



Structure and magnetic properties of $\text{Mn}(\text{Zn})\text{Fe}_{2-x}\text{RE}_x\text{O}_4$ ferrite nano-powders synthesized by co-precipitation and refluxing method

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ABSTRACT

The spinel-type MnZn ferrite nanopowders were synthesized by co-precipitation and refluxing method using $\delta\text{-FeOOH}$ as a precursor. The effects of processing parameters such as the pH value of co-precipitation solution and reflux time on the crystalline phase formation, microstructure and magnetic properties were systematically investigated. The results showed that, instead of spherical shape, $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles have square slice shape with sizes varying from <10 nm to >20 nm. The particle size can be controlled by the co-precipitation and reflux parameters. The products with saturation magnetization (M_s) of 46 emu/g were obtained when the pH value of co-precipitation solution and reflux time are 13.0 and 6 h, respectively. The effects of rare earth (RE) elements (La, Nd, Gd) doping on the structure and magnetic properties of $\text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_{2-x}\text{RE}_x\text{O}_4$ nanoparticles were investigated. Due to the differences in available magnetic moment and ion's radius for La^{3+} , Nd^{3+} and Gd^{3+} , various magnetic properties were obtained in these three series of alloys. It was also found that the particle size, M_s and the coercive force (H_c) strongly depend on the RE concentration due to the preferred occupied positions of RE ions.

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1. Introduction

As one of the important classes of soft magnetic materials, MnZn ferrites have high magnetic permeability, saturation magnetization, electrical resistivity and low power losses [1–3]. They are widely used in the field of electronics and electric devices such as deflection yoke rings, computer memory chips, magnetic recording heads, microwave devices, transducers, and transformers [4–6]. Apart from these applications, nanosized MnZn ferrites are also found potentially useful in ferrofluid technology, magnetically guided drug delivery, and magnetic resonance imaging [7]. As we know, ferrites are commonly produced by the ceramic process involving high temperature solid-state reactions between the constituent oxides/carbonates [8,9]. The disadvantages of this conventional method includes rather large and non-uniform particle size and inducing impurities, which restrict further improvement in the performance of the products [10,11]. In order to overcome these difficulties and to meet the requirements for new applications, some wet chemical processes like sol–gel citrate [12,13], hydrothermal method [14], reverse micro-emulsion process [15], co-precipitation technique [16], one solution spray [17], and the detonation of emulsion explosive [18] have been considered for production of nanoscale ferrites with excellent magnetic properties. The use of co-precipitation process to synthesize homogeneous, fine and reproducible Mn–Zn ferrites with narrow size distribution at a

relatively low reaction temperature appears to have attracted much attention in recent years [19]. For examples, Arulmurugan et al. [20] employed co-precipitation to synthesize Mn–Zn nanoparticles used for ferrofluid. Segal et al. [21] and Jeyadevan et al. [22] also reported the Mn–Zn nanoparticles with excellent properties obtained by this method. In addition, a large number of publications on Ni–Zn ferrites synthesized by co-precipitation can also be found every year [23,24]. Despite these progresses, the better understanding and better control of this process seems still the main focus of this topic in near future. In our work, MnZn ferrites were prepared by a modified co-precipitation technique, which has shown promising due to its easy operation, low cost, low temperature, controllable conditions and high reactivity of the obtained products. From the crystallography point of view, MnZn ferrite has spinel structure. The major unit cell of spinel lattice is composed of eight sub-unit cells with face centre cubic (FCC) structure. There are total 64 tetrahedral and 32 octahedral interstitial sites available within each unit cell [4], in which zinc ions occupy tetrahedral sites (A-sites) while iron and manganese ions occupy both tetrahedral sites (A-sites) and octahedral sites (B-sites) [25]. This special structure allow introduction of different metallic ions to change the magnetic, electronic and other properties considerably [26,27] since metal ions may either replace Fe^{3+} and entered into spinel crystal lattice or aggregate on the grain boundary in the form of compound. In this article the effects of rare earth (La, Nd, and Gd) doping on the structure and magnetic properties of MnZn ferrite nanoparticles are also investigated with intention to modify intrinsic properties by introducing these three elements with different atomic magnetic moments.

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2. Experimental

MnZn ferrite nanoparticles were prepared by the co-precipitation and refluxing method using ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), manganese sulfate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$), zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), sodium hydroxide (NaOH), hydrogen peroxide (H_2O_2), ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$) as the raw materials. All the materials had analytical purity and used without further purification. To synthesize $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ferrites, the required metal salts and sodium hydroxide were dissolved in deionized water separately to form aqueous solutions. First, sodium hydroxide and hydrogen peroxide were added into ferrous sulfate solution under constant magnetic stirring in order to obtain $\delta\text{-FeOOH}$ as the precursor. Then the solution of manganese sulfate and zinc sulfate in required molar ratio of $\text{Fe}^{2+}/\text{Mn}^{2+}/\text{Zn}^{2+} = 4:1:1$ were added to the above solution and the pH value of the solution was continually monitored by adding sodium hydroxide solution. The intermediate product obtained by above co-precipitation process was then transferred to a reflux system where the transformation of metal hydroxide into nano-ferrites took place upon heating at 100°C for up to 6 h. The nanoscale MnZn ferrites were then obtained after separated from the supernatant by magnetic decantation, washed three times with distilled water and dried at room temperature. During the experiments, two important processing parameters, the pH value of co-precipitation and reflux time, were adjusted to investigate their effects on the structure and properties of the final products. To synthesize $\text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_{2-x}\text{RE}_x\text{O}_4$ ($\text{RE} = \text{La}, \text{Nd}, \text{Gd}$; $x = 0, 0.04, 0.08, 0.1, 0.2$) nanoparticles, similar process was employed. In order to introduce La, Nd or Gd, La_2O_3 , Nd_2O_3 or Gd_2O_3 were first dissolved in an appropriate amount of nitric acid (HNO_3) with a continuous magnetic stirring and then the obtained nitrate were added into the co-precipitation suspension obtained by the previous process. X-ray diffraction (XRD) for all samples was carried out at room temperature to determine the phase structure and crystalline size. XRD patterns were recorded on a Philips X Pert diffractometer at the wavelength $\lambda = 0.15405$ nm of $\text{Cu-K}\alpha$ radiation. Conventional transmission electron microscope (TEM) (Philips F20) and high resolution TEM (HRTEM, Joel 3100) examination was performed to observe the morphology and determine the crystal structure and the size of the synthesized particles. The magnetic properties of the nanoparticles were measured at room temperature by a physical properties measurement system (PPMS) equipped with a high accuracy vibrating sample magnetometer (VSM).

