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Properties of Co-Ferrite Nanoparticles Synthesized by Thermal Decomposition Method

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Co-ferrite nanoparticles have been synthesized by the decomposition of iron(III) acetylacetonate, Fe(acac)$_3$ and Co acetylacetonate, Co(acac)$_2$ in benzyl/phenyl ether in the presence of oleic acid and oleyl amine at the refluxing temperature of 295 °C/265 °C for 30 min. before cooling to room temperature. Particle diameter detected by PSA can be turned from 4 nm to 20 nm by seed-mediated growth and reaction conditions. Structural and magnetic characterization of Co-ferrite were measured by use of HRTEM, SAED (selected area electron diffraction), XRD and SQUID. The as-synthesized Co-ferrite nanoparticles have a cubic spinel structure and coercivity of 20 nm $CoFe_2O_4$ nanoparticles reached 1 kOe at room temperature and 18 kOe at 10 K.

Key words : Co-ferrite nanoparticles, coercivity, seed-mediated growth, forming gas

1. Introduction

The current and potential applications for nanoparticles are growing and cover a broad range of markets which is estimated to be 1000 times in 2010 compared with in 2005 [1, 2].

The cubic spinel structured $CoFe_2O_4$ is well known to oxide magnetic materials, and nowadays its nanoprticles may have numerous applications as soft and hard magnetic materials for bio, mechanical and electronic fields.

The synthesis of magnetic nanoparticles such as Fe, FePt, Co-ferrite, magnetite etc. has scientific and technical interest [3-6].

A wide variety of different techniques are used to synthesize magnetic nanoparticles; the chemical method, mechanical size reduction, gas phase synthesis etc. All of these have their own merits and faults.

The synthesis of Co-ferrite nanoparticles was reported by many researchers, Moumen etc. obtained 2–5 nm Co-ferrite nanoparticles by control the concenturation of reactants using oil-in-micelles [2]. Chinnasamy etc. [3] synthesized 8~40, 7~100 nm Co-ferrite particles and reported average switching field (H_p), magnetic crystalline constant (K) and coercivity (H_c) at room temperature. In magnetite nanoparticles, Sun etc. synthesized monodisperse 4 and 6 nm Fe_3O_4 particles, if phenyl ether was used as solvent, 4 nm Fe_3O_4 nanoparticles were separated, while the use of benzyl ether led to 6 nm Fe_3O_4 because of different boiling point [4, 5].

Here we report a simple chemical synthesis of Co-ferrite nanoparticles with average 2 nm size in diameter and a seed-mediated growth method to make larger Co-ferrite nanoparticles.

2. Experiment

To prepare $CoFe_2O_4$ nanoparticles, we used Fe(acac)$_3$ (acac = acetylacetonate) and Co(acac)$_2$ without further purification. Fe(acac)$_3$ and Co(acac)$_2$ were purchased from Sigma-Aldrich Co. Oleic acid and oleylamine are necessary for the formation of particles.

The synthetic experiments were carried out under Ar atmosphere, Fe(acac)$_3$ (2 mmol), Co(acac)$_2$ (1 mmol), 1,2-hexadecanediol (10 mmol) and benzyl ether (20 ml) were mixed in a flask equipped with a Ar in/outlet and a thermal probe. The mixture was heated to 100 °C by 5 °C per min. After refluxing for 20 min. at 100 °C, added oleic acid (6 mmol) and oleylamine (6 mmol) as surfactants, and refluxed for 30 min. at 265 °C.

Particle size of as-synthesized powders was measured by PSA (Particle Size Analyzer, NanoTrac 250). The

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morphology and phase identification of Co-ferrite nanoparticles were analyzed by use of HRTEM and XRD. Magnetic studies were carried out using VSM and SQUID magnetometer with temperature from 10 to 300 K.

3. Results and Discussion

Benzyl ether and Phenyl ether were used as solvents. In the case of benzyl ether, we can raise the fluxing temperature because of high boiling temperature than phenyl ether, but the fluxing temperature of last step in this procedure didn't affect the size of as-synthesized particles.

The particle size of as-synthesized powders measureded by PSA was average 2 nm. Figure 1 shows particle size distribution of as- synthesized Co-ferrite nanoparticles measured by PSA.

