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Growth of ultra-fine cobalt ferrite particles by a sol–gel method and their magnetic properties

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Ultra-fine $CoFe_2O_4$ particles are fabricated by a sol–gel method and magnetic and structural properties of powders are investigated. Cobalt ferrite powders fired at and above 450 °C have only a single-phase spinel structure and behave ferrimagnetically. Powders annealed at 350 °C have a typical spinel structure and are of the paramagnetic and ferrimagnetic nature, simultaneously. With X-ray diffraction and Mössbauer spectroscopy measurements, the formation of nano-crystallized particles is confirmed when cobalt ferrite is annealed at 200 °C. In addition, the transition from the paramagnetic to the ferrimagnetic state is observed in samples fired at 200 °C as the measuring temperature decreases from the room to liquid nitrogen temperature. The magnetic behaviour of $CoFe_2O_4$ powders fired at and above 350 °C shows that an increase of the annealing temperature yields a decrease in the coercivity and, in contrast, an increase in the saturation magnetization. The maximum coercivity and the saturation magnetization of cobalt ferrite powders prepared by the sol–gel method are 2020 Oe and 76.5 e.m.u. g^{-1}, respectively. © *1998 Kluwer Academic Publishers*

1. Introduction

The preparation and characterization of nano-crystalline ferrite powders have been studied extensively in recent years [1, 2]. Ferrites are well-known magnetic compounds that have been studied for potential applications in microwave devices and as magnetic recording media using their novel physical properties [3, 4]. Cobalt ferrite, $CoFe_2O_4$, is a well-known hard magnetic material, which has been studied in detail due to its high coercivity (5400 Oe) and moderate saturation magnetization (about 80 e.m.u. g^{-1}) as well as a remarkable chemical stability and a mechanical hardness [5]. For using as high-density magnetic recording materials, the grain size of ferrite particles must be less than 10 nm to avoid the exchange interaction between neighbouring grains [6]. As the grain size becomes smaller, the magnetization direction of the ultra-fine ferrite powder cannot be fixed as in large crystals, but fluctuates spontaneously. It is very important to grow ferrite particles with homogenous magnetic properties.

Solution routines are commonly used to fabricate ultra-fine powders rather than a solid-state reaction process. One of the solution routines is the sol–gel method, which is known as a technique for the low-temperature synthesis of glass, ceramics and other materials. A few sol–gel methods for ultra-fine barium ferrite powders and LiZn-ferrite thin films have been introduced [7, 8]. One of the advantages of using the sol–gel method is the lower annealing temperature that enables smaller grained powders to be grown, e.g. nano-crystalline particles. Most researchers are interested in the growth of ultra-fine barium ferrite powders for their applications; however, ultra-fine cobalt ferrite particles have not yet been investigated to a great extent. Recently, the growth of nano-crystalline cobalt ferrite particles has been introduced by Blaskov *et al.* [2]. The particle sizes of their products (about 5 nm) were too small to behave ferrimagnetically and the effect of the change of the annealing temperatures has not been studied in detail.

In this study, a sol–gel procedure was used for the growth of ultra-fine cobalt ferrite powders and their magnetic and structural properties were characterized using an X-ray diffractometer, a vibrating sample magnetometer (VSM), a transmission electron microscope (TEM) and Mössbauer spectroscopy. X-ray diffraction and TEM measurements provide information about the formation of phases, the crystallization temperature and particle sizes. Mössbauer spectroscopy measurements were used to identify magnetic phases of ultra-fine ferrite powders. VSM measurements gave the saturation magnetization and coercivities of the

ferrite powders. The magnetic and structural properties of ultra-fine $CoFe_2O_4$ powders as a function of annealing temperature are presented in this paper.

