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


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Structure and magnetic properties of Mn(Zn)Fe$_{2-x}$RE$_x$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 δ-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, Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanoparticles have square slice shape with size varied 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 6h, respectively. The effects of rare-earth (RE) elements (La, Nd, Gd) doping on the structure and magnetic properties of Mn$_{0.4}$Zn$_{0.6}$Fe$_{2-x}$RE$_x$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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Graphical Abstract

MnZn ferrite nanopowders were synthesized by co-precipitation and refluxing method. The nanoparticles have square slice shape instead of spherical shape. Powder size can be controlled by pH value and reflux time. Doping rare earth elements had strongly effects on the magnetic properties due to preferred occupied positions of RE ions.

Highlights

- Spinel MnZn ferrite nanopowders were synthesized by co-precipitation+refluxing method.
- Instead of spherical shape, the nanoparticles have square slice shape with size of <10 ~ >20 nm.
- The particle size can be controlled by the co-precipitation and reflux parameters.
- Effects of RE (La, Nd, Gd) doping on MnZnFe$_2$O$_4$ nanoparticles were investigated.

Key words: MnZn ferrites, nanopowders, Co-precipitation, refluxing, rare earth doping, magnetic properties
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 electrics 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 he 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 8 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.

2. Experimental

MnZn ferrite nanoparticles were prepared by the co-precipitation and refluxing method using ferrous sulfate (FeSO₄·7H₂O), manganese sulfate (MnSO₄·H₂O), zinc sulfate (ZnSO₄·7H₂O), sodium hydroxide (NaOH), hydrogen peroxide (H₂O₂), ammonia (NH₃·H₂O) as the raw materials. All the materials had analytical purity and used without further purification. To synthesize Mn\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O₄ 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 δ-FeOOH as the precursor. Then the solution of manganese sulfate and zinc sulfate in required molar ratio of Fe\(^{2+}\):Mn\(^{2+}\):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 Mn$_{0.4}$Zn$_{0.6}$Fe$_{2-x}$RE$_x$O$_4$ (RE=La, Nd, 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$_2$O$_3$, Nd$_2$O$_3$ or Gd$_2$O$_3$ 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 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 Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanoparticles

The process for preparing Mn$_{0.5}$Zn$_{0.5}$Fe$_2$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 Mn$_{0.5}$Zn$_{0.5}$Fe$_2$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 4h reflux a pure spinel phase is formed. The intensities of the XRD 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 showed 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 Mn$_{0.5}$Zn$_{0.5}$Fe$_2$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 6h. Fig. 2 and Fig. 3 also show that the ferrite particles are uniform in both morphology and particle size, but agglomerated to some extend 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, which can be explained by the very small particle size of all samples. Non-zero coercivity also indicates that the critical particle size for MnZn-ferrite should be less than 10 nm, which is in agreement with other reports [30]. Fig.5a also shows that the saturation magnetization $M_s$ strongly depends on pH value and it increases with increasing pH value, reaching a maximum value at pH =13 and then decreases for pH=13.5. The reason can be well explained by XRD results. The increase of $M_s$ is attributed to the improved crystallization and the decrease of $M_s$ is probably because of the dissolution of zinc hydroxide as discussed previously. The decreasing $M_s$ with reducing particle size for pH=11-13 may also result from the well-known nano-effect. The effects of reflux time on the magnetic properties are shown in Fig.5b. The product refluxed for 6 h has a higher $M_s$ than those obtained by 2 h and 4 h, also due to the improved crystallization. A high saturation magnetization of 46 emu/g has been achieved in the MnZn ferrite nanoparticles without dopant prepared at a co-precipitation pH value of 13 and reflux time of 6 h. However this high saturation magnetization is still lower than that of coarse-grained bulk samples [31]. Several theories, including surface effects, spin-canting phenomenon, purity and particle size effects, have been proposed to account for the relatively low magnetization of nanoparticles [32].
3.3 Effects of RE doping on the structure of Mn$_{0.4}$Zn$_{0.6}$Fe$_{2-x}$RE$_x$O$_4$ ferrite nanoparticles

To investigate the effects of rare earth element addition on the magnetic properties of MnZn ferrites, Mn$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$ was chosen as the starting composition and three elements with various atomic magnetic moments, i.e. La, Nd and Gd, were selected as the dopants. The XRD patterns for Mn$_{0.4}$Zn$_{0.6}$Fe$_{2-x}$La$_x$O$_4$ products (Fig. 6a) revealed that all the peaks of the nanoparticles match well with the spinel ferrite without any other phase peaks until $x=0.1$. Fe$_2$O$_3$ peaks were detected for high content of La ($x=0.2$). XRD patterns for Mn$_{0.4}$Zn$_{0.6}$Fe$_{2-x}$Nd$_x$O$_4$ (Fig. 6b) demonstrate that Nd can enhance the crystallization of MnZn ferrite just as La and no secondary phase is detected. For the Gd doped nanoparticles, Fig. 6c shows that the peak intensity becomes stronger with the increase of $x$ up to 0.04. When the Gd concentration further increases, MnZn ferrites are partially decomposed and γ-Fe$_2$O$_3$ coexists with the cubic spinel phase.

