Research Article

Microstructural and Mössbauer Spectroscopy Studies of $\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.5, 0.7$) Nanoparticles

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Zinc substituted magnesium ferrite $\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.5, 0.7$) powders have been prepared by a sol-gel autocombustion method. XRD patterns show that the specimens with $x = 0.5$ and 0.7 exhibit single-phase spinel structure, and more content of Zn in specimens is favorable for the synthesis of pure Mg-Zn ferrites. Room temperature Mössbauer spectra of $\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ annealed at 800°C display transition from ferrimagnetic behavior to super paramagnetic behavior with increase in zinc concentration. The Mössbauer spectras of $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ annealed at different temperatures display the magnetic phase change of the ferrite particles.

1. Introduction

MgFe_2O_4 is regarded as an important candidate of the spinel ferrite family. Nanocrystalline Mg ferrite shows more enhanced magnetization than its crystalline counterpart and has been found to exhibit some unusual magnetic properties, such as super paramagnetism and a noncollinear ordering of the magnetic moments of Fe^{3+} ions, known as spin canting [1]. If the MgFe_2O_4 structure was completely inversed, its magnet moment would be zero because the magnetic moment of Mg^{2+} ion is zero. Manjurul Haque et al. [2] studied saturation of Zn^{2+} substitution on the magnetic properties of $\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ferrites. Saturation magnetization and magnetic moment are observed to increase up to $x = 0.4$ and thereafter decrease due to the spin canting in B-sites. Similar results of saturation magnetization's variation should be reported in the other literature [3, 4]. In this paper, ferrite $\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.5, 0.7$) powders were prepared by a sol-gel autocombustion method. The aim of this study is to investigate variation structural and magnetic properties of magnesium ferrite powders by partial replacement of nonmagnetic zinc cations.

2. Experimental

2.1. Sample Preparation. Zinc substituted magnesium ferrite $\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.5, 0.7$) powders were prepared

by a sol-gel autocombustion method. The analytical grade $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$), and ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$) were used as raw materials. The molar ratio of metal nitrates to citric acid was taken as 1 : 1. The metal nitrates and citric acid were dissolved into deionized water to form solution, respectively. The pH value of metal nitrates solution was changed from 7 to 9 by adding ammonia. And then, the mixed solution was maintained at 80°C in a thermostat water bath under constant stirring to transform into a dried gel. Citric acid was dropped continually in the process of heating. The gel were dried at 120°C in a dry-oven for 2 h, being ignited in air at room temperature, the dried gel burnt in a self-propagating combustion way to form loose powder. The powder was grounded and annealed.

2.2. Characterization. The crystalline structure was investigated by X-ray diffraction (D/max-2500 V/PC, Rigaku) with Cu K_α radiation ($\lambda = 0.15405 \text{ nm}$). The micrographs were obtained by scanning electron microscopy (NoVa Nano SEM 430). The Mössbauer spectrum was performed at room temperature, using a conventional Mössbauer spectrometer (American Fast Com Tec PC-mossII), in constant acceleration mode. The γ -rays were provided by a ^{57}Co source in a rhodium matrix.

FIGURE 1: Room temperature X-ray diffraction patterns of $\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ annealed at 800°C .

FIGURE 2: X-ray diffraction patterns of $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ annealed at different temperatures.

3. Results and Discussion

3.1. XRD Patterns Analysis. Figure 1 shows the XRD patterns of $\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.5, 0.7$) ferrites calcined at 800°C for 3 h. It is clear that the specimens with $x = 0.5$ and 0.7 exhibit single-phase spinel structure. Obviously, increasing the content of Zn is favorable for the synthesis of pure Mg-Zn ferrites. Similar results also are reported in the other literature [4]. Table 1 indicates that the X-ray density increases with Zn^{2+} concentration for all samples. The increase in lattice parameter is probably due to replacement of smaller Mg^{2+} ions by larger Zn^{2+} ions [5, 6].

The X-ray patterns of $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ annealed at different temperatures are shown in Figure 2. All the samples are the single-phase cubic spinel structure. No additional phase was detected. The lattice parameter showed changes for all the samples from Table 2. Average crystallite size of $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ tends to increase with the increase of the calcining temperature, due to the coalescence of small grains through grain boundary diffusion [7]. In other people's work [8], the diffraction peaks of $\text{Cu}_{0.7}\text{Mg}_{0.3}\text{Fe}_2\text{O}_4$ annealed at low temperature are not very sharp, but in our result the diffraction peaks of $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ without burning are very

sharp. The result suggests that magnesium substituted cobalt ferrite powders prepared by a sol-gel autocombustion method still have a good crystallinity without calcining.