2. Experimental procedure

A block diagram outlining the preparation process is shown in Fig. 1. Weighed amounts of $Co(CH_3CO_2)_2$ $4H_2O$ (1/200 mol) and $Fe(NO_3)_3 9H_2O$ (1/100 mol) were first dissolved in 2-methoxyethanol (100 ml) and water (15 ml) for 30 min by means of an ultrasonic cleaner. The solution was refluxed at 70 °C for 12 h to allow gel formation and then dried at 100 °C in a dry oven for 24 h. The dried powder was ground and annealed at temperatures ranging from 200–850 °C for 3 h in air. These compositions of samples fired at various temperatures were identified from an X-ray diffractometer with CuK_α radiation. Electron micrographs were taken using a transmission electron microscope. Mössbauer spectra of the powders were recorded at room and liquid nitrogen temperatures with a ^{57}Co source in a constant acceleration mode to identify magnetic phases of cobalt ferrite powders. Mössbauer spectra were analysed with Lorentzian line shapes. Coercivities and saturation magnetization of the ferrite powders as a function of annealing temperature were measured using a vibrating sample magnetometer.

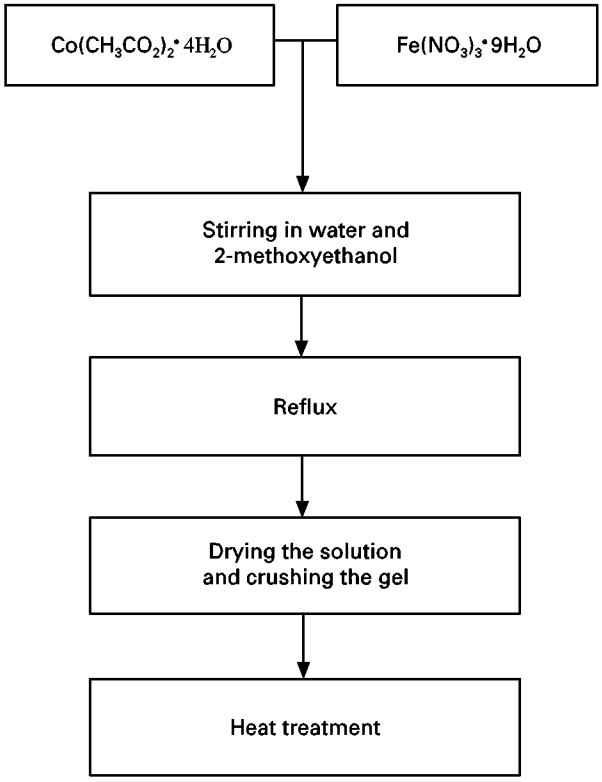

Figure 1 Preparation process for the cobalt ferrite powder.

3. Results and discussion

X-ray diffraction patterns of $CoFe_2O_4$ powders fired at various temperatures are shown in Fig. 2. The X-ray diffraction measurement shows that all peaks of $CoFe_2O_4$ powders annealed at and above 350 °C are consistent with those of a typical spinel structure of a cobalt ferrite powder prepared by a conventional solid-state reaction [9]. In addition, the increase in the annealing temperature yields an increased sharpness of the major peaks, that is, the growth of the larger grain size of cobalt ferrite powders. From Fig. 2d, the formation of $CoFe_2O_4$ powder is seen to start at and above 200 °C; however, the considerable broadening of all diffraction peaks of the samples fired at 200 °C suggests that the sizes of cobalt ferrite particles are expected to be relatively small. From the X-ray diffraction measurements of the dried powder, it is hard to say whether cobalt ferrite particles remain amorphous.

