

COERCIVITY ENHANCEMENT OF COBALT FERRITE NANOPARTICLES BY CO-SUBSTITUTION WITH COPPER AND MANGANESE

Anuchit Hunyek^{1,*} and Komkrich Chokprasombat²

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Abstract

Magnetic properties of cobalt ferrite nanoparticles can be altered by doping with transition metals. Herein, we report the effect of co-substitution with copper and manganese on the structural and magnetic properties of the cobalt ferrite. The particles were prepared by a sol-gel method with post-annealing at high temperature. The obtained particles are varied in size and shape depending on the amount of doping elements. The coercivity can be enhanced by small doping (less than 10%) whereas the saturation magnetization does not show an explicit trend. The coercivity enhancement is ascribed to the stronger magnetic moment coupling and the particle size effect.

Keywords: Magnetic nanoparticle, co-substitution, cobalt ferrite, coercivity

Introduction

Ferrite nanoparticles are of interest due to their exceptional magnetic and dielectric properties. They have been used in many applications, for examples, permanent magnets, magnetic fluids, microwave absorber, drug delivery, biosensor, and high-density magnetic recording (Chinnasamy *et al.*, 2003; Mohamed *et al.*, 2010). The general formula of the ferrites is MFe_2O_4 ; where M is a divalent cation such as Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , and Cu^{2+} . These ferrites have an inverse spinel structure

in which the tetrahedral sites (A-sites) are occupied by Fe^{3+} and the octahedral sites (B-sites) are occupied by both M^{2+} and Fe^{3+} .

Among the dominant ferrites, cobalt ferrite ($CoFe_2O_4$) has attracted much attention because of its outstanding physical properties including high coercivity (H_c), moderate saturation magnetization (M_s), high chemical stability, and good mechanical hardness (Toksha *et al.*, 2008; Sangmanee and Maensiri, 2009). Moreover, $CoFe_2O_4$ could be easily doped with

¹ Faculty of Liberal Arts, Rajamangala University of Technology Rattanakosin, Wang Klai Kangwon Campus, Prachuap Khiri Khan 77110 Thailand. Tel: +66-3261-8500 ext. 4820, e-mail: anuchit.hun@rmutr.ac.th

² Department of Physics, Faculty of Science, Thaksin University, Phatthalung 93210 Thailand.

* Corresponding author

various transition metals, leading to the alterations in the physical properties. Balavijayalakshmi *et al.*, (2012) substituted Cu into the CoFe_2O_4 structure by a co-precipitation method. They found that the crystallite sizes of the particles range between 37 and 52 nm, and the M_S and H_C decrease with increasing Cu content. The decrease in magnetic properties of CoFe_2O_4 is also found in the case of Ni substitution (Mozaffari *et al.*, 2014). Additionally, increase of Mn in the CoFe_2O_4 structure exhibits the lower H_C , but the M_S does not show the explicit trend (Koseoglu *et al.*, 2010). Recently, Jadhav *et al.* (2015) demonstrated that co-substitution of Cu and Mn in cobalt-substituted nickel ferrite also reduces the crystallite size and H_C of the particles. However, co-substitution with Cu and Mn in CoFe_2O_4 nanoparticles has not been investigated, particularly in the case of small doping.

The aim of this work is to determine the structural and magnetic properties of CoFe_2O_4 nanoparticles co-doped with small amounts of Cu and Mn. The sol-gel method was employed to prepare the nanoparticles with required compositions. In contrast to the previous works, the H_C of the doped CoFe_2O_4 increases even though in the case of single doping. In addition, $\text{Co}_{0.92}\text{Cu}_{0.02}\text{Mn}_{0.06}\text{Fe}_2\text{O}_4$ exhibits the high H_C of around 1.4 kOe which is higher than that of the undoped CoFe_2O_4 more than two times.

Experimental

The $\text{Co}_{0.92}\text{Cu}_x\text{Mn}_y\text{Fe}_2\text{O}_4$ ($x+y = 0.08$) ferrites were synthesized by the PVA glue sol-gel method (Hunyek *et al.*, 2012). In a typical experiment, designed amount of metal nitrates were dissolved in the poly vinyl alcohol (PVA) glue with a ratio of 1:12. The solution was then heated at around 80°C for 6-8 h. After that, the product was annealed at 700°C for 4 h in air. The dried product was ground to obtain the sample powder. The six samples were named according to the doping percentage of Cu and Mn, i. e. Cu_0Mn_0 for CoFe_2O_4 , Cu_8Mn_0 for $\text{Co}_{0.92}\text{Cu}_{0.08}\text{Fe}_2\text{O}_4$, Cu_6Mn_2 for $\text{Co}_{0.92}\text{Cu}_{0.06}\text{Mn}_{0.02}\text{Fe}_2\text{O}_4$, Cu_4Mn_4 for $\text{Co}_{0.92}\text{Cu}_{0.04}\text{Mn}_{0.04}\text{Fe}_2\text{O}_4$, Cu_2Mn_6 for

$\text{Co}_{0.92}\text{Cu}_{0.02}\text{Mn}_{0.06}\text{Fe}_2\text{O}_4$, and Cu_0Mn_8 for $\text{Co}_{0.92}\text{Mn}_{0.08}\text{Fe}_2\text{O}_4$.

