

铁酸钴纳米微粒的共沉淀法制备和磁性质

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Cobalt Ferrite Nanoparticles: Coprecipitation Synthesis and Magnetic Properties

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Abstract: The cobalt ferrite nanoparticles were prepared by coprecipitation in the presence of poly (N-vinylpyrrolidone) (PVP) and characterized by XRD, TEM, EDX and magnetometry. XRD results suggest the formation of pure cobalt ferrite. The mean particle sizes of CoFe_2O_4 samples annealed at 400 °C and 600 °C were *ca.* 6 and 25 nm, respectively as obtained by transmission electron microscopy (TEM). The magnetic measurements indicated that nano-particles obtained at 400 °C were superparamagnetic while that prepared at 600 °C were ferri-magnetic.

Key words: cobalt ferrite; coprecipitation; magnetic properties

0 Introduction

Magnetic nanomaterials have attracted great attentions due to their novel properties and applications. It is well known that some magnetic properties, such as saturation magnetization and coercivity, depend on the particle size, shape and microstructure of the nanomaterials, which are determined to a great degree by the preparation method. New preparative methods are of intense current interest to give rise to nanopar-

ticles with well-controlled size, morphology and chemical homogeneity.

Ferrites are a group of technologically important magnetic materials. The nanoparticles of CoFe_2O_4 have received special attention due to the remarkable properties observed for bulk CoFe_2O_4 : strong cubic magnetocrystalline anisotropy, high saturation magnetization and coercivity along with good mechanical hardness and chemical stability^[1,2]. A variety of methods for preparation of CoFe_2O_4 nanoparticles have been re-

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ported such as coprecipitation^[3-5], hydrothermal^[6], microemulsion^[7,8], high-energy ball milling^[9], sonochemical^[10], combustion^[11] and sol gel^[12] processes. Coprecipitation without any additives is a very useful method to prepare CoFe_2O_4 nanoparticles^[3-5], however it usually gives larger particles with wide size distribution. The use of a polymer in the coprecipitation preparation of nanoparticles has been developed to solve this problem. Polymers such as poly(vinyl alcohol) (PVA) and polyacrylic acid (PAA) have been effectively used in the preparation of uniform nanoparticles of Fe_3O_4 ^[13] and $\text{BaFe}_{12}\text{O}_{19}$ ^[14], respectively.

We report herein the preparation of CoFe_2O_4 nanoparticles by the coprecipitation method using PVP and subsequent heat treatment. The magnetic properties of these new CoFe_2O_4 nanoparticles are also discussed.

1 Experimental

1.1 Preparation of cobalt ferrite nanoparticles

$\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ (1.2 mmol) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (2.4 mmol) were dissolved in 2-propanol (280 mL). PVP (K30) with addition of a 1:12 molar PVP/($\text{Fe}^{3+} + \text{Co}^{2+}$) into this solution at room temperature under vigorous stirring. The mixture was hydrolyzed by adding 420 mL of $0.03 \text{ mol} \cdot \text{L}^{-1}$ NaOH solution in 2-propanol at room temperature, and then refluxed for 5 h. The formed precipitates were centrifuged at 10 000 rpm for 20 min, and washed twice with deionized water and once with ethanol before being dried in air. The solid precursors were then annealed to 300 °C (denoted as S300), 400 °C (denoted as S400) and 600 °C (denoted as S600), respectively, at a rate of $5 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$, and were kept at the set temperature for 3 h in order to study the temperature effect on particle size and magnetic properties of the nanoparticles thus produced.

1.2 Characterization

The crystalline phase of the samples were investigated by powder X-ray diffraction (XRD) on a X'PERT X-ray diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$). The morphology and particle size of the samples were studied by a JEM-200CX transmission electron microscopy. The sample composition was determined by energy-dispersive X-ray analysis (EDX)

on a JEOL JSM-6400 scanning electron microscope. The measurement of magnetic properties was conducted on a Lakeshore 7307~9309 vibrating sample magnetometer.

