Research Article

Magnetic Properties of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ Nanoparticles Synthesized by a Template-Assisted Hydrothermal Method

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In the present paper, nickel cobalt ferrite ($\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$) nanoparticles were synthesized using a template-assisted hydrothermal method. Carboxymethyl cellulose was used as the templating agent for controlling the morphology of the $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles. The synthesized nanoparticles were characterized using X-ray diffraction, scanning electron microscopy, and a vibrating sample magnetometer. The results indicated that the morphology of the nanoparticles changed from granular and superparamagnetic to platelike and ferromagnetic with the addition of the template. The $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles synthesized without the template exhibited a saturation magnetization and coercivity 2.81 T and $0.2 \text{ kA} \cdot \text{m}^{-1}$, while when the template was used, the saturation magnetization and coercivity increased to 3.13 T and $76.6 \text{ kA} \cdot \text{m}^{-1}$ as the template proportion increased to 0.3.

1. Introduction

Over recent decades, the fabrication of spinel ferrite nanoparticles has been intensively investigated due to their excellent magnetic and electrical properties, and their potential uses in many areas, such as magnetic devices, recording tapes or disks, microwave absorbers, and active components of ferrofluids [1–5]. Among spinel ferrites, Zn^{2+} substituted CoFe_2O_4 nanoparticles ($\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$) exhibit improved properties such as excellent chemical stability, high corrosion resistivity, magnetocrystalline anisotropy, magnetostriction, and magneto-optical properties [6–8].

Since the magnetic property of spinel ferrites is associated with their morphology and size, modern data storage, microwave protection, and biomedical applications require strict control over the morphology of the particles and a considerable reduction in their dimensions to the single domain and superparamagnetic size [9].

To date, many methods have been developed to prepare $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ nanopowders, such as the coprecipitation method [6, 8, 10], the standard solid-state reaction technique [7, 11], the forced hydrolysis method [12], the microwave-hydrothermal method [13], and the hydrothermal method

[14]. However, research on the template-assisted synthesis of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ nanoparticles is comparatively limited. In the current study, focus was placed on development of a synthesis route for $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles via a template-assisted hydrothermal method and examining the magnetic properties (magnetization and coercivity) and morphology dependence on the template.

2. Experimental

$\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ powders were synthesized from cobalt chloride, zinc acetate, and iron (III) nitrate with carboxymethyl cellulose (CMC) as a template. The chemicals were weighted according to the required stoichiometric proportions, and three solutions of cobalt chloride, zinc acetate, and iron (III) nitrate were prepared in deionized water with continuous stirring. The template was added to the solutions with constant stirring to achieve molar ratios of CMC monomer: metal ions (CMC:M) of 0:1, 0.1:1, and 0.3:1. When the template was dissolved, the solutions were heated to 80°C and held for 8 h. The solutions were then adjusted to $\text{pH} > 9$ with aqueous NaOH and transferred into autoclaves

FIGURE 1: XRD patterns of the powders synthesized with different molar ratios of CMC monomer to metal ions.

TABLE 1: Lattice parameters, density, and orientation degree (O_{hko}) of the $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ particles determined with XRD data analysis.

CMC : M	a (Å)	c (Å)	c/a	D ($\text{g}\cdot\text{cm}^{-1}$)	O_{hko}
0 : 1	8.3913	8.6038	1.0253	5.214	1.260
0.1 : 1	8.4210	8.1811	0.9715	5.445	1.337
0.3 : 1	8.4204	8.2398	0.9685	5.407	1.359

(volume: 100 mL, degree of filling: 80% V). After sealing, the hydrothermal reaction was then carried out in hydrothermal ovens at 170°C for 30 h, the heating rate was about 20 K·min⁻¹. After natural cooling in the furnace, the products were washed repeatedly with distilled water and then dried for 24 h at ambient temperature.

The crystalline structure of the synthesized $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ powders was identified at room temperature using X-ray diffractometry (XRD, Cu-K α_1 , $\lambda = 0.15406$ nm, Model no. D/Max-2200PC, Rigaku, Japan). The morphology of the particles was analyzed using scanning electron microscopy (SEM, Model no. JXM-6700F, Japan). The magnetic property was measured with a vibrating sample magnetometer (VSM, Model no. Versa Lab, Quantun Design, USA)

3. Results and Discussion

Figure 1 shows the XRD patterns of the synthesized powders. All the diffraction peaks were indexed to zinc cobalt ferrite with spinel structure, indicating that the final products consisted of single-phase $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ without any other impurities.

The lattice parameters of the powders were calculated with the relation for tetragonal structures using:

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}. \quad (1)$$

A $c/a = 1$ ratio would indicate a perfect cubic structure in the powder, but the calculated results (Table 1) show that

(a)

(b)

(c)

FIGURE 2: SEM micrographs of the powders synthesized with molar ratios of CMC monomer to metal ions to (a) 0 : 1, (b) 0.1 : 1, and (c) 0.3 : 1.

the powders had varying anisotropies depending on the amount of template that was added. Without any template, the c/a ratio was greater than 1, but as the template was added, the ratio decreased below 1. This is a common occurrence for structures prepared through special synthesis processes. For example, the c/a ratios of some films with c -orientation texture, are all relatively large as reported in literature [15–17]. Each lattice cell contains eight

FIGURE 3: Molecular structure of the carboxymethyl cellulose (CMC).