Figure 2 shows the TEM images of the 10 nm and 20 nm Co-ferrite nanoparticles grown by seed-mediated growth method. Seed-mediated process was carried out by adding the as-synthesized nanoparticles (average 2 nm shown in Figure 1), 4, 8 nm etc. as seeds in the same starting reagents and heated, and particle size increased ~2 nm or more in each seed-mediated reaction. This method has been recently applied to larger nanoparticles synthesis, through slow, continuous nucleation and fast, autocatalytic surface growth [7, 8].

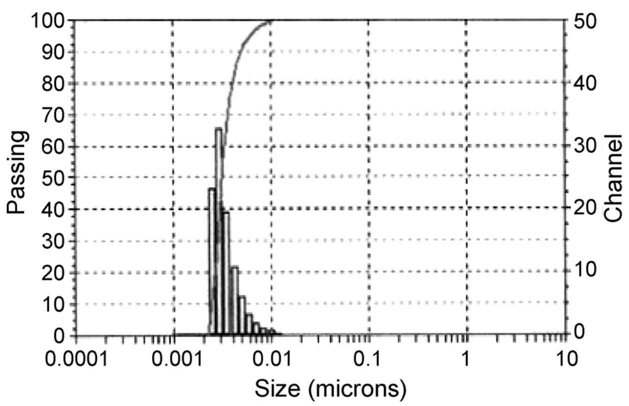

Fig. 1. Particle size distribution of as-synthesized Co-ferrite nanoparticles measured by PSA.

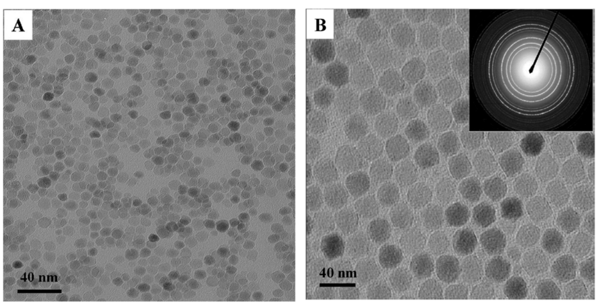

Fig. 2. TEM images and SAED patterns of Co-ferrite nanoparticles. (A) 10 nm (B) 20 nm.

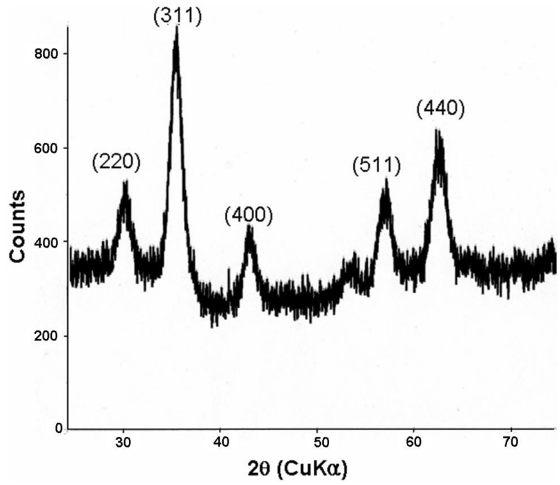

Fig. 3. XRD pattern of 10 nm Co-ferrite nanoparticles.

Figure 3 shows the XRD pattern of 10 nm Co-ferrite particles grown by seed-mediated growth method from 8 nm particles. It was found that all the peaks of nanoparticles synthesized by seed-mediated growth method

