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Structure and magnetic properties evolution of cobalt–zinc ferrite with lithium substitution

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ABSTRACT

$Li_xCo_{0.5}Zn_{0.5-x}Fe_2O_4$ ($0.0 \le x \le 0.3$) is obtained by calcining precursor oxalates at 900 °C in air. The precursor and its calcined products are characterized by thermogravimetry and differential scanning calorimetry, X-ray powder diffraction, scanning electron microscopy, and vibrating sample magnetometer. A high-crystallized $Li_xCo_{0.5}Zn_{0.5-x}Fe_2O_4$ with a cubic structure is obtained when the precursor is calcined at 900 °C in air for 3 h. Lattice parameters decrease with the increase of Li^+ addition amount. The magnetic properties of $Li_xCo_{0.5}Zn_{0.5-x}Fe_2O_4$ depend on Li^+ doped amount and calcination temperature. $Li_{0.3}Co_{0.5}Zn_{0.2}Fe_2O_4$ obtained at 900 °C has the highest specific saturation magnetization value, 70.24 emu/g. However, $Li_{0.3}Co_{0.5}Zn_{0.2}Fe_2O_4$ obtained at 800 °C has the highest remanence (8.29 emu/g) and coercivity value (97.8 Oe).

1. Introduction

Cobalt ferrite ($CoFe_2O_4$) with inverse spinel structure is a well-known hard magnetic material, which has many unique properties, such as high coercivity, large magnetocrystalline anisotropy, moderate specific saturation magnetization, high mechanical hardness, high chemical stability, and high Curie temperature (~520 °C). Thus, $CoFe_2O_4$ has been widely used as audio and videotape, high-density digital recording disks, magnetic separation, ferrofluids, catalysts, magnetic resonance imaging, gas sensor, and drug targeting [1–11], etc. The doped $CoFe_2O_4$ can improve its magnetic performance. Therefore, doped $CoFe_2O_4$ caused great concern.

Various synthetic approaches have been pursued to prepare spinel $CoFe_2O_4$ and doped $CoFe_2O_4$ with different particle sizes and morphological features, including solid-state reaction at low temperatures [1–3], sol–gel synthesis [4,6,12–14], co-precipitation [5,15,16], hydrothermal treatment [7,17], ball milling method [8,18,19], ceramic method [20,21], citrate precursor method [22,23], solvothermal method [24,25], microwave combustion method [26,27], and polyol process [28]. The crystallite diameter, morphology, and crystalline phases of $CoFe_2O_4$ associated with its performances highly depend on the synthesis method, calcination temperature, and doping elements. Lopes-Moriyama et al. [29] synthesized nano-octahedral grains of cobalt ferrite ($CoFe_2O_4$) with size around 20 nm by a hydrothermal route. Jia et al. [24] synthesized $Co_{1-x}Zn_xFe_2O_4$ nanorods by the solvothermal annealing method. $Co_{1-x}Zn_xFe_2O_4$ has the maximal specific saturation magnetization value, 43.0 emu g^{-1}. Singhal et al. [14] prepared $Co_{0.5}Zn_{0.5}Al_xFe_{2-x}O_4$ nanoparticles via sol–gel route. The results showed that $Co_{0.5}Zn_{0.5}Fe_2O_4$ obtained at 1000 °C had the highest specific saturation magnetization value, 64.33 emu/g; $Co_{0.5}Zn_{0.5}AlFeO_4$ had the highest coercivity value, 162 Oe. Although many researchers have made great efforts to prepare single phase $Co_{1-x}Zn_xFe_2O_4$ with high performance, facile and scalable synthesis of $Co_{1-x}Zn_xFe_2O_4$ with high specific saturation magnetization, higher coercivity, and lower remanence values is still a significant challenge. Therefore, it is highly desirable and necessary to explore new synthetic methods for the preparation of $Co_{1-x}Zn_xFe_2O_4$ and/or doped $Co_{1-x}Zn_xFe_2O_4$. To the best of our knowledge, the synthesis and magnetic properties of $Li_xCo_{0.5}Zn_{0.5-x}Fe_2O_4$ by thermal decomposition of oxalates has rarely been reported in previous studies.

