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Crystallographic and Magnetic Properties of Nanocrystalline Cobalt Ferrite Particles

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Ultrafine cobalt ferrite particles have been synthesized using a microemulsion method. All peaks of X-ray diffraction patterns are fairly broad but correspond to a cubic spinel structure with the lattice constant 8.39 Å. The coercivity measured at 5 K is 15.1 kOe. The maximal magnetizations measured at 5 and 300 K are 13.2 and 10.7 emu/g, respectively. The particles behave ferrimagnetically at 5 K but superparamagnetically at 300 K. Superparamagnetic behavior of the particles at room temperature was confirmed by the coincidence of the M vs. H/T at different temperatures and the Mössbauer spectrum.

Key words : Ultrafine Particle, Superparamagnetism, Mössbauer

I. Introduction

Ultrafine particles have attracted considerable interest recently because of the wide range of potential applications, including magnetic recording media, ferrofluids, catalysts, medical diagnostics, drug delivery systems, and pigments in paints and ceramics.[1] The physical properties of the disordered system of such particles differ from those of the free atoms or molecules themselves as well as from the properties of the bulk solids.

Cobalt ferrite is specially interesting material for magnetic investigations. The bulk material of cobalt ferrite is known to be a typical oxide with a spinel structure and have a cubic magnetocrystalline anisotropy with three easy axes, [100][2]. The saturation magnetization is 93.9 emu/g at 5 K and 80.8 emu/g at 300K[3]. But, in the case of ultrafine cobalt ferrite particles, the different values of coercivity and saturation magnetization have been reported by several authors.[4-6]. The reason is that the properties of ultrafine particles depend on the particle size and the method of preparation.

In many electronic and magnetic applications, it is the most important to fabricate a ceramic material of desirable microstructure, with the high sintered density, the small particle size and the narrow particle size distribution.[7] Various techniques have been developed in synthesizing ultrafine ferrite particles. For example, there are precipitation/coprecipitation method,[8] sol-gel process,[9] hydrothemal processing[10] and microemulsion method.[11]

The purpose of the present work is to investigate the magnetic properties of ultrafine cobalt ferrite particles prepared by the microemulsion method. The term "microemulsion" was introduced by the English chemist J. H. Schulman in 1943, and the technique has recently been developed which enable the synthesis of nano-scaled magnetic particles using the micellar reaction method.[12,13]

II. Experimental Procedure

Ultrafine cobalt-iron hydroxide carbonate particles have been synthesized in aerosol OT/water/iso-octane inverse microemulsion systems. 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 both metallic salts(Fe(III)/Co(II)) in the stoichiometric molar ratio (2:1) in the water phase, and the other with the precipitating agent(Na_2CO_3) in excess with respect to the iron and manganese salts. The precipitate, cobalt-iron hydroxide carbonate particle, was achieved by mixing the two microemulsion; one containing Fe(III)/Co(II) and the other Na_2CO_3. The precipitate was washed with solvent and dried at about 100. The nanophase precursor particles were readily calcinated at about 330 into metal oxide.[14]

X-ray diffraction patterns of the sample were obtained with Cu-$K\alpha$ radiation. A SQUID magnetometer was used to study the magnetic properties of the particles in temperature range 5300 K and in fields up to 50 kOe. Mössbauer data was obtained with a constant acceleration spectrometer using a ^{57}Co(Rh) source at room temperature. The data were used to determine the superparamagnetic state and give information regarding the ionic state of iron ion in ultrafine cobalt ferrite particles.

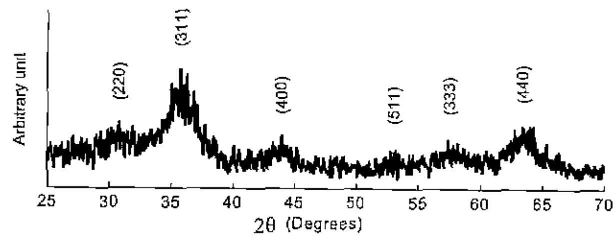

Fig. 1. X-ray diffraction pattern for the ultrafine Co ferrite particles at room temperature.

III. Results and Discussion

The X-ray diffraction pattern of ultrafine cobalt ferrite particles was taken at a slow scanning speed, *i.e.*, 0.02° advance in 2θ per min., and shown in Fig. 1. The pattern of the sample consists of fairly broad but still resolved peaks. Each peak in the patterns can be indexed on a cubic spinel structure. The broadening of all diffraction peaks indicates that the particle sizes prepared are very small. There is no evidence of extra crystalline or amorphous phases present. The lattice constant a_0 was found to be 8.39 Å by plotting a_0 (θ) versus the Nelson-Riley function[15] and extrapolating to θ=90°. The average particle size, determined from X-ray diffraction line-broadening using Scherrer's equation, is 46 Å.

