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Mössbauer study of cobalt ferrite nanocrystals substituted with rare-earth Y^{3+} ions

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ABSTRACT

Mössbauer spectroscopy is used to characterize the crystallite size and structure of $CoFe_{2-x}Y_xO_4$ ($x = 0$, 0.1, 0.3, 0.5) ferrite nanocrystallites synthesized by the sol–gel auto-combustion method. The effect of the substitution of Fe^{3+} ions by Y^{3+} ions on the structure of cobalt ferrite nanocrystallites is investigated. The Mössbauer spectra showed two sets of six-line hyperfine patterns for all the samples, indicating the presence of Fe in both A and B-sites. On increasing the concentration of doped Y, the hyperfine field strength and the isomer shift first increase and then decrease, whereas the quadrupole splitting continuously increases. The superparamagnetism was observed for all the samples and the change of ratio of the superparamagnetism component reflects the size of crystal grain.

1. Introduction

Ferrimagnetic cubic spinels, with the possession of the combined properties of magnetic materials and insulators, are found to be important in technological applications. Their electrical and magnetic properties depend on magnetic interactions and cation distribution in the two sub-lattices, i.e. tetrahedral (A) and octahedral (B) sites [1]. Cobalt ferrite, a well-known hard magnetic material, is also one of the candidates for high-density recording media. It has a high coercivity of ~5400 Oe, moderate saturation magnetization of about 80 emu/g and remarkable chemical stability and mechanical hardness, which are important properties for high-density recording media [2]. Nanosized spinel ferrite particles have received considerable attention during the past several years because of their interesting magnetic properties [3]. Co-ferrite crystallites in partially inverse spinel structure were represented as $(Co_xFe_{1-x})[Co_{1-x}Fe_{1+x}]\ O_4$, where x depends on thermal history and preparation conditions [4,5]. Cation distribution in octahedral and tetrahedral sites of the ferromagnetic spinel $CoFe_2O_4$ has been studied for two extremes: quenched and slowly cooled samples, respectively [6,7]. As the magnetic recording performance of the magnetic material is improved for well-crystallized materials with nanodimensions, the effect of rare-earth ions substitution seems to be extremely valuable in this aspect. The magnetic properties, cation distribution and grain size of $CoFe_2O_4$ crystallites substituted with rare-earth ions like Gd, Pr, Dy, Ho and Er are reported [8–10]. In the present paper, we studied the local environments of the Fe atoms of cobalt-rich yttrium-substituted cobalt ferrite powders $CoFe_{2-x}Y_xO_4$ for $x = 0$–0.5 as a function of yttrium concentration by transmission Mössbauer spectroscopy.

2. Experimental

The analytical grade $Fe(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Y(NO_3)_2 \cdot 6H_2O$ and citric acid ($C_6H_8O_7 \cdot H_2O$) were used as raw materials. Appropriate amounts of metal nitrates and citric acid were dissolved in deionized water to form a mixed solution, ammonia was added to adjust the pH of the solution around 7–8 under heating to 60 °C. Then the mixed solution was stirred for 1 h to form a sol. The sol was heated to 100 °C in order to obtain it as a dried gel. Then, the gel was heated to 500 °C for 1 h to obtain $CoFe_{2-x}Y_xO_4$ ($x = 0$, 0.1, 0.3, 0.5) as powder. Isothermal calcinations of $CoFe_{1.9}\ Y_{0.1}O_4$ were performed for 1 h at different

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annealing temperatures (Auto-combustion, 300, 500 and 700 °C), where the sample became black-brown colored. X-ray diffraction (XRD) measurements were carried out on Rigaku D/max Powder XRD with Cu K_α ($\lambda = 0.15406$ nm) radiation. The tube current was 150 mA, with a tube voltage of 50 KV. The Mössbauer spectra were recorded at room temperature on transmission OXFORD MS-500, using a ^{57}Co(Pd) source mounted in a constant-acceleration drive unit with a demarcated velocity with α-Fe. The Mössbauer spectra were fitted by with least-square methods according to the Lorentz pattern.

3. Results and discussion

Fig. 1 shows the XRD patterns of spinel ferrite Co $Fe_{2-x}Y_xO_4$ ($x = 0$, 0.1, 0.3, 0.5) after annealing at 500 °C. As can be seen, higher concentrations of doped Y led to lower crystallinity of the sample. This is because more dopant concentration leads to a higher potential barrier that rare-earth ion has to overcome for entering the spinel crystal lattice. As a result, crystal lattice distortion and local strains appeared. Table 1 shows that as the concentrations of doped Y increase, lattice constant decreases. This is because more dopant concentration leads to higher defect and hole in the crystal structure, which lower the degree of alignment of lattice fringes. According to the Scherrer equation, the sizes of crystal grain of $CoFe_{2-x}Y_xO_4$ ($x = 0$, 0.1, 0.3, 0.5) are from 23.4 to 6.1 nm. More-doped Y resulted in the smaller size of crystal grain, indicating that doped Y suppresses crystal grain's growth. Moreover, when the amount of doped Y is more than 0.2, the unexpected $YFeO_3$ forms (as shown in the XRD pattern(c) and (d) in Fig. 1), which makes the formation of the spinel structure more difficult. Thus, the pure cobalt ferrite of spinel structure can be obtained when the concentration of doped Y is below 0.2.

