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Structural and magnetic studies of Mg substituted cobalt composite oxide catalyst $Co_{1-x}Mg_xFe_2O_4$

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ABSTRACT

The article synthesized the $Co_{1-x}Mg_xFe_2O_4$ sample of single phase spinel structure with sol-gel auto-combustion. The lattice parameter increases, the X-ray density and average crystal sized decrease with an increase in the Magnesium content. The average crystallite size increases with an increase in the calcinating temperature. The ferrimagnetic behaviour of all samples is confirmed by room temperature Mössbauer spectra, and the magnetic hyperfine field decrease with an increase in Mg substitution, which can be attributed to the decrease of the A-B super-exchange interaction. The calcining temperature influences the magnetic hyperfine field and the distribution of Fe^{3+} ions at the tetrahedral A site and the octahedral B site. The saturation magnetization and coercivity have significant change with increasing Mg^{2+} ions, the decrease in the coercivity suggests that the sample towards soft magnetic material transformation. Magnesium substituted for Cobalt both having preference to occupy B sites (octahedral sites) reduces. Besides that increased particle size with Mg substitution causes increased distance, and reduces magnetic moment of the B sublattice.

1. Introduction

Ferrite is an important magnetic material. $CoFe_2O_4$ is a kind of hard magnetic ferrite materials [1]. Some of typical physical parameters of $CoFe_2O_4$ are listed: a moderate saturation magnetization of about 80 emu/g, a high coercivity of 5000 Oe. Moreover, cobalt ferrites exhibit high electromagnetic performance, show a distinct magneto-optic effect, and hold excellent chemical and physical properties [2]. Therefore, $CoFe_2O_4$ has been widely used in the field of recording materials [3,4]. The above properties of cobalt ferrites can be further tuned by partial replacement of non-magnetic magnesium cations. Franco et al. reported that the saturation magnetization and the effective anisotropy constant of $Co_{1-x}Mg_xFe_2O_4$ ferrite nano-materials decreased with increasing the substitution of Co^{2+} ion by nonmagnetic Mg^{2+} ions in the spinel structure [5]. The decrease in the saturation magnetization is due to a stronger preference of nonmagnetic Mg^{2+} in the octahedral sites than Fe^{3+} and Co^{2+}, which leads to a decrease in super interactions between the tetrahedral sites and octahedral sites in the spinel structured materials [6]. Dippong et al. synthesized $Co_xFe_{3-x}O_4$ ferrites and $CoFe_2O_4/SiO_2$ nanocrystallites using sol-gel method, and observed the structural and magnetic properties of samples [4,7]. Joshi et al. synthesized $Co_{1-x}Mg_xFe_2O_4$ ferrites by coprecipitation, and observed that the Mössbauer spectrum consisted of paramagnetic doublet and magnetic sextets for wet samples, and the ferrites were in an ordered magnetic structure after calcination at a high temperature [8]. Ahmed et al. further concluded that the crystal size and the magnetic properties of the Mg^{2+} -substituted cobalt magnesium ferrites were enhanced [9]. The variation of lattice parameter was interpreted on the basis of cation distribution, the general trend of molar magnetic susceptibility with Mg content is the decrease, which was also interpreted on the basis of redistribution of iron ions between the two sublattices.

In the previous studies, hydrolysis method, wet chemical method and standard ceramic preparation techniques have been used to prepare the $Co_{1-x}Mg_xFe_2O_4$. Ferrites prepared by Nlebedim et al. have a secondary phase, which influences the magnetism of the sample [6]. Due to the sol-gel auto-combustion method not only has excellent sinterability with a single phase, but also requires relatively simple

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equipment at a lower cost [10]. Furthermore, Ahmed et al. did not use the Mössbauer spectroscopy to investigate the magnetic properties of $Co_{1-x}Mg_xFe_2O_4$ ferrite [9]. The magnetic properties of the ferrite can be modified by replacement of metal cation, especially nonmagnetic ion substitution. In addition, the non-magnetic Mg^{2+} ions can be distributed at the tetrahedral A-sites and octahedral B-sites, the magnetism will change when cations take the different spinel lattice. Therefore, the variation structural and magnetic properties of cobalt ferrite powders can be investigated by the replacement of non-magnetic magnesium (Mg^{2+}) cations.

In the current work, we aimed to investigate the variation structural and magnetic properties of cobalt ferrite powders $Co_{1-x}Mg_xFe_2O_4$ (x = 0, 0.1, 0.3, 0.5, 0.7, 0.9) by partial replacement of non-magnetic magnesium cations. The main objectives of this study were four folds: (1) to synthesy the sample of single phase spinel structure with sol-gel auto-combustion and investigate the influence of doping content on the structure and calcining temperature on the structure; (2) to synthesy the sample of the grains are homogeneously distributed and well crystallized, and the average grain size of ferrite powers are in the nanometer scale; (3) to investigate the magnetic properties of the different doping content and calcining temperature sample by Mössbauer spectroscopy, and confirm the magnetic behavior for all samples; (4) to investigate the influence of doping content on both saturation magnetization and coercivity.

