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The structural and magnetic properties of cobalt ferrite nanoparticles formed *in situ* in silica matrix

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ABSTRACT

Cobalt ferrite ($CoFe_2O_4$) nanoparticles were successfully prepared *in situ* in an amorphous silicon matrix by sol–gel method. The magnetic and structural properties of the powders were investigated by varying the annealing temperature and the weight ratio of cobalt ferrite and silica. The samples, with 40 wt.% cobalt ferrite annealed at 873 K and above, are found in a single spinel phase structure and behave ferrimagnetically. However, the samples annealed below 773 K show superparamagnetic behavior. The magnetic parameters, such as saturation magnetization (Ms), remanent magnetization (Mr) and coercivity (Hc), increase monotonically with annealing temperature with the corresponding maximums of 21.09 emu g^{-1}, 5.671 emug g^{-1} and 1.15 kOe, respectively. The samples annealed at 1073 K are ferromagetic, except for the one with 10 wt.% cobalt ferrite, which is superparamagnetic. The corresponding maximum is 34.28 emu g^{-1}, 10.41 emu g^{-1} and 1207 Oe, respectively. The Ms and Mr increase with content of cobalt ferrite, except for the Hc values. The isomer shifts show that the iron atoms are ferric at the tetrahedral (A) and the octahedral (B). The nature of magnetic phase was analyzed by Mossbauer spectra.

1. Introduction

Cobalt ferrite is a cubic oxide with high coercivity and moderate saturation magnetization, as well as excellent chemical stability and mechanical hardness, which is a good candidate for recording media [1–4]. The main barrier for the application is the large media noise existing in polycrystallines. It has been confirmed that the refinement of the grain size is an effective way to reduce the noise [5]. For the use as high density magnetic recording materials, the grain size of ferrite particles must be smaller than 10 nm to avoid the exchange interaction between neighboring grains [6]. However, if the grain size becomes smaller than the critical size, the magnetization direction of the ultrafine ferrite powder can never be fixed as those in large crystals, but fluctuates spontaneously [1]. Recently, many approaches have been used to synthesize ferrite ultrafine powders [7–11], but the tendency of nanocrystallites to aggregate and coarsen at elevated temperature is still a critical obstacle. Hence, the methods of dispersing nanoparticles in a suitable matrix, such as resin [12], polymer films [13], and silica glass [14–16], have been applied to prevent from crystallite coarsening and particle aggregation. The sol–gel-derived amorphous silica matrix is an excellent host for supporting different type of guest nanoparticles. If nonreactive species were inserted into the initial solution (called "sol"), the solid oxide network gradually grew around the species during the sol–gel reaction and finally obtained a doped gel with dispersed species encaged in the pores of the gel [17].

In this study, cobalt ferrite ($CoFe_2O_4$) nanoparticles are dispersed *in situ* in silica matrix in a sol–gel process. The structural and magnetic properties of nanoscale composite powders as a function of annealing temperature and cobalt ferrite weight percentage are characterized by using an X-ray diffractometry, Mossbauer spectroscopy, and vibrating sample magnetometry (VSM).

2. Experimental

Nanocomposites of cobalt ferrite formed *in situ* in silica matrix are prepared via a sol–gel process using tetraethylorthosilicate (TEOS) and metallic nitrates as the precursors of the silica and the ferrite, respectively. Firstly, cobalt nitrate and iron nitrate were dissolved in the deionized water in a molar ratio of 1:2 according to the stoichiometric proportion of Co and Fe in $CoFe_2O_4$. Then the aqueous solution of metallic nitrates was mixed with TEOS and ethanol, in which the weight percentages (wt.%) of $CoFe_2O_4$ to SiO_2 were designed as 10%, 20%, 30%, 40%, 50% and 60%. The resulting mixture was placed in air for slow gelation. Then, the alcogel was put into an oven for further drying at 383 K for 24 h before being annealed at temperatures ranging from 673 K to 1073 K for 2 h, leading to samples for further characterizations. The phase of the samples is determined by the X-ray diffraction method (XRD) using a Rigaku D/MAX-3B powder diffractometer with Cu k_α radiation ($\lambda = 1.5418$ Å). The crystalline size is estimated by using the Scherrer equation: $d = k\lambda/(\beta \cos\theta)$. The Mossbauer spectra were recorded at room temperature to identify the magnetic

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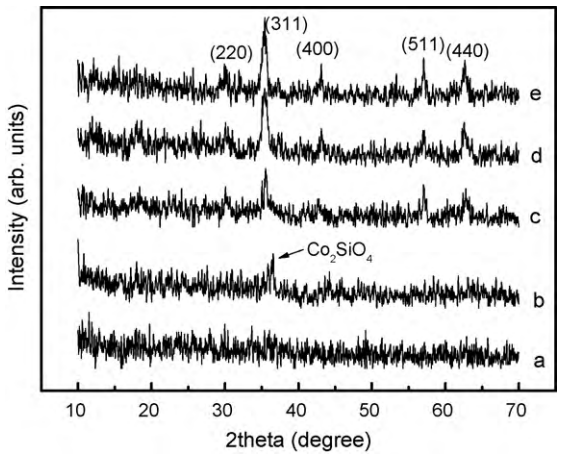

Fig. 1. XRD patterns of cobalt ferrite/silica samples annealed at (a) 673 K, (b) 773 K, (c) 873 K, (d) 973 K and (e) 1073 K and for 2 h, respectively.