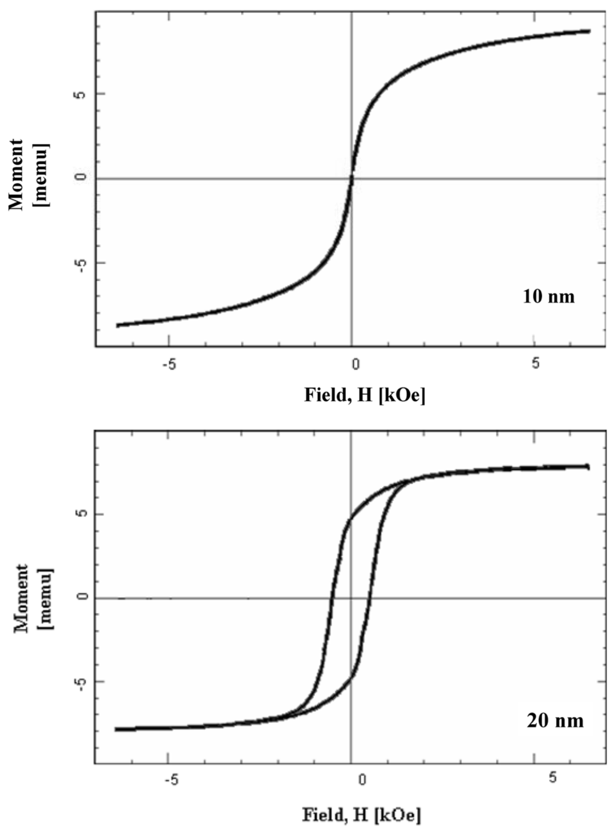

Fig. 4. Hysteresis loops of Co-ferrite nanoparticles at room temperature.

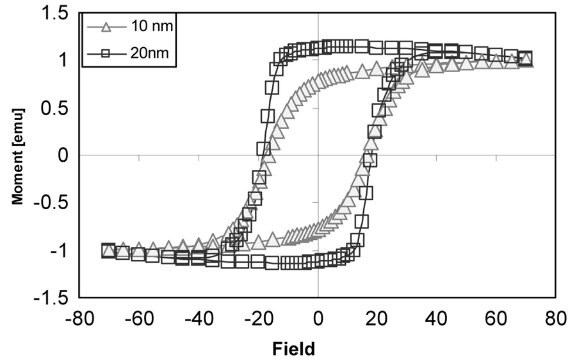

Fig. 5. Hysteresis loops of Co-ferrite nanoparticles at 10 K.

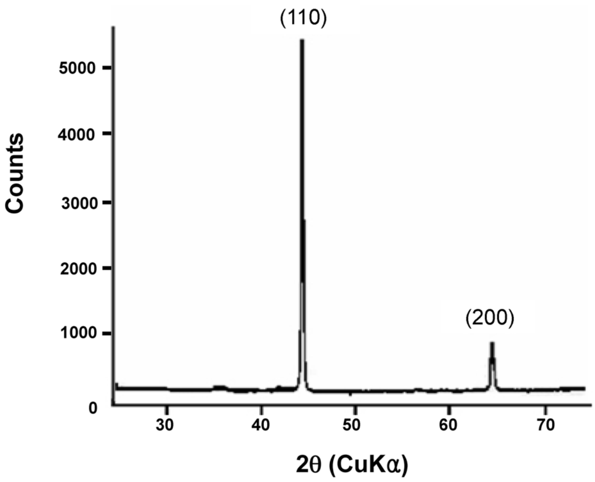

Fig. 6. XRD pattern of nanoparticles after annealing at 600 °C for 30 min. under forming gas.

were appeared typical patterns of the cubic structured Co-ferrite.

We can see the magnetic values of particles in Fig. 4 that the coercivity (H_c) on the hysteresis loop reveals 635 Oe and 1 kOe, respectively. And also Fig. 5 shows the coercive force of the same sized particles in Fig. 4, but at 10 K are 16.2 and 18.5 kOe, respectively, so at low temperature they all show strong magnetic behavior.

Cubic structured Co-ferrite transformed to cubic FeCo phase which has main (110) peak by annealing at 600 °C for 30 min. in the Ar+H_2 forming gas and the resulting of annealing is shown in Figure 6. It provides that FeCo nanoparticles obtained by reduction of Co-ferrite can be applied to the exchange-coupled nanocomposite magnets such as FePt/FeCo materials.

4. Conclusion

2 nm sized Co-ferrite nanoparticles were synthesized by chemical process and grew to 10 nm, 20 nm particles by seed-mediated growth method. Structural and magnetic characterization of Co-ferrite were measured by use of HRTEM, SAED, XRD, VSM and SQUID. The as-synthesized Co-ferrite nanoparticles have a cubic spinel structure and coercivity of 10 nm, 20 nm Co-ferrites reached 626 Oe, 1 kOe at room temperature and 16.2, 18.5 kOe at 10 K, respectively.

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