3. Results and discussion

3.1. Effect of preparation process on the structure of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles

The process for preparing $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles was systematically studied. Fig. 1a shows XRD patterns for final products prepared under various co-precipitation pH values and same refluxing time of 6 h. It shows that all the samples have a pure spinel structure (JCPDS 74-2401) without any other phases being detected, which indicates that pure MnZn ferrite can be successfully synthesized by the method of co-precipitation and refluxing. XRD peaks of all samples are broaden, but the peak width decreases with the increase of pH value, which indicates that the mean crystalline size of synthesized ferrites is fine and gradually increases with increasing pH value until 13, which is different from the optimized pH value of 11 reported in Ref. [28]. When the pH value is 13.5, the peak intensities became weaker due to the dissolution of zinc hydroxide in the high pH solution. The optimized pH value of 13 was then set for further study. Fig. 1b is the XRD patterns for the co-precipitation precursor and $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ particles with different reflux time from 2 to 6 h. It can be found that the co-precipitation intermediate products are in amorphous status and after 4 h reflux a pure spinel phase is formed. The intensities of the XRD

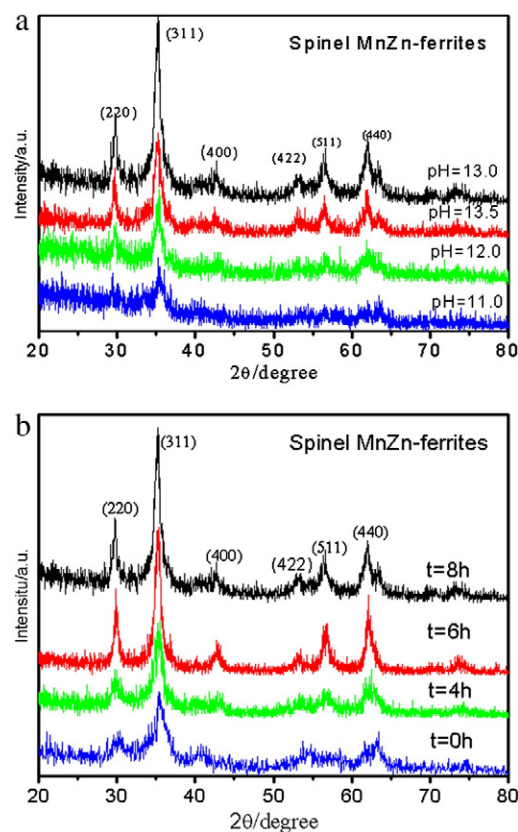


Fig. 1. XRD patterns for the samples produced at various co-precipitation pH values (a) and with different reflux time (b).

peaks increase with prolonging react time, suggesting that a relative long time is beneficial to the crystallization of ferrite particles.

The morphologies observed by TEM for the MnZn ferrites produced at various pH values of 11, 12, 13 and 13.5 are shown in Fig. 2. It is clearly found that the particle size ranges from less than 10 nm to above 20 nm with increasing pH value from 11 to 13.5. Higher co-precipitation pH value enhances the growth of grain, which is in good agreement with the XRD results. The TEM photographs of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ferrites with different reflux time (0–6 h) at pH 13 are shown in Fig. 3. The particle size increases with extending reaction time and reach about 20 nm when time is 6 h. Figs. 2 and 3 also show that the ferrite particles are uniform in both morphology and particle size, but agglomerated to some extent due to the interaction between magnetic nanoparticles.

To clearly observe the morphology and confirm the phase structure of the products, selected samples were examined by high magnification TEM and high-resolution TEM (HRTEM), as shown in Fig. 4. Interestingly, Fig. 4a demonstrates that the nanoparticles are not in spherical shape but in square slice shape with small thickness, which is different from other reports [29]. It is believed that the shape of the crystal reflects the FCC structure of MnZn ferrites, and our result here is helpful for clarifying the microstructure of nanoparticles prepared by this method. Fig. 4b shows a selected area electronic diffraction (SAED) pattern of the nanoparticles and indexed diffraction rings confirm the crystal planes of MnZn ferrite. The HRTEM image (Fig. 4c) clearly shows the crystal plane of (111) with d -space of 0.470 nm, which also indicates the nanoparticles are well crystallized. No secondary phase was detected by HRTEM.

3.2. Effect of preparation process on the magnetic properties of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles

The magnetic hysteresis loops for all samples prepared at different pH values are shown in Fig. 5a. All hysteresis loops exhibit very small coercive field indicating a behavior approaching to superparamagnetism,

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