The magnetization curves measured at 5 and 300 K is shown in Fig. 2. It is seen from the figure that the sample does not saturate even in a field of 50 kOe. The coercivity measured at 5 K is 15.1 kOe. The maximal magnetizations measured at 5 and 300 K are 13.2 and 10.7 emu/g, respectively. These maximal magnetization measured in the maximal field of 50 kOe is much lower than the saturation magnetization, 93.9 emu/g at 5 K and 80.8 emu/g at 300 K, for bulk cobalt ferrite at the same temperature. This reduction of the magnetization is examined by V. Blaskov *et al.* as relating to the possible local canting of magnetic moments due to the imperfect structure, and mainly to the contributions of the surface spins.[16] In this figure, there is hysterisis for the magnetization curve measured at 5 K: i.e., both retentivity and coercivity are not zero. This indicates that the particles behave ferrimagnetically at 5 K. But, at 300 K, the particles do have enough thermal energy to come to complete thermal equilibrium with the applied field during the time required for the measurement, and hysterisis does not appears. This indicates that the particles behave superparamagnetically at 300 K.

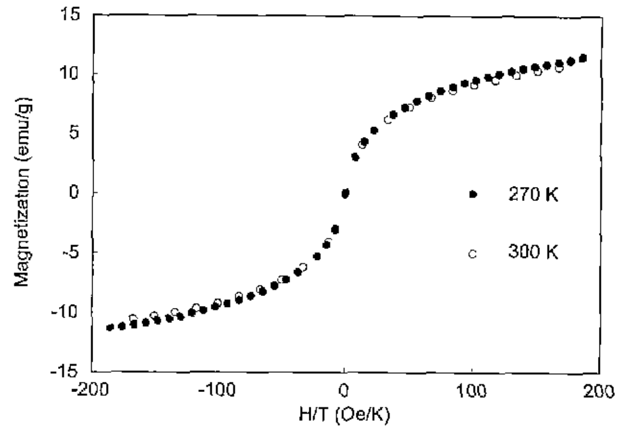

Fig. 3. Magnetization curves measured at 270 and 300 K superimpose when *M* is plotted as a function of *H*/*T*.

Superparamagnetic behavior of the particles is additionally confirmed by the coincidence of the M vs. H/T plots for 270 and 300 K shown in Fig. 3. The some discrepancies of the curves could be mainly related to the particle-size distribution[17]. The superparamagnetic behavior of the particles at room temperature is also made evident from their Mössbauer spectrum. Fig. 4 shows the Mössbauer spectrum of ultrafine cobalt ferrite particles measured at room temperature. The spectrum shows a typical paramagnetic doublet. Using a least-squares fitting procedure, a quadrupolar doublet was fitted to the spectrum. The isomer-shift value is 0.35 mm/s relative to iron metal, indicating that the iron ions are ferric.[18] The quadrupole splitting value is 0.78 mm/s.

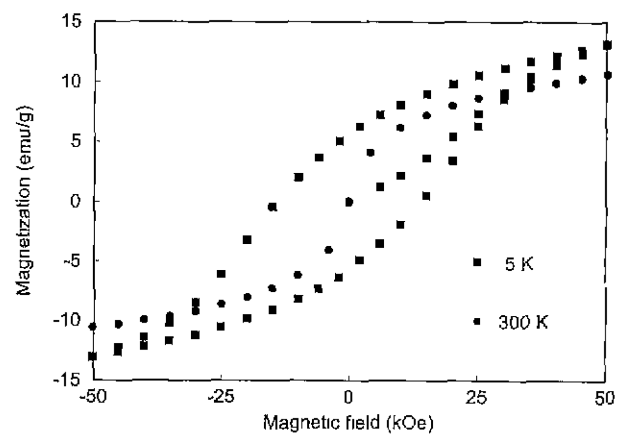

Fig. 2. Magnetization curves measured at 5 and 300 K.

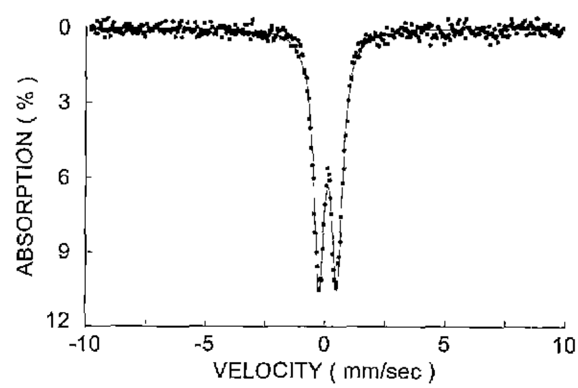

Fig. 4. Mössbauer spectrum measured at RT.

IV. Conclusions

Ultrafine cobalt ferrite particles have been prepared by the microemulsion method. The crystal is found to have a cubic spinel structure with the lattice constant 8.39 Å. All peaks of X-ray diffraction patterns observed are very broad but still resolved. The coercivity measured at 5 K is 15.1 kOe. The maximal magnetizations measured at 5 and 300 K are 13.2 and 10.7 emu/g, respectively. The particles behave ferrimagnetically at 5 K but superparamagnetically at 300 K. Superparamagnetic behavior of the particles at room temperature was confirmed by the coincidence of the M vs. H/T and the Mössbauer spectrum. The isomer-shift value is 0.35 mm/s relative to iron metal, indicating that the iron ions are ferric.

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