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SUPERPARAMAGNETIC RELAXATION IN COBALT FERRITE NANOPARTICLES SYNTHESIZED FROM HYDROXIDE CARBONATE PRECURSORS

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Abstract. Cobalt ferrite nanoparticles having various sizes have been synthesized from hydroxide carbonate precursors. The Mössbauer absorption patterns of all the samples consist of a ferromagnetic component superposed on a superparamagnetic doublet. The intensity of the superparamagnetic doublet is smaller for particles having large average particle size and the Curie temperatures increase linearly with increasing average particle size.

1. INTRODUCTION

Research on nanosized spinel ferrite particles currently has been received considerable attention during the past several years because of the difference of their physical and chemical properties from those of the free atoms or molecules, as well as from the properties of the bulk solids [1], and the wide range of potential applications toward magnetic recording media, ferrofluids, catalysts, medical diagnostics, drug delivery systems, and pigments in paints and ceramics [2,3].

In many electronics and magnetic applications, it is mostly important to fabricate a ceramic material of desirable microstructure, with a high sintered density, a small particle size and a narrow particle size distribution [4]. Various preparation methods have been developed in obtaining nanosized ferrite particles as follows: sonochemical reactions [5], sol-gel [6], microwave plasma [7], host template [8], corprecipitation [9] and microemulsion method [10].

The purpose of the present work is to report the dependence of the average particle size on the superparamagnetic phenomena observed in cobalt ferrite nanoparticles having various sizes, which have been synthesized from hydroxide carbonate precursors.

2. EXPERIMENTAL

All the materials used in this work were of the purest quality commercially available and were used without further purification: $FeCl_2 \cdot 6H_2O$ (Merk), $CoCl_2 \cdot 6H_2O$ (Merk), Na_2CO_3 (Hayashi), bis(2-ethylhexyl) sulfosuccinate sodium salt (Sigma). The mixed solution of Co(II) and Fe(II) ion in the molar ratio 1:2 was prepared by dissolving 0.01 mol $CoCl_2 \cdot H_2O$ and 0.02 mol $FeCl_2 \cdot 6H_2O$ in 300 mL distilled and deionized water.

The general method of the preparation of particles in these media consists mainly in mixing two microemulsions with the same structure and composition, except the content of their aqueous phase: one of them contains the mixture of the metallic salts (Co(II)/Fe(II)) in the stoichiometric molar ratio (1:2) in the water phase, and the other with the precipitating agent ($NaCO_3$) in excess with respect to the iron and cobalt salts.

A solution of AOT in isooctane was mixed with a mixed metal salt aqueous solution or a Na_2CO_3 aqueous solution which were previously prepared. The

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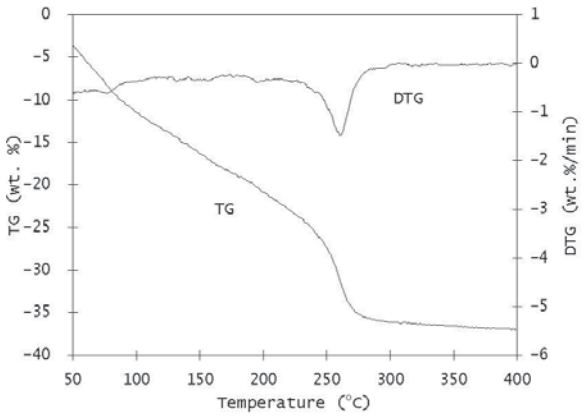

Fig. 1. TG and DTG analysis furves of ferrite precusor dried at room temperature.

preparation of the colloidal cobalt-iron hydroxide carbonate precursor particles was achieved by mixing and stirring the two microemulsion solutions at room temperature. The solution was stirred for one hour. After the synthesized magnetic precipitates settled down, the supernatant was removed and replaced by pure bulk solvent. Subsequently, the precipitate was washed with acetone and alcohol, and dried at room temperature. The samples were dried again at 110 °C for a day and then annealed isothermally for 6 hrs at 330 °C .

To identify the dried samples, Fourier transformation infrared (FTIR) spectra were recorded in air at room temperature using Bio-Rad 135 FTIR and KBr pellets. The as-dried precursors were characterized using TG/DTG (Chyo Balance, TRDA3-N) at a heating rate of 5 °C/min. The XRD analysis was performed using a powder diffractometer with CuK_{α} radiation to determine the crystal structure. TEM measurements were performed using Philips CM12/STEM. A Mössbauer spectroscopy of the electromechanical type was used in the constant-acceleration mode. A ^{57}Co single-line source in a rhodium matrix was used at room temperature.

3. RESULTS AND DISCUSSION

The precursor sample dried at 100 °C was characterized by FTIR spectroscopy. The characteristic feature of metal carbonate complex is the splitting of the doubly degenerated vibrations for ν_3(carbonate group C_S, unidentate) or ν_4(carbonate group C_{2v}, bidentate). The splitted bands correspond to asymmetric stretching and in-plane deformation vibration. The two bands of 1075 and 1352 cm^{-1} are significantly observed in the FTIR spectra of the precursor sample. Therefore, we confirm that metal hydroxide carbonate complexes are synthesized in reverse micelles.

The TG and DTG profiles of the as-dried precursor sample show significant transition about 260 °C (Fig.1). A continuous and broad peak is also observed between 50 and 240 °C. It is known that the thermal decompositions of iron (III) hydroxide carbonate and cobalt (II) hydroxide carbonate are registered around 135 °C and 240 °C. Fig. 1 shows that the weight loss from room temperature to 240 °C is due to the loss of residual solvent and water, and the decomposition of iron (III) hydroxide carbonate in the as-dried precursor powder. Sharp transitions in TG and DTG about 260 °C are caused by the decomposition of cobalt(II) hydroxide carbonate.