Crystalline structures of the samples were identified by X-ray diffraction (XRD). The X-ray source was Cu K_α ($\lambda = 1.54058 \text{ \AA}$), and the scattering angle (2θ) was varied from 20 to 70 degree with the scanning rate of 0.02 degree/0.2 s. The crystallite sizes were estimated from the apparent peaks by using the Scherrer's formula. Lattice parameters and X-ray density were analyzed by the methods described in (Salunkhe *et al.*, 2014). Scanning electron microscope (SEM) was employed to determine the particle morphology. The elemental compositions were obtained by the energy dispersive X-ray spectroscopy (EDS) equipped with the SEM. The magnetic properties were measured by the vibrating sample magnetometer (VSM) with applied magnetic field ranging between -10,000 and 10,000 Oe at room temperature.

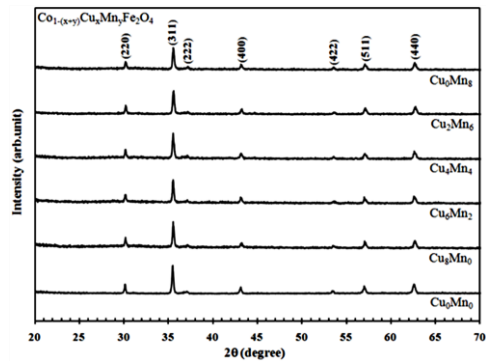


Figure 1. XRD patterns of the samples

Results and Discussion

XRD patterns (Figure 1) indicate that all samples are of cubic spinel cobalt ferrite. No secondary phases occur in all spectra, and the apparent peaks can be specified to the (220), (311), (222), (400), (422), (511) and (440) planes (JCPDS no. 22-1086). Doping with small amount of Cu and Mn does not alter the XRD patterns, however EDS results (Table 1) show

the variation of Cu and Mn according to the designed doping percentages. These results demonstrate the presence of Cu and Mn in the crystalline structure of the cobalt ferrites. In addition, the crystallite sizes determined from the highest peak in each spectrum are in the range of 30-45 nm (Table 2) which are comparable to the case of single Cu doping (Balavijayalakshmi *et al.*, 2012). Figure 2. illustrates the effect of doping on lattice parameter and X-ray density. The lattice parameters decrease when the concentration of Cu is higher than that of Mn because the ionic radius of Cu^{2+} (0.73 Å) is smaller than that of Co^{2+} (0.78 Å). However, when the amount of Mn^{2+} is equal or higher than that of Cu^{2+} , the lattice parameter is increased (Figure 2). This result is also ascribed to the larger ionic radius of Mn^{2+} (0.83 Å) compared to that of Cu^{2+} (Adeela *et al.*, 2015). Because the X-ray density is inversely proportional to the lattice parameter (Salunkhe, 2014), the sample with smaller lattice

to the previous reports (Sanpo *et al.*, 2013; Balavijayalakshmi, 2012; Adeela, 2015), however, in the case of co-doping, the concentrations of both substituted elements should be appropriate. In this study, the presence of small concentration

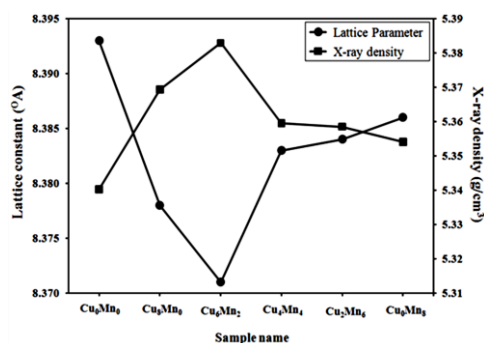


Figure 2. Lattice parameters and X- ray density of the samples

Table 1. Elemental compositions of the samples

Sample	Weight Percent				
	Co	Cu	Mn	Fe	O
Cu ₀ Mn ₀	15.9	-	-	29.6	45.4
Cu ₈ Mn ₀	20.1	1.8	-	43.5	28.1
Cu ₆ Mn ₂	21.3	1.3	0.3	43.7	27.6
Cu ₄ Mn ₄	22.5	0.9	0.8	45.9	24.3
Cu ₂ Mn ₆	17.4	0.4	0.9	35.6	36.2
Cu ₀ Mn ₈	11.0	-	0.8	24.1	47.2

parameter generates the higher X-ray density.

