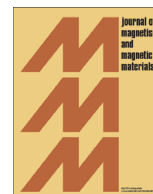




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Structure and magnetic properties evolution of nickel–zinc ferrite with lanthanum substitution

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ABSTRACT

La³⁺-doped Ni–Zn ferrites with a nominal composition of Ni_{0.5}Zn_{0.5}La_xFe_{2–x}O₄ (where x=0–0.3) are prepared by solid-state reaction at low temperatures. X-ray diffraction data shows that single phase Ni_{0.5}Zn_{0.5}Fe₂O₄ is obtained at 600 °C, but all samples consist of the main spinel phase in combination of a small amount of a foreign LaFeO₃ phase after doping. When the precursor is calcined at 900 °C, the lattice constants of the ferrites initially increase after La³⁺ doping, but then become smaller with additional La³⁺ doping. The addition of La³⁺ results in a reduction of crystallite size. Magnetic measurement reveals that the specific saturation magnetization (Ms) of the as-prepared ferrites decreases with increasing La³⁺ substitution, while the coercivity (Hc) of Ni_{0.5}Zn_{0.5}La_xFe_{2–x}O₄ obtained above 800 °C increases with increasing La³⁺ substitution.

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1. Introduction

Spinel ferrites M²⁺Fe₂O₄ (M²⁺=Cu²⁺, Mn²⁺, Mg²⁺, Zn²⁺, Ni²⁺, Co²⁺, etc.) are a technologically important group of materials owing to their diverse applications in high-density magnetic recording, ferrofluids technology, biomedical drug delivery, catalysis, energy storage, gas sensors, and magnetic resonance imaging (MRI) [1–14]. Within this group, Ni–Zn ferrites is a kind of very important soft magnetic material. Ni–Zn ferrites have many advantages, such as low cost, high resistivity, mechanical hardness, high Curie temperature, and chemical stability. So, Ni–Zn ferrites are attractive for microwave device applications and other relevant fields. Therefore, Ni–Zn ferrites are always the focus of research. Compared to other composition Ni–Zn ferrites, Ni_{0.5}Zn_{0.5}Fe₂O₄ has higher specific saturation magnetizations [5]. Ni–Zn ferrites properties were highly dependent on the composition, synthesis methods, and doped elements. Rare earth oxides are good electrical insulators with high electrical resistivity. The occupation of rare earth ions on 'B' sites impedes the motion of Fe²⁺ in the conduction process, thus causing an increase in resistivity [1]. Doped rare earth in ferrites was considered to be an

effective means to improve the performance of ferrites [1,15–22].

Various synthetic approaches have been pursued to prepare spinel Ni_{1–x}Zn_xFe₂O₄ and doped Ni_{1–x}Zn_xFe₂O₄ with different particle sizes and morphological features, including ceramic technique [17,23], solid-state reaction at low temperatures [5,24], hydrothermal method [25,26], co-precipitation method [15,27,28], citrate precursor method [29,30], high energy ball milling method [31], sol–gel synthesis [16,18,32], self-combustion method [33], molten salt method [34], refluxing method [35], reverse micelle method [36,37], solvothermal method [38], flash combustion technique [39], and chitosan method [40]. In the synthesis of Ni_{0.5}Zn_{0.5}Fe₂O₄, the crystallite diameter, morphology, and crystalline phases of Ni_{0.5}Zn_{0.5}Fe₂O₄ associated with its performances highly depend on the synthesis method and calcination temperature. Dey et al. [31] synthesized nanosized Ni_{0.5}Zn_{0.5}Fe₂O₄ by the high energy ball milling method. The value of specific saturation magnetization at 27 °C is 30.7 emu/g. The sample does not show any detectable hysteresis at 27 °C, indicating superparamagnetic behavior of Ni_{0.5}Zn_{0.5}Fe₂O₄. Gao et al. [32] obtained irregular polyhedrons Zn_{0.5}Ni_{0.5}Fe₂O₄ with a size of 29 nm by the sol–gel method, followed by calcination at 900 °C. The values of specific saturation magnetization and coercivity at room temperature are 53 emu/g and 40 Oe, respectively. Peng et al. [17] prepared Pr³⁺-doped Ni–Zn ferrites with a nominal composition of Ni_{0.5}Zn_{0.5}Pr_xFe_{2–x}O₄ (x=0–0.08) by the ceramic technique. The results showed that the specific saturation magnetization (Ms) of

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the as-prepared ferrites decreased, while the coercivity (H_c) increased with increasing Pr^{3+} substitution. Although many researchers have made great efforts to obtain high-performance Ni–Zn ferrites and/or doped rare earth ferrites, facile and scalable synthesis of Ni–Zn ferrites at a low cost is still a significant challenge.