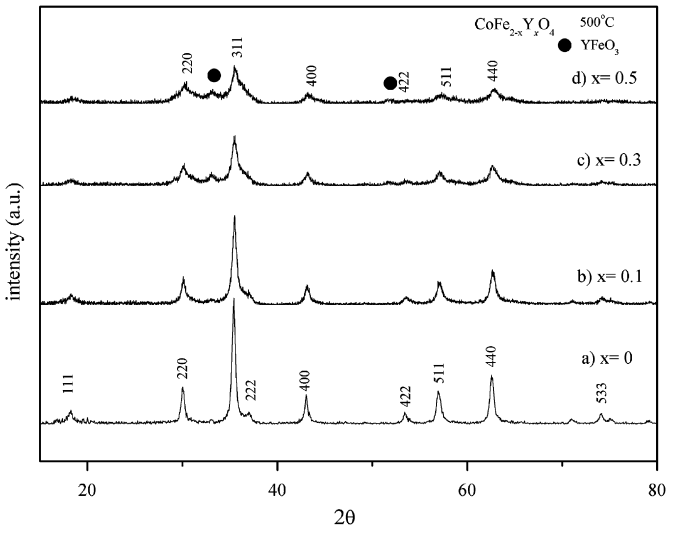

Fig. 1. XRD patterns of Co $Fe_{2-x}Y_xO_4$ after annealing at 500 °C: (a) $x = 0$ (b) $x = 0.1$ (c) $x = 0.3$ and (d) $x = 0.5$.

Table 1
Relationship of lattice constant of cobalt ferrite doped Y with x value and annealing temperature.

$CoFe_{2-x}Y_xO_4$	Lattice constant (nm)	Annealing temperature (°C)	Lattice constant ($CoFe_{1.9}Y_{0.1}O_4$) (nm)
$x = 0$	0.8375	Auto-combustion	0.8374
$x = 0.1$	0.8366	300	0.8360
$x = 0.3$	0.8353	500	0.8366
$x = 0.5$	0.8358	700	0.8379

The lattice constant is calculated according to five indices of crystallographic plane and angle of diffraction for all the samples.

Fig. 2 displays the XRD patterns of $CoFe_{1.9}Y_{0.1}O_4$ obtained after annealing at different temperatures (auto-combustion, 300, 500 and 700 °C) as the annealing temperature increases the width of diffraction peaks becomes narrower and the intensity increases indicating higher crystallinity due to smaller microscopic strains in the lattice upon heating. Table 1 shows that as the annealing temperature increases, the lattice constant of $CoFe_{1.9}Y_{0.1}O_4$ increases. As can be seen, higher annealing temperature helps Y to enter the crystal lattice.

Fig. 3 shows the Mössbauer spectroscopy of $CoFe_{2-x}Y_xO_4$ ($x = 0$, 0.1, 0.3, 0.5) after annealing at 500 °C, and Tables 2 and 3 list the fitted data. Fig. 4 shows two Fe sites in the crystal structure, which helps one to understand the following discussion. The magnetic hyperfine split component was only found in the $x = 0$ spectrum of a sample, whereas the spectra of the Y-doped samples (b–d) showed a quadrupols splitting, which has an increased area, which becomes more significant when the

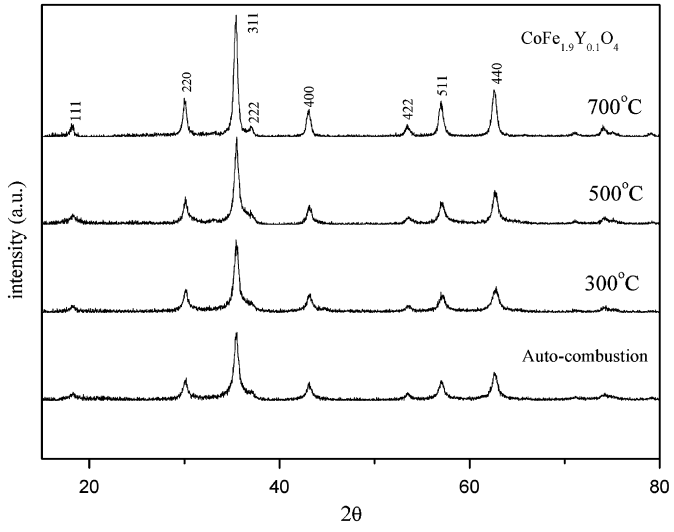

Fig. 2. XRD patterns of $CoFe_{1.9}Y_{0.1}O_4$ annealed at different temperatures: auto-combustion at 300, 500 and 700 °C.

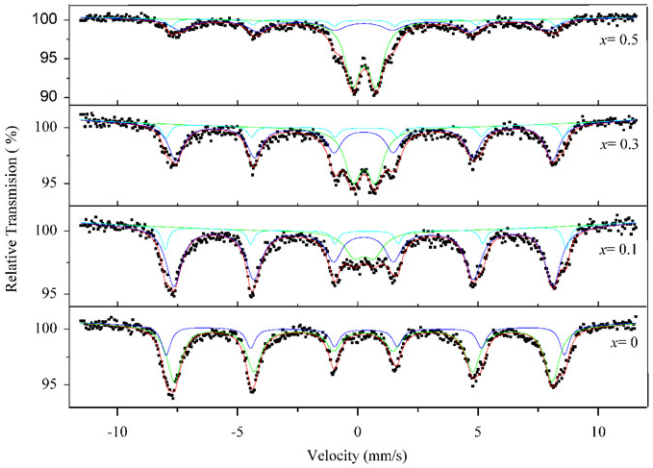

Fig. 3. Mössbauer spectra of Co $Fe_{2-x}Y_xO_4$ after annealing at 500 °C and its fitting curves (blue, red and green), where (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.3$ and (d) $x = 0.5$.