This study aims to prepare $Li_xCo_{0.5}Zn_{0.5-x}Fe_2O_4$ by calcining oxalates in air and study effect of composition and calcination temperature on magnetic properties of $Li_xCo_{0.5}Zn_{0.5-x}Fe_2O_4$. Our results clearly show that the magnetic properties, in particular the specific magnetizations (*Ms*) and coercivity (*Hc*) of $Li_xCo_{0.5}Zn_{0.5-x}Fe_2O_4$, can be precisely tailored by controlling Li^+

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doped amount and calcination temperature.

2. Experimental

2.1. Reagent and apparatus

All chemicals used are of reagent-grade purity (purity > 99.9%). The TG/DSC measurements were conducted using a Netzsch Sta 409 PC/PG thermogravimetric analyzer under continuous flow of air (35 mL min^{-1}). The sample mass was approximately 12 mg. X-ray powder diffraction (XRD) was performed using a X′pert PRO diffractometer equipped with a graphite monochromator and a Cu target. The radiation applied was Cu Kα (λ=0.15406 nm), operated at 40 kV and 50 mA. The XRD scans were conducted from 5° to 70° in 2θ, with a step size of 0.01°. The morphologies of the synthesis products were observed using a S-3400 scanning electron microscope (SEM). The specific saturation magnetizations (*Ms*) of the calcined sample powders were carried out at room temperature using a vibrating sample magnetometer (Lake Shore 7410).

2.2. Preparation of $Li_xCo_{0.5}Zn_{0.5-x}Fe_2O_4$

The $Li_xCo_{0.5}Zn_{0.5-x}Fe_2O_4$ (x=0, 0.1, 0.2, and 0.3) samples were prepared by calcining precursor oxalates in air using $Li_2C_2O_4$, $CoC_2O_4\cdot 2H_2O$, $ZnC_2O_4\cdot 2H_2O$, and $FeC_2O_4\cdot 2H_2O$ as raw materials. In a typical synthesis ($Co_{0.5}Zn_{0.5}Fe_2O_4$), $CoC_2O_4\cdot 2H_2O$ (4.62 g), $ZnC_2O_4\cdot 2H_2O$ (4.78 g), and $FeC_2O_4\cdot 2H_2O$ (18.15 g) were placed in a mortar, and the mixture was thoroughly ground by hand with a rubbing mallet for 35 min. The strength applied was moderate. The resulting material was determined to be $0.5CoC_2O_4$–$0.5ZnC_2O_4$–$2FeC_2O_4\cdot 7.32H_2O$ by TG and inductively coupled plasma atomic emission spectrometry. A similar synthesis procedure was used to synthesize other $Li_xCo_{0.5}Zn_{0.5-x}Fe_2O_4$ precursor. Cubic $Li_xCo_{0.5}Zn_{0.5-x}Fe_2O_4$ was obtained by calcining the precursor at 900 °C in air for 3 h.

3. Results and discussion

3.1. Composition analysis of the precursor

0.0310 g precursor sample was dissolved in 10 mL 50 vol% HCl solution, then diluted to 100.00 mL with deionized water. Cobalt (Co), zinc (Zn), and ferrum (Fe) in the solution were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, Perkin Elmer Optima 5300 DV). The results showed that the Co, Zn, and Fe mass percentage were 5.17%, 5.74%, and 19.60%, respectively. In other words, molar ratio of Co:Zn:Fe in the precursor is 0.5:0.5:2.00.

3.2. TG/DSC/DTG analysis of the precursor

Fig. 1 shows the TG/DSC/DTG curves of the precursor at a heating rate of 10 °C min^{-1}. The TG/DSC/DTG curves show that the thermal transformation of $0.5CoC_2O_4$–$0.5ZnC_2O_4$–$2FeC_2O_4\cdot 7.32H_2O$ below 900 °C occurred in five well-defined steps. The first step started at about 126.2 °C and ended at 157.1 °C, which can be attributed to the dehydration of the one water from $0.5CoC_2O_4$–$0.5ZnC_2O_4$–$2FeC_2O_4\cdot 7.32H_2O$ (mass loss: observed, 3.22%; theoretical, 3.16%). The second transformation step started at 157.1 °C and ended at 220.1 °C, attributed to the dehydration of the 6.32 waters from $0.5CoC_2O_4$–$0.5ZnC_2O_4$–$2FeC_2O_4\cdot 6.32H_2O$ (mass loss: observed, 20.18%; theoretical, 19.98%). The third transformation step started at 220.1 °C and ended at 265.2 °C, attributed to the reaction of $2FeC_2O_4$ with $1.5O_2$ into Fe_2O_3 and the four CO_2 molecules (mass loss: observed, 21.62%; theoretical, 22.47%). The fourth transformation step started at 265.2 °C and ended at 316.5 °C, attributed to the reaction of $0.5CoC_2O_4$ with $1/3O_2$ into $0.5/3Co_3O_4$ and the one CO_2 (mass loss: observed, 6.16%; theoretical, 5.85%). The fifth transformation step started at 316.5 °C and ended at 392.9 °C, attributed to the reaction of $0.5/3Co_3O_4$ and $0.5ZnC_2O_4$ with $1/6O_2$ into 0.5CoO, 0.5ZnO, and one CO_2 (mass loss: observed, 6.96%; theoretical, 6.79%).

