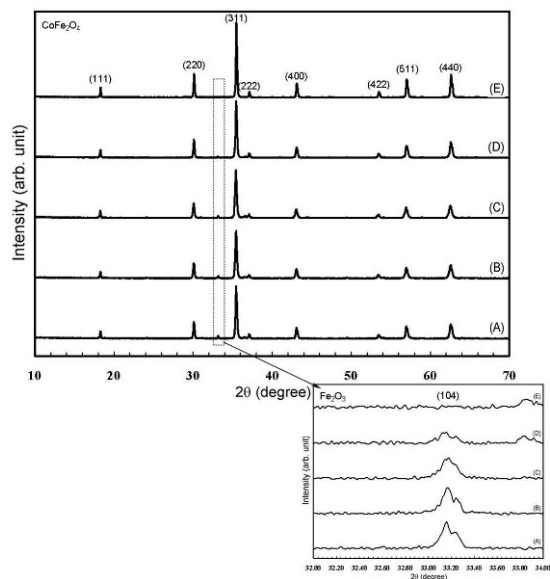


Fig. 1. XRD patterns of ferrite products for varying sol-gel compositions. Data between 32 and 34 degree are magnified to compare the  $\text{Fe}_2\text{O}_3$  peak.

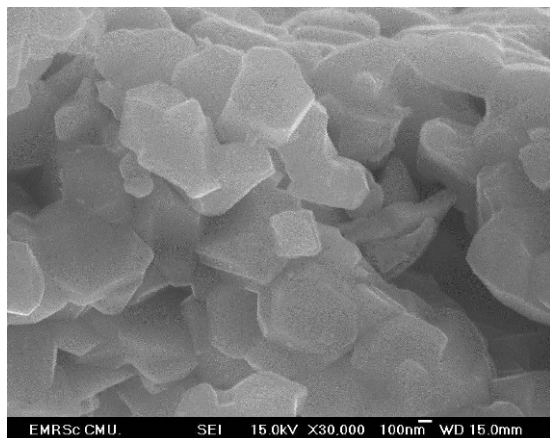


Fig. 2. SEM micrograph showing morphology of the ferrite product (Sample A).

conditions lead to comparable ferromagnetic characteristics without superparamagnetic behaviors. Nevertheless, a complete saturation is not obtained even in a 440 kA/m field. The highest magnetization corresponds to about 50 emu/g, comparable to the value recently reported for nanosized  $\text{CoFe}_2\text{O}_4$  synthesized by the sol-gel technique [10]. Both coercive field and squareness (the ratio of remanence to

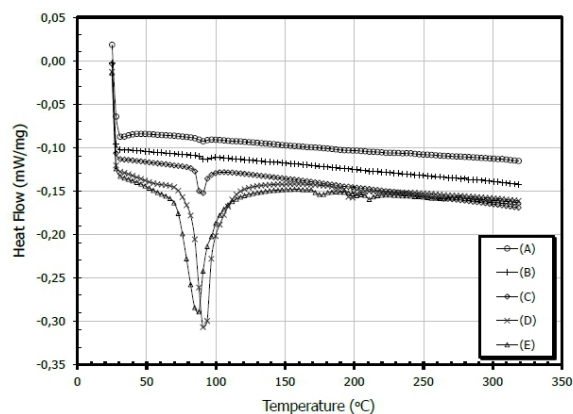


Fig. 3. DSC curves of ferrite products with different sol-gel compositions.

Table 1. Magnetic parameters of ferrite products with varying sol-gel compositions.

Sample Code	PVA powder: water (% w/v)	Ratio of cobalt nitrate: iron nitrate: PVA solution	Coercive field (kA/m)	Squareness
A	5%	1:2:6	28.24	0.28
B	5%	1:2:10	16.86	0.20
C	5%	1:2:12	27.20	0.26
D	10%	1:2:12	32.69	0.31
E	15%	1:2:12	38.74	0.36

saturation magnetization) are substantially raised with increasing PVA content. The amount of PVA powder in water, whose function is to cleave the metal atoms during the water evaporation, controls the viscosity of the gel. Interestingly, the 5 % PVA gel has the lowest viscosity but is still able to encapsulate the metal atoms, although an increase in PVA content improves the crystallinity of  $\text{CoFe}_2\text{O}_4$  as shown by the XRD results. While the gel viscosity is controlled by the amount of PVA in water, the degree of reaction is dependent on the ratio of cobalt and iron nitrates per gel. When the PVA content in water is 5 %, the lowest values for coercive field (16.86 kA/m) and squareness (0.20) are obtained when the ratio of cobalt and iron nitrates to PVA is 1:2:10. This difference in magnetic behavior is connected to the differences in size and structure of ferrite products.

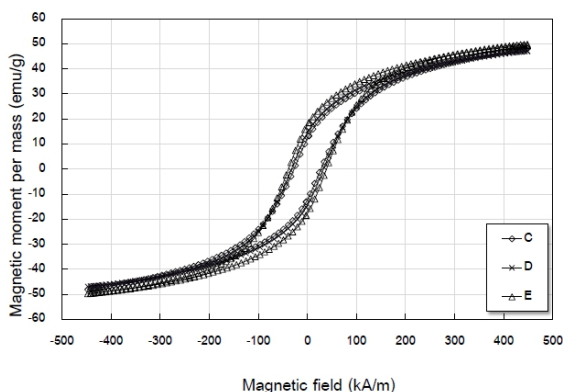


Fig. 4. Hysteresis loops of ferrite products with different PVA content in water (Samples C, D, E).

## 4. Conclusions

Cobalt ferrites were synthesized by a PVA sol-gel reaction with five different compositions of precursors. Single phase  $\text{CoFe}_2\text{O}_4$  with large crystallite size was obtained from the synthesis with 10 and 15 % PVA powder in the water whereas 5 % PVA resulted in mixtures of  $\text{CoFe}_2\text{O}_4$  and  $\alpha\text{-Fe}_2\text{O}_3$ . However, the sintered product from cobalt and iron nitrates in a 5 % PVA with a ratio of 1:2:10 exhibited the lowest coercive field and squareness, which are desirable characteristics for some magnetic applications. The increase in PVA content significantly increased the magnetization, squareness and coercive field of  $\text{CoFe}_2\text{O}_4$ , which are required in other applications. Thus, for each application, the magnetic properties of  $\text{CoFe}_2\text{O}_4$  can be tailor-made by variation of sol-gel compositions.

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