Fig. 7 shows the relationship between average crystal size $D$ which is calculated from XRD data using Scherrer’s equation and RE content for Mn$_{0.4}$Zn$_{0.6}$Fe$_{2-x}$RE$_x$O$_4$ (RE=La, Nd and Gd) nanoparticles. The results imply that RE substitutions for Fe can greatly affect the crystallization during reflux process. $D$ almost decreases linearly with increasing La concentration up to $x=0.1$ and then increases sharply for $x=0.2$. There are some possible explanations to account for this decrease of $D$. First, in the crystal structure of MnZn ferrite, Zn$^{2+}$ and Mn$^{2+}$ occupy tetrahedral sites (A-sites) and octahedral sites (B-sites) respectively. Fe$^{3+}$ occupies either tetrahedral or octahedral sites. La$^{3+}$ ions have a tendency to enter into B-sites, but the ionic radius (1.22Å) of La$^{3+}$ is much larger than the ionic radius of Fe$^{3+}$ (0.67Å) and it needs more activation energy for La$^{3+}$ to enter B-sites than Fe$^{3+}$ since the bond energy of La-O is higher than that of Fe-O. Hence it is difficult for La$^{3+}$ to substitute Fe$^{3+}$. The extra stress coming from partial La$^{3+}$ enter the lattice at interstitial sites instead of occupying Fe$^{3+}$ sites in the lattice will suppress the crystallization of MnZn ferrites. On the other hand, some excess La in the form of La$_2$O$_3$ or LaFeO$_3$ separating from the lattice as solid solute in
MnZn ferrites, although not detected by XRD, will lead to abnormal grain growth. The details, however, are in need of further investigation. The relationship between crystal size and Nd content for $\text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_{2-x}\text{Nd}_x\text{O}_4$ shows that $D$ decreases sharply with increasing Nd concentration up to 0.1 which is similar to La-doping. After $x>0.1$, $D$ decreases gently possibly due to the limited solution of Nd in cubic structure. The relationship for Gd doping was similar to that for Nd doping except for the point of $x=0.04$, which can be attributed to abnormal grain growth.

Fig. 8 shows the relationships between lattice constant $a$ and RE content for $\text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_{2-x}\text{RE}_x\text{O}_4$ (RE=La, Nd and Gd) nanoparticles. The lattice constant $a$ is calculated from the peaks in XRD patterns according to the following equation $a = d_{hkl} \sqrt{h^2+k^2+l^2}$, where $d$ is the interspace of crystal plane ($hkl$). It is found that $a$ decreases with increasing RE doping concentration for all RE addition samples. These results confirm that La, Nd and Gd can enter the lattice while keeping the spinel structure unchanged. The decrease in lattice constant may be due to the iron vacancies in these samples, as described in ref.[33].

3.4 Effects of RE doping on the magnetic properties of $\text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_{2-x}\text{RE}_x\text{O}_4$ ferrite nanoparticles

The magnetic properties for the MnZn ferrite nanoparticles with various La, Nd and Gd doping were measured by VSM. Figs. 9 show the dependences of magnetic properties ($M_s$ and $H_c$) on the concentrations of La, Nd and Gd. Fig. 8a illustrates that the $M_s$ for $\text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_{2-x}\text{La}_x\text{O}_4$ decreases sharply and $H_c$ increase linearly with increasing concentration of $\text{La}^{3+}$. The result may be related to the weak super-exchange interaction of A-O-B since $\text{Fe}^{3+}$ was substituted by $\text{La}^{3+}$ whose magnetic moment is zero. For $\text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_{2-x}\text{Nd}_x\text{O}_4$ nanoparticles (Fig. 9b), the higher content of Nd will lead to higher $M_s$ until $x=0.1$ and then it will decrease rapidly while $H_c$ increases continuously with increasing concentration of Nd. This can be ascribed that Nd have a larger magnetic moment ($3.62 \mu_B$) than that of Fe ($2.3 \mu_B$),
so the $M_s$ increases with Nd substitution for Fe. Too high Nd content may give rise to a lattice distortion of spinel ferrite and this is probably the reason why there is a sharp decline of $M_s$ for $x>0.1$. $\text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_{2-x}\text{Gd}_x\text{O}_4$ nanoparticle has similar dependence of Ms on the Gd concentration (Fig. 9c) with $\text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_{2-x}\text{Nd}_x\text{O}_4$ and the maximum value of $M_s$ is located at $x=0.08$. Large magnetic moment of Gd ion (7.94 $\mu_B$) leads to a higher $M_s$ for Gd doped ferrite than La and Nd doped ferrites. The dependence of coercivity show similar behavior for three series of alloys except one composition of $\text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_{2-x}\text{Gd}_x\text{O}_4$. Defects such as vacant position, dislocation and stacking fault occurred in the spinel ferrites when RE dissolved in the cubic structure and these defects will induce increased $H_c$ with the introduction of RE. The exemption of $\text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_{2-x}\text{Gd}_x\text{O}_4$ may be related to its abnormal grain growth as shown earlier. Overall, by doping of La, Nd and Gd, the highest Ms values of 44, 53 and 60 emu/g in the La, Nd and Gd doped nanosized MnZn ferrite particles, respectively, have been obtained in this work. It is believed that doping by RE is feasible approach for modifying the structure and magnetic properties of MnZn ferrite nanoparticles.