An analysis of the X-ray diffraction patterns showed that all the four samples had the cubic spinel structure. The particle sizes were analyzed by least-square fitting to a lognormal distribution [11]. The average particle sizes of the four samples obtained from these results are listed in Table 1.

Superparamagnetic behaviour of the particles was confirmed by line broadening and the presence of a pronounced central peak in Mössbauer absorption lines. The Mössbauer hyperfine spectra of all the four samples were taken at various temperatures from 15K to the Curie temperature. The Mössbauer lines at 15K for all the four samples are relatively sharp and consist of two well-defined sextets corresponding to Fe ions in tetrahedral and octahedral sites of the spinel crystal lattice. These lines become broader with increasing temperature until a pronounced central doublet appears, suggesting the appearance of superparamagnetic relaxation.

Fig. 2 shows the Mössbauer spectra taken at 150K for four samples. As evident from the figure,

Table 1. Average particle sizes and Curie temperature for the four nanosized cobalt ferrite particles.

sample	*Average particle size* (nm)	*Curie temperature* (K)
1	4.9	200
2	6.9	300
3	7.8	320
4	10.0	440

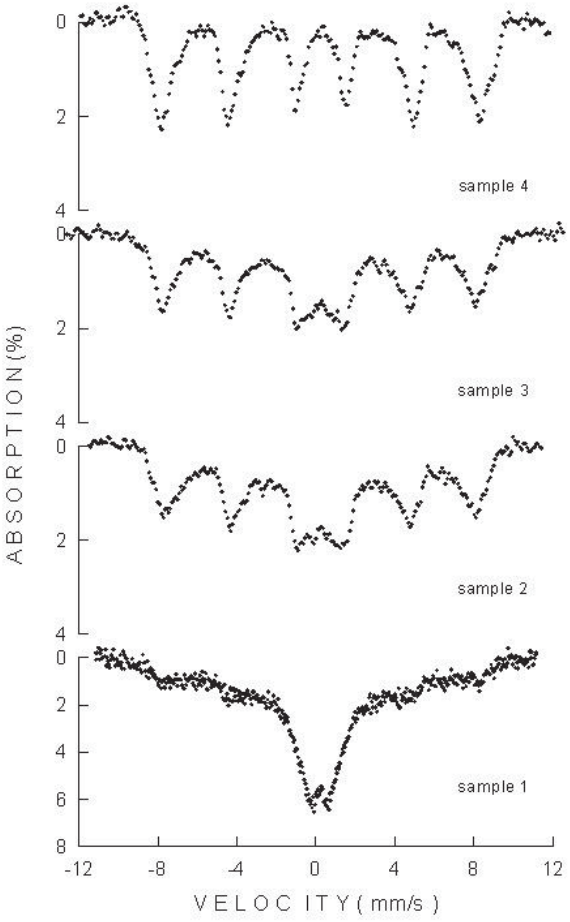

Fig. 2. Mössbauer spectra of the four samples having different sizes at 150K (Mössbauer spectra of sample 1 were obtained at 140K).

the spectrum for sample 1 shows a very strong central doubled superposed on a very weak sextet patterns. A pronounced central doublet for sample 2 and 3 appears near 150K, suggesting the appearance of superparamagnetic relaxation. On the other hand, there is no superparamagnetic doublet in the Mössbauer spectra for sample 4. From these results, one can see that the intensity of the sextet pattern decreases with decreasing particle size, while that of the central superparamagnetic doublet increases with decreasing particle size. This shows that the fraction of superparamagnetic particles increase with decreasing particle size. The results are in good agreement with those reported by earlier reports [12].

Curie temperature is defined as the temperature at which the magnetic hyperfine fields completely have collapsed. Therefore, we measured the temperature which the magnetic hyperfine fields completely had collapsed, and the obtained Curie temperatures for the four samples are listed in Table 1. Fig. 3 shows particle size dependence of the fluctuation. From this figure, one can see that Curie temperatures increase linearly with increasing the average particle size.

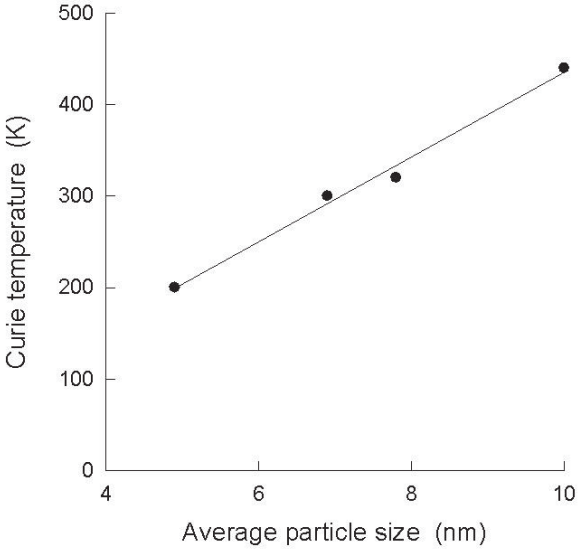

Fig. 3. Average particle size dependence of the Curie temperature.

4. CONCLUSIONS

Cobalt ferrite nanoparticles having sizes varying from 4.9 to 10.0 nm have been synthesized from hydroxide carbonate precursors. The crystal structure of the samples was investigated with XRD technique and the particle sizes and size distributions were examined by a transmission electron microscopy. The Mössbauer absorption patterns of all the samples consist of a ferromagnetic component superposed on a superparamagnetic doublet. The intensity of the superparamagnetic doublet is smaller for particles having large average particle size and the Curie temperatures increase linearly with increasing the average particle size.

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