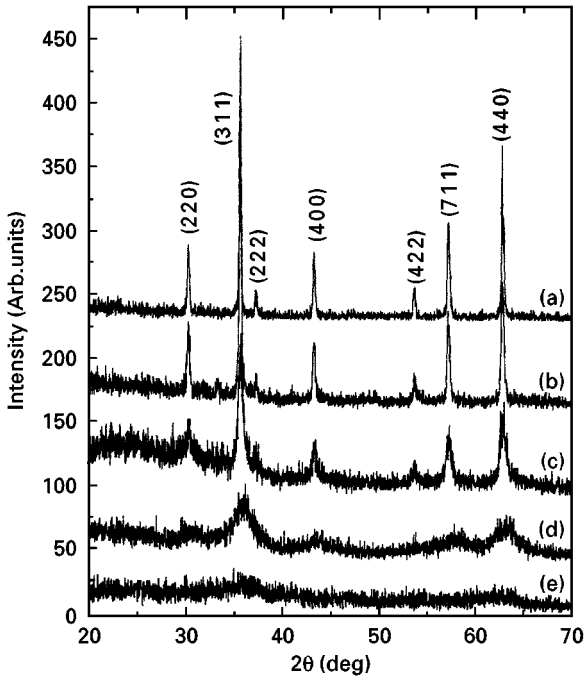

Figure 2 Changes in the X-ray diffraction patterns of $CoFe_2O_4$ powders at various annealing temperatures: (a) 750 °C, (b) 600 °C, (c) 350 °C, (d) 200 °C, and (e) pre-heated.

Mössbauer absorption spectra measured at room temperature for cobalt ferrite powders annealed at different temperatures are shown in Fig. 3a. Spectra of all samples annealed at and about 450 °C are fitted with two six-line subpatterns that are assigned to A-ions in tetrahedral sites and B-ions in octahedral sites of a typical spinel crystal structure. However, the spectrum for the sample annealed at 350 °C consists of two six-line subspectra and a large absorption of a doublet with very small magnetically split patterns, as shown in Fig. 3c. It is suggested that the sample fired at 350 °C is of the paramagnetic and ferrimagnetic nature, simultaneously. Half of the powder has a volume too small to maintain the ferrimagnetic property and the other has a size large enough to become ferrimagnetic. The ratio of the different magnetic phases is based on the calculated absorption ratio of the two subspectra. The Mössbauer spectrum measured at room temperature for the powder annealed at 200 °C, as shown in Fig. 3d, is mainly attributable to the paramagnetic behaviour of $CoFe_2O_4$ powders. That is, most of the cobalt ferrite particles fired at

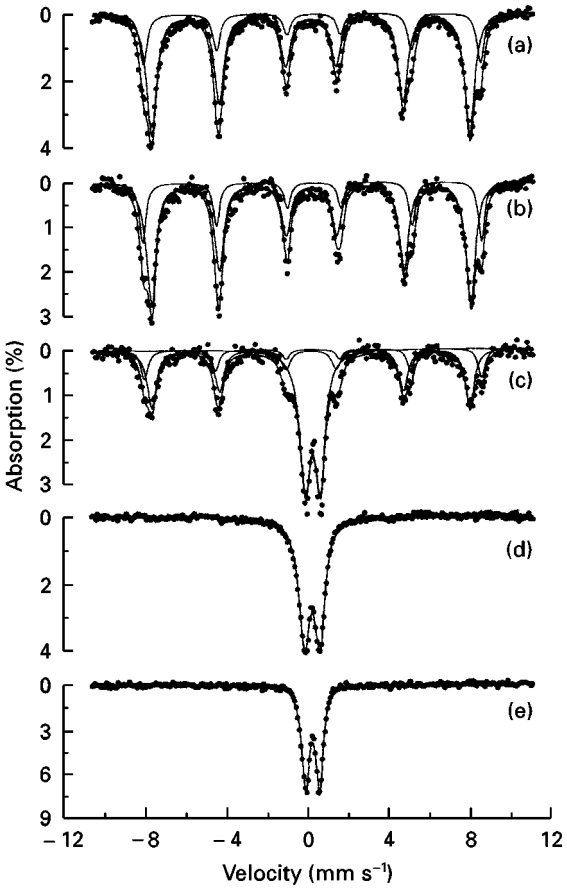

Figure 3 Room-temperature Mössbauer spectra of $CoFe_2O_4$ powders annealed at (a) 600 °C, (b) 450 °C, (c) 350 °C, (d) 200 °C, and (e) pre-heated.