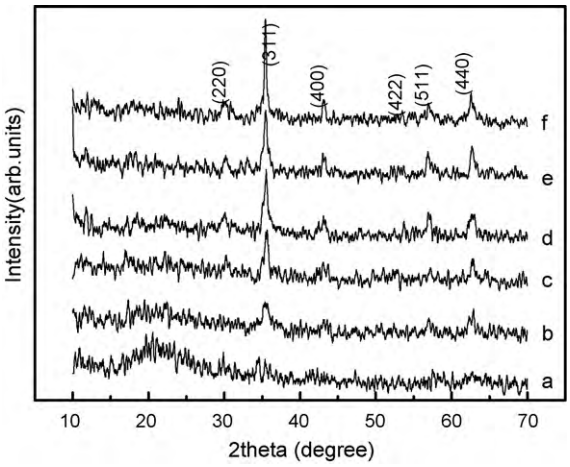

Fig. 2. XRD patterns of cobalt ferrite/silica samples with different cobalt ferrite weight percentage (a) $w = 0.1$, (b) $w = 0.2$, (c) $w = 0.3$, (d) $w = 0.4$, (e) $w = 0.5$ and (f) $w = 0.6$ annealed 1073 K for 2 h.

phase of cobalt ferrite powders using a constant acceleration mode with a 30 mCi ^{57}Co radioactive source in a rhodium matrix. The coercivity and the magnetization of the samples were measured using a vibrating sample magnetometer (VSM, LDJ 9600, USA) with a maximum field of 20 kOe.

3. Results and discussion

X-ray diffraction patterns of the samples with 40 wt.% cobalt ferrite annealed at various temperature for 2 h are shown in Fig. 1. The sample annealed at 673 K is amorphous, which remains unaltered at 773 K where the diffraction peak from (3 1 1) plane of cobalt ferrite becomes visible, suggesting that the particles of cobalt ferrite have been nucleated in the silica matrix with the appearance of the intermediate phase of Co_2SiO_4. After being annealed at 873 K, the peak of the intermediate phase disappears and the pure spinel structured product has been obtained. The intensity of peaks (3 1 1) of the samples increases with the annealing temperature indicative of the growth of crystals. The crystallite size is estimated as 9.2–12.6 nm from the strongest diffraction peak of (3 1 1) by the Scherrer equation in the annealing temperature range from 873 K to 1073 K, as shown in Table 1.

Similarly, we also investigated the evolution of XRD patterns of the samples with different cobalt ferrite contents annealed at 1073 K for 2 h shown in Fig. 2. Samples with 10 wt.% cobalt ferrite exhibit only shoulders at 23°, showing the feature of amorphous silica. The crystalline cobalt ferrite starts to form at and above the content of 20 wt.% with the appearance of sharper and narrower (3 1 1) diffraction peaks suggestive of the growth of crystallite size. The average crystallite size is estimated from the (3 1 1) diffraction peak to be 7–34 nm corresponding to the weight percentages from 20 wt.% to 60 wt.%, as shown in Table 2.

The morphology and microstructure of the sample with 40 wt.% $CoFe_2O_4$ annealed at 1073 K for 2 h were investigated by transmission electron microscopy (TEM). TEM and HRTEM (high resolution transmission electron microscope) micrograph are shown in Fig. 3(a) and (b), respectively, from which we can see that uniformly dispersed spherical $CoFe_2O_4$ crystalline nanoparticles are embedded in the silica network. The average particle size was approximately 15 nm estimated by a statistical method, closed to the value from XRD analysis, i.e. 12.6 nm. So the particles observed in TEM should be $CoFe_2O_4$ single crystallites. Fig. 3(c) is an associated selected area diffraction (SAD) pattern, where the diffraction dots and diffuse rings are assigned to the (3 1 1), (4 2 2) and (5 1 1) crystal plane of $CoFe_2O_4$ and amorphous silica, respectively.

Table 1
Room temperature Mossbauer parameters of samples with 40 wt.% cobalt ferrite annealed at various temperatures.

T (K)	Crystalline size (nm)	Relative area (%)		H_{hf} (KOe)		QS (mm s^{-1})		IS (mm s^{-1})	
		A	B	A	B	A	B	A	B
1073	12.6	47.1	52.9	473.3	428.8	0.004	−0.025	0.299	0.342
973	10.6	49.1	50.9	471.0	422.5	0.008	−0.025	0.303	0.328
873	9.20	42.3	57.7	472.3	412.4	0.002	−0.096	0.303	0.325
773	–	–	–	472.2	419.4	0.007	−0.029	0.306	0.334
	–	0.870	0.342						
673	–	–	–	–	0.855	0.336			

Table 2
Room temperature Mossbauer parameters of samples with various cobalt ferrite weight percent annealed at 1073 K for 2 h.

$CoFe_2O_4$ content (wt.%)	Crystalline size (nm)	Relative area (%)		H_{hf} (KOe)		QS (mm s^{-1})		IS (mm s^{-1})	
		A	B	A	B	A	B	A	B
10	–	–	–	426.2	484.4	−0.049	−0.039	0.302	0.319
	–	0.713	0.338						
20	8.70	36.4	63.6	462.8	413.8	−0.006	−0.019	0.302	0.312
30	11.8	46.0	54.0	473.0	426.7	0.016	−0.060	0.301	0.337
40	12.6	46.6	53.4	461.1	394.4	0.006	−0.041	0.305	0.356
50	19.5	48.7	51.3	473.2	435.9	0.009	−0.041	0.297	0.324
60	36.9	24.6	75.4	483.6	439.7	−0.006	−0.042	0.306	0.331