This study aims to prepare $Ni_{0.5}Zn_{0.5}La_xFe_{2-x}O_4$ by calcining carbonates precursor in air and study structure and magnetic properties evolution of $Ni_{0.5}Zn_{0.5}La_xFe_{2-x}O_4$. Our results clearly show that the magnetic properties, in particular the specific magnetizations (M_s) and coercivity (H_c), can be precisely tailored by controlling the composition as well as the calcination temperature.

2. Experimental

2.1. Reagent and apparatus

All chemicals used are of reagent-grade purity (purity > 99.9%). The TG measurement was conducted using a Netzsch Sta 409 PC/PG thermogravimetric analyzer under continuous flow of air (40 mL min^{-1}). The sample mass was approximately 12 mg. X-ray powder diffraction (XRD) was performed using a Rigaku D/Max 2500V diffractometer equipped with a graphite monochromator and a Cu target. The radiation applied was $Cu K\alpha$ ($\lambda = 0.15406 \text{ nm}$), operated at 40 kV and 50 mA. The XRD scans were conducted from 5° to 70° in 2θ , with a step size of 0.02° . The morphologies of the synthesis products were observed using a S-3400 scanning electron microscope (SEM). The specific magnetization (M) of the calcined sample powders were carried out at room temperature using a vibrating sample magnetometer (Lake Shore 7410).

2.2. Preparation of $Ni_{0.5}Zn_{0.5}La_xFe_{2-x}O_4$

The $Ni_{0.5}Zn_{0.5}La_xFe_{2-x}O_4$ ($x = 0, 0.1, 0.2, \text{ and } 0.3$) precursor samples were prepared by solid-state reaction at low temperatures [24] using $NiSO_4 \cdot 7H_2O$, $ZnSO_4 \cdot 7H_2O$, $FeSO_4 \cdot 7H_2O$, $La(NO_3)_3 \cdot 6H_2O$, and $Na_2CO_3 \cdot 10H_2O$ as raw materials. In a typical synthesis, $NiSO_4 \cdot 7H_2O$ (8.86 g), $ZnSO_4 \cdot 7H_2O$ (9.07 g), $FeSO_4 \cdot 7H_2O$ (35.08 g), $Na_2CO_3 \cdot 10H_2O$ (62.28 g), and surfactant polyethylene glycol-400 (3.0 mL, 50 vol%) 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 reactant mixture gradually became damp, and a paste was formed immediately. The reaction mixture was kept at 30°C for 1.5 h. The mixture was washed with deionized water to remove soluble inorganic salts until SO_4^{2-} ion cannot be visually detected with a 0.5 mol L^{-1} $BaCl_2$ solution. The solid was then washed with a small amount of anhydrous ethanol. A red-brown solid was obtained after dried at 80°C in air for 4 h, implying that Fe^{2+} in the precipitate was oxidized into Fe^{3+} . The resulting material was determined to be $Ni_{0.5}Zn_{0.5}CO_3-Fe_2O_3 \cdot 1.7H_2O$. A similar synthetic procedure was used to synthesize other $Ni_{0.5}Zn_{0.5}La_xFe_{2-x}O_4$ precursor. A high-crystallized $Ni_{0.5}Zn_{0.5}La_xFe_{2-x}O_4$ was obtained when the precursor was calcined over 600°C for 3 h in a muffle furnace.

3. Results and discussion

3.1. TG/DTG analysis of $Ni_{0.5}Zn_{0.5}CO_3-Fe_2O_3 \cdot 1.7H_2O$

Fig. 1 shows the TG/DTG curves of the precursor at a heating rate of $10^\circ\text{C min}^{-1}$, from ambient temperature to 800°C . The TG/DTG curves show that the thermal transformation of $Ni_{0.5}Zn_{0.5}CO_3-Fe_2O_3 \cdot 1.7H_2O$ below 800°C occurred in two well-