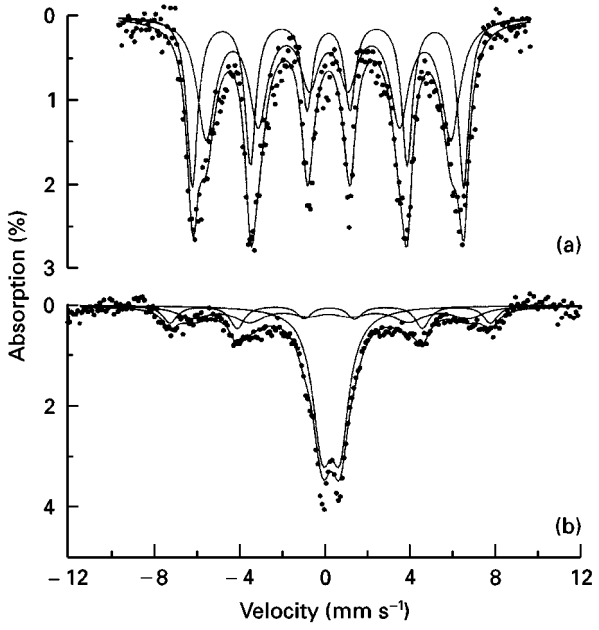

Figure 4 Mössbauer spectra recorded at (a) liquid nitrogen temperature, and (b) 200 K, for $CoFe_2O_4$ powders annealed at 200 °C.

200 °C are too small to become ferrimagnetic. The magnetic phase change of the ferrite powders can be explained with the variation of particle sizes as a function of annealing temperature. Fig. 4 shows the Mössbauer spectra of the sample fired at 200 °C that were taken at 80 and 200 K. The change in the spectrum is typical for superparamagnetic materials as the measuring temperature decreases. These Mössbauer results are similar to those obtained by Blaskov *et al.* [2]. The spectrum recorded at liquid nitrogen temperature is fitted with two six-line subpatterns; however, two subspectra have broad absorption lines that are related to the relaxation phenomena. The spectrum taken at 200 K is similar to that measured at room temperature for the sample fired at 350 °C, as shown in Fig. 3c. The transition of magnetic properties can be explained with the relation between the volume of the particle and the measuring temperature. As the measuring temperature is lowered, the critical volume to maintain the ferrimagnetic property becomes smaller so that some of the super-paramagnetic cobalt ferrite particles become ferrimagnetic [1].

Fig. 5 shows that the sample annealed at 350 °C consists of ultra-fine particles, of average diameter 12 nm. The particle size distribution is not uniform in the range of 6–20 nm and some of them are in the aggregate state. The broad size distribution is one reason why the sample annealed at 350 °C becomes paramagnetic and ferrimagnetic at room temperature, simultaneously [2].

The magnetic properties of annealed powders have been determined at room temperature using a vibrating sample magnetometer. Fig. 6 shows the annealing temperature dependence of saturation magnetization and coercivity in the maximal field of 15 kOe. The saturation magnetization increases drastically with increasing annealing temperature, however, the coercivity decreases when the annealing temperature is higher than 350 °C. This magnetic behaviour is related to the variation of the particle size. The sample fired at 200 °C shows only a small amount of saturation magnetization. With the Mössbauer spectroscopy measurement, it is known that most of the cobalt ferrite particles have particle sizes smaller than the critical size to maintain their magnetic properties.