3.3. XRD analyses of the calcined products

Fig. 2 shows the XRD patterns of calcined samples from different calcination temperatures for 3 h. Fig. 2a shows that part of characteristic diffraction peaks of cubic $ZnFe_2O_4$ appeared when $Li_xCo_{0.5}Zn_{0.5-x}Fe_2O_4$ precursor (x=0 and 0.1) was calcined at 700 °C. Characteristic diffraction peaks of cubic $ZnFe_2O_4$ become strong and those of impurity (Fe_2O_3, ZnO, and/or Co_3O_4) become weak and/or disappear with the increase of calcination temperature. When the precursor was calcined at 900 °C, all other diffraction peaks in the pattern agreed with those of cubic $ZnFe_2O_4$ with space group Fd-3m (227) from PDF card 22-1012 except for one weak diffraction peak of rhombohedral Fe_2O_3 at 33.05 for 2θ. No diffraction peaks of crystalline $CoFe_2O_4$ were observed, which implied that $ZnFe_2O_4$ and $CoFe_2O_4$ formed a solid solution. Fig. 2c and d shows that single phase $CoFe_2O_4$ with cubic structure [space group Fd-3m (227)] can be obtained when $Li_xCo_{0.5}Zn_{0.5-x}Fe_2O_4$ (x=0.2 and 0.3) precursor was calcined at 900 °C. No diffraction peaks of crystalline $ZnFe_2O_4$ and/or $Li_{0.5}Fe_{2.5}O_4$ were observed, implying that $ZnFe_2O_4$, $Li_{0.5}Fe_{2.5}O_4$, and $CoFe_2O_4$ formed a solid solution. The lattice parameters of the sample were refined by the Rietveld analysis using MDI Jade (ver. 5.0) software. The refined lattice parameters of $Li_xCo_{0.5}Zn_{0.5-x}Fe_2O_4$ obtained at 900 °C were $a=b=c$=0.843901 nm for x=0; $a=b=c$=0.840565 nm for x=0.1;

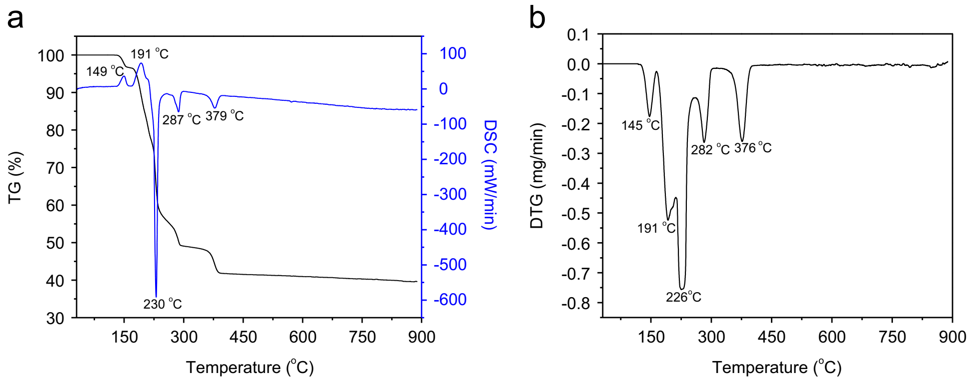

Fig. 1. TG/DSC/DTG curves of $0.5CoC_2O_4$–$0.5ZnC_2O_4$–$2FeC_2O_4\cdot 7.32H_2O$ at a heating rate of 10 °C/min in air.