2 Results and discussion

2.1 Characterization of CoFe_2O_4 nanoparticles

The X-ray diffractograms of S300, S400 and S600, which were obtained by annealing the solid precursor at 300, 400 and 600 °C, respectively, are shown in Fig.1. S300 shows a broad and unresolved peak (35°) (Fig.1a) suggesting that the crystalline phase had started to nucleate. S400 and S600 show the clear XRD patterns, which match the standard pattern of CoFe_2O_4 (JCPDS No.22-1086) (Fig.1b and 1c). The broad nature of the peaks implies the small particle size of S400 and S600. The mean particle sizes of S400 and S600 were roughly estimated from diffraction peak (311) by the Scherrer formula to be 6 nm and 25 nm, respectively. The calculated cell parameter (0.839 nm) obtained from diffraction peaks in Fig.1c was close to that of bulk ferrite (0.839 5(5) nm)^[12]. EDX analysis showed that the Co/Fe ratio in S300, S400 and S600 was *ca.* 1/2, in good agreement with the formula of CoFe_2O_4 .

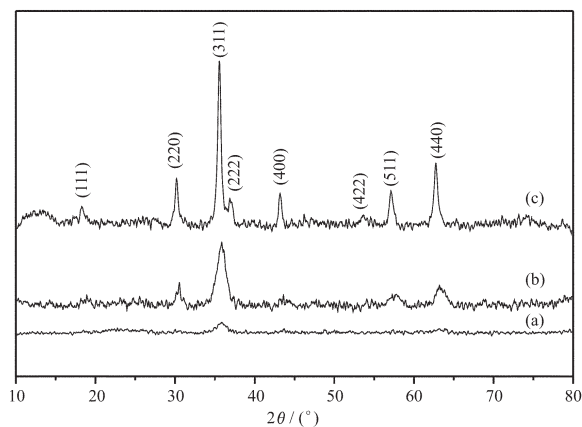


Fig.1 X-ray diffraction patterns for (a) S300, (b) S400 and (c) S600

The transmission electron micrographs for S400 and S600 are shown in Fig.2. They show that S400 and S600 contain highly aggregated particles with roughly estimated size of 5 and 30 nm, respectively. These results were in a good agreement with those of XRD studies of S400 and S600. Therefore, with the

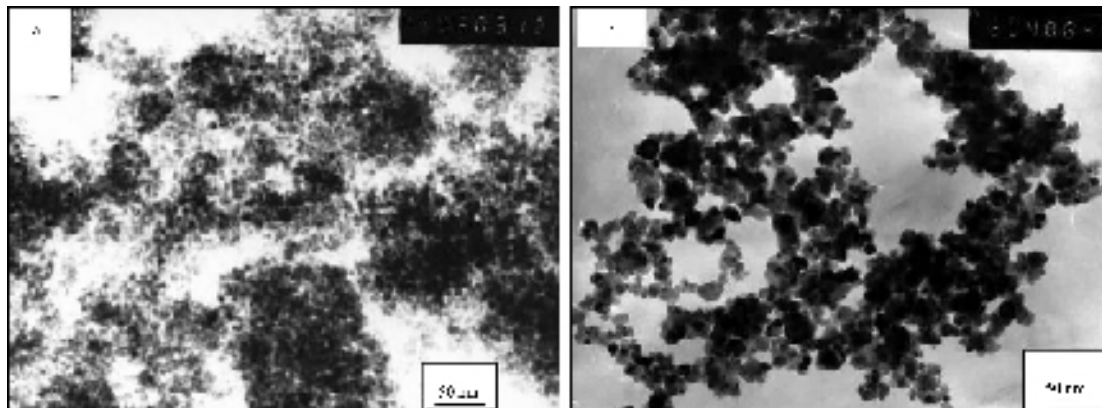


Fig.2 TEM images of samples (a) S400 and (b) S600

assistance of PVP, the coprecipitation and subsequent heat treatment gave CoFe_2O_4 nanoparticles with relatively narrow size distribution.