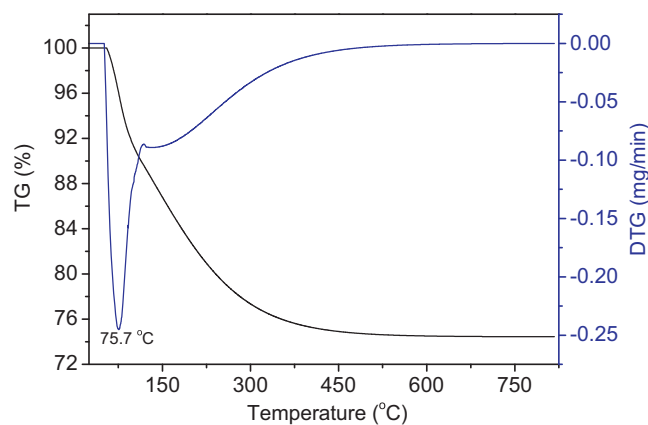


Fig. 1. TG/DTG curves of $Ni_{0.5}Zn_{0.5}CO_3-Fe_2O_3 \cdot 1.7H_2O$, at a heating rate of $10^\circ\text{C min}^{-1}$ in air.

defined steps. The first step started at about 54°C and ended at 114.7°C , which can be attributed to the dehydration of the 1.7 waters from $Ni_{0.5}Zn_{0.5}CO_3-Fe_2O_3 \cdot 1.7H_2O$ (mass loss: observed, 9.80%; theoretical, 9.81%). The second transformation step started at 114.7°C and ended at 400°C , attributed to the thermal decomposition of $Ni_{0.5}Zn_{0.5}CO_3-Fe_2O_3$ into $Ni_{0.5}Zn_{0.5}Fe_2O_4$ and the one CO_2 molecule (mass loss: observed, 14.9%; theoretical, 14.09%).

3.2. XRD analyses of the precursor and the calcined products

Fig. 2 shows the XRD patterns of calcined samples from different calcination temperatures for 3 h. Fig. 2a shows that when $Ni_{0.5}Zn_{0.5}CO_3-Fe_2O_3 \cdot 1.7H_2O$ was calcined at 600°C for 3 h, a diffraction pattern with strong intensity and smoothed baseline was observed. The calcined product therefore has a high degree of crystallinity. All the diffraction peaks in the pattern agreed with those of cubic $Ni_{0.5}Zn_{0.5}Fe_2O_4$ with space group $Fd-3m$ (227) from PDF card 52-0278. Fig. 2b–d shows the XRD patterns of $Ni_{0.5}Zn_{0.5}La_xFe_{2-x}O_4$ ($x = 0.1, 0.2, \text{ and } 0.3$) from different calcination temperatures for 3 h. The results showed that all samples consisted of the main spinel phase in combination of a small amount of a foreign $LaFeO_3$ phase after doping. Similar phenomenon was also observed for La^{3+} -doped ferrites [1,18,20,41]. Compared with solid-state reaction at high temperature using a mixture of oxides, the crystallization temperature of $Ni_{0.5}Zn_{0.5}La_xFe_{2-x}O_4$ in our paper is lower, and higher degree of crystallinity of $Ni_{0.5}Zn_{0.5}La_xFe_{2-x}O_4$. The reason is that direct high temperature solid-state reaction exists difficult penetration between the solid particles, resulting in crystallization of $Ni_{0.5}Zn_{0.5}La_xFe_{2-x}O_4$ at a higher temperature, and a lower degree of crystallinity. However, in our study, a mixture of $NiSO_4 \cdot 7H_2O$, $ZnSO_4 \cdot 7H_2O$, $FeSO_4 \cdot 7H_2O$, $La(NO_3)_3 \cdot 6H_2O$, and $Na_2CO_3 \cdot 10H_2O$ was grinded at room temperature, precursor carbonates can be obtained with molecular-level scale and the uniform mixing at first, crystalline $Ni_{0.5}Zn_{0.5}La_xFe_{2-x}O_4$ can be obtained at lower temperature when the precursor was calcined in air.

The crystallite diameter of $Ni_{0.5}Zn_{0.5}La_xFe_{2-x}O_4$ was estimated using the following Scherrer formula [42]:

$$D = K\lambda/(\beta \cos \theta), \quad (1)$$

where D is the crystallite diameter, $K = 0.89$ (the Scherrer constant), $\lambda = 0.15406 \text{ nm}$ (wavelength of the X-ray used), β is the width of line at the half-maximum intensity, and θ is the corresponding angle. The crystallite sizes of $Ni_{0.5}Zn_{0.5}La_xFe_{2-x}O_4$ from calcining the precursor at 600°C , 700°C , 800°C , and 900°C are shown in Fig. 3. The crystallite size of $Ni_{0.5}Zn_{0.5}La_xFe_{2-x}O_4$

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