4. Conclusions

MnZn ferrite nanopowders without and with RE doping were successfully synthesized by co-precipitation and refluxing method using $\delta$-FeOOH as a precursor. The square slice shaped nanoparticles with the average particle size ranging from less than 10 nm to more than 20 nm were obtained through controlling the parameters of process. It is found that the optimum co-precipitation pH value is 13.0 and reflux time is 6h. Rare-earth (La, Nd, Gd) doping has important effects on the structure and magnetic properties of MnZn ferrite nanoparticles. It is revealed that grain size and $M_s$ depends strongly on the content of RE and the coercive force ($H_c$) increased with RE ion doping. Good magnetic properties have been obtained in these nanosized ferrites. Meanwhile, the square sliced nanoparticles may find important application as building block for magnetic nanostructures.
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References


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

Figure 2. The morphologies for the samples prepared at various pH values: a. pH=11; b. pH =12; c. pH =13; d. pH =13.5

Figure 3. TEM images for the nanosized MnZn-ferrites prepared at different refluxing time: a. 0 h; b. 2 h; c. 4 h; d. 6 h

Figure 4. High magnification TEM image (a), selected area electronic diffraction pattern (b) and HRTEM image (c) of MnZn ferrite nanoparticles synthesized at pH=13.5 and reflux time of 6 h

Figure 5. Magnetic hysteresis loops for the samples produced (a) at different pH values with 6h refluxing and (b) with different reflux time at pH=13

Figure 6. XRD patterns for Mn$_{0.4}$Zn$_{0.6}$Fe$_{2-x}$RE$_x$O$_4$ nanoparticles with RE doping: a. RE=La; b. RE=Nb; c. RE=Gd

Figure 7. Relationship of the average crystal size $D$ and RE content for Mn$_{0.4}$Zn$_{0.6}$Fe$_{2-x}$RE$_x$O$_4$ nanoparticles (RE=La, Nd, Gd)

Figure 8. Relationship of lattice constant $a$ and RE content for Mn$_{0.4}$Zn$_{0.6}$Fe$_{2-x}$RE$_x$O$_4$ nanoparticles (RE=La, Nd, Gd)

Figure 9. Relationship between magnetic properties and RE content for Mn$_{0.4}$Zn$_{0.6}$Fe$_{2-x}$RE$_x$O$_4$ nanoparticles: a. RE=La, b. RE=Nd, c. RE=Gd
Figure 4a
Figure 4b
Figure 6a
Figure 6b

The figure shows X-ray diffraction patterns for different compositions of the compound $\text{Mn}_{x}\text{Zn}_{1-x}\text{Fe}_{2-x}\text{Nd}_{x}\text{O}_{4}$, where $x$ varies from 0 to 0.20.

- For $x=0$, the pattern shows broad peaks, indicating a non-ordered or amorphous structure.
- As $x$ increases, the peaks become sharper and more defined, indicating a transition to a more ordered structure.
- The peaks at specific 20 values correspond to the crystallographic planes (220), (311), (400), (422), (511), and (440).

The diagram also includes labels for different phases, such as "Spinel," indicating the crystal structure.

The intensity is measured in arbitrary units (a.u.).
Figure 6c
Figure 8

The graph shows the variation of lattice parameter $a$ (Å) with $x$ (RE content) for different rare earth (RE) elements: La, Nd, and Gd. The lattice parameter decreases as the RE content increases. The La curve is represented by black squares, the Nd curve by red circles, and the Gd curve by blue triangles.