2.2 Magnetic properties

Room-temperature magnetization curves in fields up to 10 000 Oe for the as-prepared CoFe_2O_4 nanoparticles annealed at different temperature are shown in Fig.3. In the curve of S400, no hysteresis was found, indicating the superparamagnetic nature of S400. The distinguishable hysteresis phenomenon appeared for S600, suggesting that S600 particles were ferrimagnetic. The values of maximum magnetization in the field of 10 000 Oe were 18.6 and 55.5 $\text{emu} \cdot \text{g}^{-1}$ for S400 and S600, respectively. However, they were not saturated even at 10 000 kOe. The value for S600, even not saturated in the field of 10 000 kOe, is close to the saturation magnetization of bulk cobalt ferrite, 65 $\text{emu} \cdot \text{g}^{-1}$ [15]. When the annealing temperature rose from 400 °C to 600 °C, the sample changed from

superparamagnetic to ferrimagnetic with increase of the particle size. The coercivity for S600 was 723 Oe, which was smaller than that of bulk ferrite, 980 Oe [12]. The remanent magnetizations for S600 was 19.3 $\text{emu} \cdot \text{g}^{-1}$.

References:

- [1] Kodama T, Kitayama Y, Tsuji M, et al. *J. Appl. Phys.*, **1992**, **71**:5926~5929
- [2] Cornejo D R, Medina-Boudri A, Bertorello H R, et al. *J. Magn. Magn. Mater.*, **2002**, **242**:194~196
- [3] Medina-Boudri A, Bueno-Baqués D, Fuentes-Cobas L, et al. *J. Appl. Phys.*, **2000**, **87**:6235~6237
- [4] Ferreira T A S, Waerenborgh J C, Mendonca M H R M, et al. *Solid State Sci.*, **2003**, **5**:383~392
- [5] Kim Y, Kim D, Lee C S. *Physica B*, **2003**, **337**:42~51
- [6] CHEN Xing(陈 兴), DENG Zhao-Xiang(邓兆祥), LI Yu-Peng(李宇鹏), et al. *Wuji Huaxue Xuebao(Chinese J. Inorg. Chem.)*, **2002**, **18**(5):460~464
- [7] Rondinone A J, Samia A C S, Zhang Z J. *J. Phys. Chem. B*, **1999**, **103**:6876~6880
- [8] Ngo A T, Pileni M P. *Adv. Mater.*, **2000**, **12**:276~279
- [9] Mekala S R, Ding J. *J. Alloys Compds.*, **2000**, **296**:152~156
- [10] Shafi K V P M, Gedanken A, Prozorov R, et al. *Chem. Mater.*, **1998**, **10**:3445~3450
- [11] Yan C H, Xu Z G, Cheng F X, et al. *Solid State Commun.*, **1999**, **111**:287~291
- [12] Lee J G, Park J Y, Kim C S. *J. Mater. Sci.*, **1998**, **33**:3965~3968
- [13] Lee J, Isobe T, Senna M. *J. Colloid Interface Sci.*, **1996**, **177**:490~494
- [14] Chen D, Chen Y. *J. Colloid Interface Sci.*, **2001**, **235**:9~14
- [15] Bate G. *Ferromagnetic Materials, Vol.2*. Wohlfarth E P ed., Amsterdam Press, **1983**.431~507

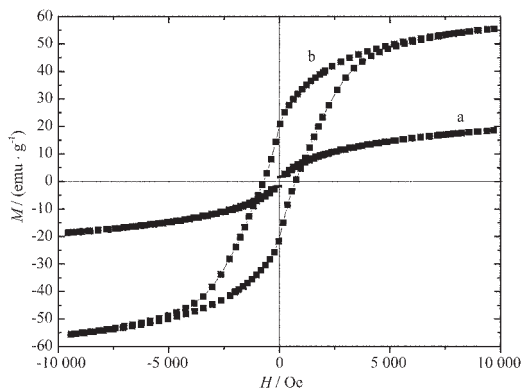


Fig.3 Magnetization versus applied magnetic field measured at room temperature for CoFe_2O_4 samples: S400(a) and S600(b)