SEM images reveal that the particles are irregular in shape with wide size distribution (Figure 3). The particle sizes are considerably larger than the crystallite sizes determined from the XRD indicating that the particles are agglomerated. The particle agglomeration is not avoidable due to the high temperature annealing and mechanical mastication. However, the amount of doping elements influences the particle morphology; doping with 2% Cu and 6% Mn (Cu₂Mn₆) generates the particles with the smallest size distribution whereas the other concentrations result in the large and non-uniform particles. It is likely that doping with Mn provides the more uniform particles compared to the Cu doping according

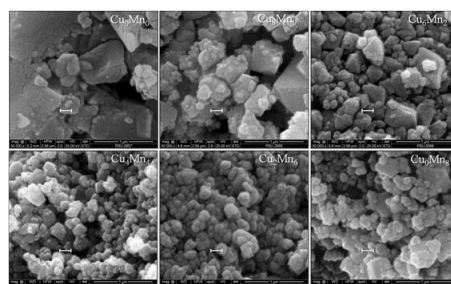


Figure 3. SEM images of the samples. Scale bars are of 200 nm.

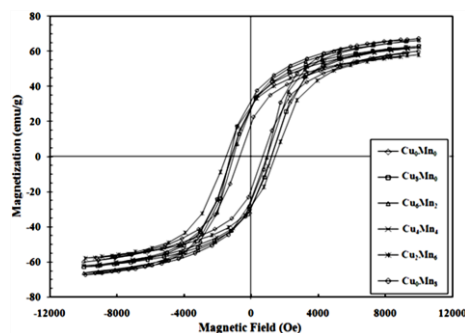


Figure 4. Magnetic hysteresis loops of the samples

of Cu with higher Mn concentration gives the

Table 2. Crystallite sizes and magnetic properties of the samples

Sample	Crystallite size (nm)	Saturation Magnetization (emu/g)	Coercivity (Oe)
Cu ₀ Mn ₀	45	60.09	641
Cu ₈ Mn ₀	31	62.83	1169
Cu ₆ Mn ₂	35	66.22	942
Cu ₄ Mn ₄	43	62.22	1194
Cu ₂ Mn ₆	39	58.00	1458
Cu ₀ Mn ₈	37	67.28	1257

smallest size and shape distributions.

Figure 4 illustrates the magnetic properties of the samples in which all samples exhibit ferromagnetic properties. Interestingly, single doping with Cu or Mn increases the coercivity to be about 2 times higher than that of the undoped sample (Table 2). Co-substitution with Cu and Mn also increase the coercivity of the cobalt ferrite; the highest coercivity is obtained in the case of Cu₂Mn₆ (~ 1.4 kOe).

Magnetic properties of the cobalt ferrite nanoparticles have been reported that depend on the synthesis procedure as well as the particle size (Sharifi *et al.*, 2012). In the past, a number of works reported that doping with Cu and Mn decrease the coercivity of the cobalt ferrite. However, with a small doping (less than 20%) the Cu-doped and Mn-doped cobalt ferrite exhibit the increasing in coercivity (Adeela, 2015). The metal cations distribution between the tetrahedral (A) sites and the octahedral (B) sites is the important factor for the magnetic moment coupling. High concentration of doping elements decreases the Fe³⁺ at the B sites leading to the decrease of anisotropy constant and hence the lowering coercivity (Adeela, 2015). In addition, within the multidomain region, the small particles exhibit the higher coercivity compared with the large particles due to the stronger surface effect of the small particles (Maaz *et al.*, 2007); The small particles have more disorder near the surface result in the large surface anisotropy. Regarding these factors, the Cu₂Mn₆ sample that possesses the small particles with the narrowest size distribution displays the highest coercivity.

Conclusions

Cobalt ferrite nanoparticles co-doped with Cu and Mn have been prepared by the sol-gel method. The concentration of doping elements influences the morphology and magnetic properties of the particles. At 2% Cu and 6% Mn, the sphere-like particles with the smallest size distribution and the highest coercivity are obtained. The coercivity is enhanced by doping with the small amount of Cu and Mn (less than 10%). The results suggest that the physical properties of cobalt ferrite can be adjusted by doping via the simple sol-gel method.

Acknowledgements

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