2. Materials and methods

2.1. Sample preparation

Magnesium substituted cobalt ferrite of composition $Co_{1-x}Mg_xFe_2O_4$ (x = 0, 0.1, 0.3, 0.5, 0.7, 0.9) were prepared by the sol-gel auto-combustion method [11]. The raw materials, $Co(NO_3)_2 \cdot 6H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, citric acid ($C_6H_8O_7 \cdot H_2O$) and ammonia ($NH_3 \cdot H_2O$), were of analytical grade. The molar ratio of metal nitrates to citric acid was adjusted to be 1:1 [11]. Deionized water was added in citric acid and metal nitrate to form two solutions. Ammonia was used to adjust the pH value of the solution of metal nitrate to be about 7. The mixed solution was placed in a thermostat water bath at 80 °C, and the solution was stirred until it became dried gel. Citric acid solution was continuously dropped into the metal nitrate solution during the process of heating. The gel was further dried at 120 °C in a dry-oven for 2 h. A small amount of alcohol was added for sample ignition in air, and the samples became fluffy after burning in an auto - combustion way. The fluffy material was ground into powder and the powder was annealed in a muffle furnace according to two different temperatures (400 and 800 °C).

2.2. Characterization

The structure and crystallite sizes were characterized by XRD (D/max-2500 V/PC, Japan) in the 2 θ range 20–70 ° using Cu-K_α radiations (λ = 0.15405 nm). The crystallite sizes were calculated with Scherrer's formula: D = kλ/hcos θ where D, k, h, θ are the average diameter, the shape factor, the half intensity width of the relevant diffraction peak and diffraction angle, respectively. The micrographs were obtained by SEM (Hitachi S-4800). Saturation magnetization was measured by Quantum Design MPMS series XL-7. The Mössbauer spectrum was performed by Fast Com Tec PC-mossII, in constant acceleration mode. The γ-rays were provided by a ^{57}Co source in rhodium matrix. The hyperfine parameters, magnetic hyperfine field (H_{hf}), isomer shift (I.S.), quadrupole doublet (Q.S.), relative area (A_0) and line width (Γ), were obtained by the fitted spectra through Mösswinn3.0 program and calibration is relative to 25 μm thick high purity alpha iron.

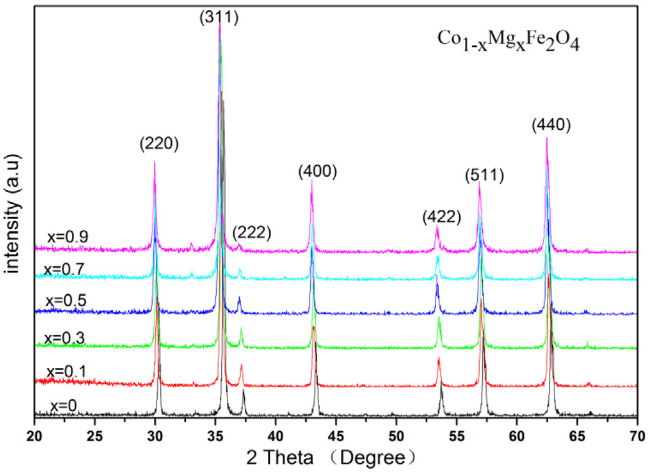

Fig. 1. XRD patterns of $Co_{1-x}Mg_xFe_2O_4$ annealed at 800 °C.

3. Results and discussion

3.1. The X-ray diffraction analysis

The X-ray diffraction (XRD) spectra of $Co_{1-x}Mg_xFe_2O_4$ (x = 0, 0.1, 0.3, 0.5, 0.7, 0.9) ferrites calcined at 800 °C for 3 h are shown in Fig. 1. The XRD patterns show a single phase spinel structure for all samples and all diffraction peaks can be indexed to the cubic spinel structure $CoFe_2O_4$ and $MgFe_2O_4$ can be indexed by JCPDS Card No. 22-1086 and JCPDS Card No. 73-2211, respectively. The impurity in these samples is undetectable. The lattice parameters for all samples are summarized in Table 1 and it has no significant change when the magnetism content increases from 0.0 to 0.9, which is probably due to a similar ionic radius of Co^{2+} and Mg^{2+}. It is also noticed that the lattice parameter increases slightly with an increase in the substitution of Co^{2+} by Mg^{2+}. The lattice parameter increases can be interpreted as a change of the cation occupancy, which agrees well with the Ahmed's study [9].

The X-ray density was determined from the formula [12]:

$$\rho_x = \frac{8M}{Na^3} \tag{1}$$

where M is the relative molecular mass, N is the Avogadro's constant and a is the lattice parameter. The calculated X-ray density is shown in Table 1 for all samples. A decrease in the X-ray density is clearly seen as the extent of Mg^{2+} substitution increases. From the Eq. (1), there are two factors contributing to the decrease in the X-ray density. The relative molecular weight, M, decreases as more Co^{2+} is replaced by Mg^{2+} since the atomic weight of Co is greater than that of Mg. Another factor is the increasing lattice parameter as the Mg^{2+} content increases, which leads to a decrease in the X-ray density.

The crystallite size is determined from the highest intensity peak (3 1 1) of the XRD patterns using the Debye Scherrer formula [13]:

Table 1
Lattice parameters, Average crystallite size, density date of $Mg_xCo_{1-x}Fe_2O_4$ annealed at 800 °C.

Sample (x)	Lattice parameter (Å)	Average Crystallite size (nm)	Density ($g\ cm^{-3}$)
0	8.355	56	5.347
0.1	8.386	46	5.208
0.3	8.387	48	5.050
0.5	8.406	48	4.860
0.7	8.401	49	4.713
0.9	8.408	36	4.547