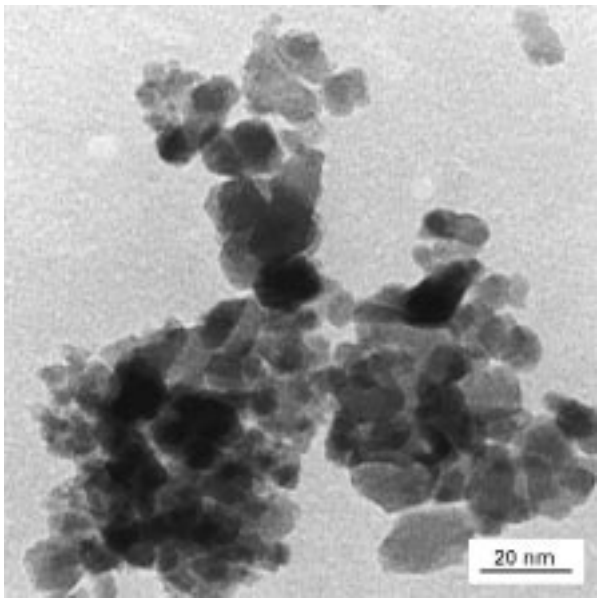

Figure 5 Transmission electron micrograph of cobalt ferrite annealed at 350 °C for 3 h.

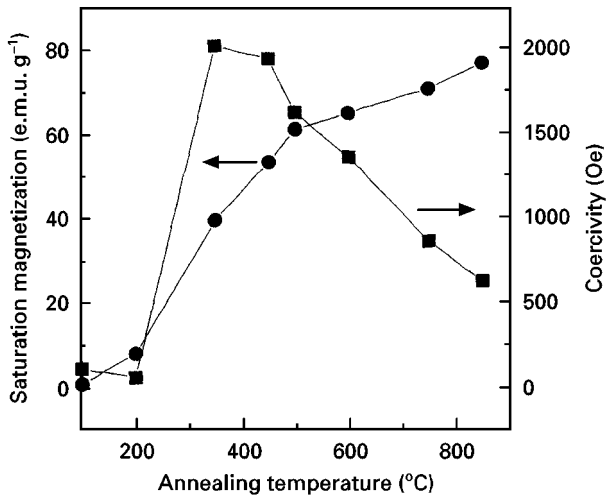

Figure 6 Changes of saturation magnetization and coercivities for $CoFe_2O_4$ powders as a function of annealing temperature.

However, when a strong magnetic field is applied to powders annealed at 200 °C, most of them remain paramagnetic due to the thermal fluctuation. Some of them are aligned along the applied field and become ferrimagnetic. The maximum coercivity and the saturation magnetization of cobalt ferrite powders are 2020 Oe and 76.5 e.m.u. g^{-1} in the maximum external field of 15 kOe, respectively. Our measured coercivities are in the range of 500 Oe to 4.5 kOe that have been reported previously [3] for the bulk of cobalt ferrite powders; however, the coercivities are relatively small compared with the theoretically estimated one [5]. The saturation magnetization is also small compared to the maximum one for bulk cobalt ferrite prepared by the combustion method [3].

4. Conclusion

Ultra-fine cobalt ferrite powders were grown using a sol–gel method and their structural and magnetic properties were investigated. X-ray diffraction and Mössbauer spectroscopy measurements revealed that $CoFe_2O_4$ powders fired at and above 200 °C began to crystallize and that the size of the cobalt ferrite powders annealed up to 200 °C was too small to be ferrimagnetic. That is, the samples behaved superparamagnetically at room temperature; however, at liquid nitrogen temperature they became ferrimagnetic. Samples annealed at 350 °C were of the ferrimagnetic and paramagnetic nature, simultaneously and the formation of the magnetically and structurally well-crystallized cobalt ferrite fired at and above 450 °C was confirmed. The saturation magnetization and the coercivity of ferrite powder strongly depended on the annealing temperatures and can be directly related to the variation of cobalt ferrite particle sizes. Cobalt ferrite powders prepared by our sol–gel method have magnetic properties necessary for use as high-density magnetic recording media.

Acknowledgements

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