3.2. Structures and Grain Sizes. The SEM micrographs of $\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.5$) annealed 800°C for 3 h are shown in Figure 3. It can be observed the distribution of grains with almost uniform size, well crystallized for $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$. Some particles are agglomerated due to the presence of magnetic interactions among particles [9].

Figure 4 shows the histogram of grain size distribution of $\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.5$) ferrites. The average grain size of $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ estimated by a statistical method is approximately 90.74 nm, respectively. It shows that the ferrite powders are nanoparticles, and the average grain size decreases with the increase of Zn content. The average grain size is slightly larger than the average crystallite size determined by XRD. This shows that every particle is formed by a number of crystallites [10, 11].

3.3. Mössbauer Spectroscopy. Mössbauer absorption spectra measured at room temperature for $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ powders

FIGURE 3: SEM micrographs depict $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ($x = 0.5$) ferrites with diameters of 100 μm (a), 50 μm (b), 20 μm (c), 10 μm (d), 5 μm (e), and 3 μm (f).

annealed at different temperatures are shown in Figure 5. All samples have been analyzed using Mösswin 3.0 program.

Spectra of the samples without calcining and annealed at 400°C are fitted into a single sextet and a central paramagnetic doublet, and the sample annealed at 800°C was analyzed to only a single sextet. The Mössbauer spectra of $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ sample show a paramagnetic doublet, which is due to the super paramagnetic relaxation, in other words, some particles are a single domain. Table 3 shows that the Mössbauer absorption area of paramagnetic doublet decreases with the increase of the annealed temperature; it is attributed to the change in particle size as a function of heat treatment [12]. Therefore the Mössbauer spectra of $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ annealed at different temperatures display the magnetic phase change of the ferrite particles.

4. Conclusion

The analysis of XRD patterns for $\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ annealed at 800°C shows that the specimens with $x = 0.5$ and 0.7 exhibit single-phase spinel structure, and more content of Zn in specimens is favorable for the synthesis of pure Mg-Zn ferrites. The XRD patterns of $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ annealed at different temperatures indicate that all $\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ferrite powders prepared by a sol-gel autocombustion method have good crystallinity. SEM results indicate the distribution of grains and morphology of the samples. Room temperature

TABLE 1: Lattice parameters, average crystallite size, and X-ray densities date of $\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ annealed at 800°C.

Sample (X)	Lattice parameter (Å)	Average crystallite size (Å)	Density ($\text{g}\cdot\text{cm}^{-3}$)
0.5	8.43133	377	4.8879
0.7	8.43576	385	5.0620

TABLE 2: Lattice parameters, average crystallite size, and X-ray densities date of $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ annealed at different temperatures.

$\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$	Lattice parameter (Å)	Average crystallite size (Å)	Density ($\text{g}\cdot\text{cm}^{-3}$)
0°C	8.42130	298	4.9054
400°C	8.41157	274	4.9224
800°C	8.43133	377	4.8879

Mössbauer spectra of $\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ annealed at 800°C display transition from ferrimagnetic behavior to super paramagnetic behavior with increase in zinc concentration. Furthermore, the Mössbauer spectra of $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ annealed at different temperatures display the magnetic phase change of the ferrite particles.

FIGURE 4: Histogram of grain size distribution of $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ annealed at 800°C.

FIGURE 5: Room temperature Mössbauer spectra of $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ annealed at different temperatures.

TABLE 3: Mössbauer parameters of isomer shift (IS), quadrupole splitting (QS), magnetic hyperfine field (H), line width (Γ), and absorption area (A_0) for $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ annealed at different temperatures.

$\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$	Component	IS (mm/s)	QS (mm/s)	H (T)	Γ (mm/s)	A_0 (mm/s)
0°C	Sextet (B)	0.313	-0.027	28.556	0.288	91.8
	Double	0.348	1.05	—	0.547	8.2
400°C	Sextet (B)	0.306	0.032	28.503	0.322	95.6
	Double	0.333	0.570	—	0.376	4.4
800°C	Sextet (B)	0.318	0.005	24.234	0.268	100

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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