$\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ molecules. With these lattice parameters, the density of the powders (D , $\text{g}\cdot\text{cm}^{-3}$) can be calculated by the following:

$$D = \frac{8G_m N_a}{a^2 b \cdot 10^{24}}, \quad (2)$$

where G_m is gram molecular weight (236.300 for the $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$) and N_a is Avogadro constant ($6.022 \cdot 10^{23}$). As-calculated densities are also listed in Table 1.

The orientation degree of the (hk_0) plane was calculated from (3) deduced from a formula in literature [15]

$$O_{hk_0} = \frac{(I_{220} + I_{440})/I_{311\text{sample}}}{(I_{220} + I_{440})/I_{311\text{standard}}}. \quad (3)$$

The larger the O_{hk_0} value, the larger the abundance of crystallites oriented in the (hk_0) direction. The calculated results (Table 1) indicate that the template obviously affected the orientation degree of (hk_0) plane, and the O_{hk_0} increased with the increase in template proportion from 0 : 1 to 0.3 : 1.

From the SEM micrographs of the powders (Figure 2), the average grain size was $\sim 35\text{--}45$ nm, and the grain morphology changed from granular to platelike with increasing template proportion. This change in the morphology was consistent with the variation of orientation degree with the template proportion.

The change in morphology can be related to the structure of the CMC monomer, which contained two substituted cyclohexane hexagonal rings with some substituted radicals (Figure 3). The substituted radicals were composed of a hydroxyl radical and a sodium acetate radical on two sides of the hexagonal ring. By partial substitution of the radicals, the CMC molecules could react with each other or with the as-produced polymer at appropriate temperatures. Polymerization in two dimensions may take place because the cyclohexane hexagonal ring appears a platelike morphology. The substituted radicals then could adsorb, before and after the polymerization, the metal hydroxides through hydrogen bonding and substituting sodium ions with Co, Zn, and Fe ions to polymerize into platelike hydroxide layers. In the hydrothermal reaction, the hydroxide layers transformed into the (hk_0) -oriented $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ particles.

Figure 4 shows the room temperature hysteresis loops of the $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ powders. The powder synthesized without the template was superparamagnetic, while the powders become ferromagnetic with the addition of the template. As the template proportion increased from 0 to 0.1 and 0.3, the saturation magnetization of the powder

FIGURE 4: Variation of magnetization with applied field. The insert shows the part of the curve near the origin.

increased from 2.81 T to 3.00 T and 3.13 T ($60.3 \text{ emu}\cdot\text{g}^{-1}$), while the coercivity markedly increased from $0.2 \text{ kA}\cdot\text{m}^{-1}$ to $7.6 \text{ kA}\cdot\text{m}^{-1}$ and $76.6 \text{ kA}\cdot\text{m}^{-1}$ (Figure 5). These variations in the magnetic nature could be attributed to the corresponding change in the structural morphology.

The magnetization of the $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles increased with increasing applied field, but it did not reach the saturation state, even under high magnetic fields of $239 \text{ kA}\cdot\text{m}^{-1}$ (30 KOe). This characteristic was also reported for the $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanospheres prepared *via* the solvothermal method, and the saturation magnetization of the nanoparticles was close to that observed for the nanospheres at an applied field of 5 kOe ($64.6 \text{ emu}\cdot\text{g}^{-1}$) [18]. The saturation magnetization of these samples was smaller than that observed for the bulk material though ($\sim 80 \text{ emu}\cdot\text{g}^{-1}$) [12, 14]. These differences in the magnetization value (such as saturation magnetization, remanent magnetization, and coercivity) between the nanosized ferrites and bulk ferrites can be attributed to the finite size effect [19]. Additionally, the lack of oxygen to mediate the superexchange mechanism between nearest iron ions on the surface can lead to a decrease in exchange coupling, resulting in slanted spins and a decrease in the nanoparticles' saturation magnetization [20]. They can also be attributed to the enhancement of the surface barrier potential due to distortion of the crystal lattice caused by the atoms deviating from normal positions in the surface layers [21].

4. Conclusions

$\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ferrites were synthesized using a template-assisted hydrothermal method with CMC as the templating agent. The average particle size was found to be $\sim 35\text{--}45$ nm, and room temperature X-ray diffraction confirmed the formation of single-phase Zn–Co ferrite at 170°C for all

FIGURE 5: Variations of saturation magnetisation and coercivity with molar ratio of CMC monomer: metal ions (CMC : M).

template proportions used in this experiment. The FE-SEM results showed that the morphology of the $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ powder changed from granular to platelike with increasing template proportion, and the room temperature VSM results showed that the $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles synthesized without the template exhibited superparamagnetic behavior with a saturation magnetization of 2.81 T. The addition of the template resulted in the powder becoming ferromagnetic with the saturation magnetization and coercivity being 3.13 T and $76.6 \text{ kA} \cdot \text{m}^{-1}$ when the template proportion was 0.3. Additionally, the morphology and magnetic properties of the $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticle could be controlled by using low template proportions. The synthesized $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ would be useful in several technological applications such as soft magnets, low loss materials at high frequencies, and magnetic fluids.

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