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Xuesong Zhu

Anhui University of Technology

Chunxiang Cao

Anhui University of Technology

Shubing Su

Ningbo University of Technology

A.L. Xia (✉ alxia@126.com)

Anhui University of Technology <https://orcid.org/0000-0002-5223-519X>

Huiyan Zhang

Anhui University of Technology

Hailing Li

Anhui University of Technology

Zhiyuan Liu

Anhui University of Technology

Chuangui Jin

Anhui University of Technology

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A comparative study of spinel ZnFe_2O_4 ferrites obtained via a hydrothermal and a ceramic route: structural and magnetic properties

Xuesong Zhu¹, Chunxiang Cao², Shubing Su³, Ailin Xia^{1,*}, Huiyan Zhang¹, Hailing Li¹,

Zhiyuan Liu¹, Chuangui Jin^{1,*}

1 School of Materials Science and Engineering, Anhui University of Technology, Maanshan 243002, China

2 Analysis and Testing Central Facility, Anhui University of Technology, Maanshan 243002, China

3 School of Electronic and Information Engineering, Ningbo University of Technology, Ningbo 315016, China

* Corresponding author: Ailin Xia, Email: alxia@126.com; Tel: 86-13665557919; Chuangui Jin,

Email: jcg@ahut.edu.cn

Abstract

The spinel ZnFe_2O_4 specimens were obtained via a hydrothermal and a ceramic method, respectively, and their structural and magnetic properties were comparatively studied. It was found that all the specimens exhibited a single-phase and mixed spinel structure. The magnetism of specimens synthesized via the hydrothermal method is obviously greater than that of specimen prepared via the ceramic method. This can be ascribed to the occupancy of Fe ions resulted from the loss of Zn during the hydrothermal process.

Key words

Spinel; ZnFe_2O_4 ferrite; hydrothermal method; magnetic properties

1. Introduction

The spinel structure with a formula of AB_2O_4 is widely studied and used in the fields of electronics, magnetism, catalyst, energy storage and so on [1-8]. Generally, A denotes the divalent metal ions, such as Mg^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+} and Zn^{2+} , and B denotes the trivalent metal ions, such as Al^{3+} , Fe^{3+} , Co^{3+} and Cr^{3+} . Spinel ferrites (AFe_2O_4) are usually used as the magnetically soft materials, such as $MgFe_2O_4$ [6], $MnFe_2O_4$ [7], $NiFe_2O_4$ [8] and so on. Their magnetic properties are related to the site occupancy of cations. There are 8 and 16 occupied tetrahedral A sites and octahedral B sites in a spinel unit cell of 32 oxygen ions, respectively. Different cation distribution will result in different magnetic properties due to the different superexchange interaction of A-O-B and B-O-B [9].

Spinel $ZnFe_2O_4$ (ZFO) ferrite is widely studied as a kind of potential catalytic or anodic material [10-13]. Theoretically, ZFO is a typical normal spinel ferrite with a cation distribution in lattice sites as the following:

Where Zn^{2+} in A site is nonmagnetic, and the magnetic moment of two Fe^{3+} ions in B sites presents an antiparallel arrangement as described by the Yafet-Kittle configuration[14, 15], which results in the zero magnetic moment in ZFO. Therefore, if partial Fe^{3+} ions in B sites are forced to locate in A sites, the magnetism in ZFO could transform from antiferromagnetism to ferrimagnetism. This is instructive to the study of magnetism in spinel structures, and consequently the magnetism in ZFO also aroused the interest of some researchers [16-18]. It has been proved that the sintering

temperature should be a key factor for the site occupancy of Fe^{3+} [16, 17]. In this study, we prepared the ZFO specimens via a hydrothermal method and a traditional ceramic method, respectively, and proved that the Zn-deficiency can also cause the transition of magnetism from antiferromagnetism to ferrimagnetism in ZFO.

2. Experimental

2.1 Synthesis of ZFO via a hydrothermal route (HZFO)

A common hydrothermal route was used to prepare ZFO specimens with a nominal composition of ZnFe_2O_4 . All the chemical reagents used were analytically pure without further treatment.

First, the mixed $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with the Fe/Zn atomic ratio (R_a) of 2:1 were uniformly dissolved in deionized water and then coprecipitated by using the NaOH solution with the $\text{OH}^-/\text{NO}_3^-$ molar ratio of 3:1[19]. Then, the precipitates and aqueous solution were moved to a Teflon liner and hydrothermally reacted at a temperature (T_h) of 160°C, 180°C and 200°C, respectively. Finally, the obtained powders after the hydrothermal reaction were used as the specimens after washing by deionized water and absolute ethylalcohol for 3 and 2 times, respectively. For convenience, the specimens obtained with a T_h of 160°C, 180°C and 200°C were denoted as HZFO-160, HZFO-180 and HZFO-200, respectively.

2.2 Preparation of ZFO via a ceramic route (CZFO)

First, analytically pure ZnO and Fe_2O_3 powders were mixed uniformly with the R_a of 2:1. Then, the mixed powders were roughly pressed into circular tablets with a

diameter of about 10 mm. Finally, these circular tablets were sintered at 750°C for 2 hours to be used as the CZFO-750 specimen in this study.

2.3 Characterization

The phase composition of specimens were identified and confirmed by using an X-ray diffractometer (XRD, Rigaku D/max-2550V/PC) using Cu K α radiation and a Fourier transformed infrared spectrometer (FTIR, Nicolet 6700), respectively. The content, distribution and chemical state of metal elements were investigated by using an inductively coupled plasma-atomic emission spectrometer (ICP, Agilent 720), an energy dispersive spectrometer (EDS, Oxford X-Max 20) and an X-ray photoelectron spectroscopy (XPS, Escalab 250Xi), respectively. The micrographs were obtained by using a transmission electron microscope (TEM, Thermo Scientific Talos F2100X) and a field emission scanning electron microscope (FESEM, Zeiss omega 500). The Room-temperature (RT) magnetic properties were obtained through the magnetic hysteresis loops measured on a vibrating sample magnetometer (VSM, Quantum Design Versalab) with the maximum external field of about 2388 kA·m⁻¹ (30,000 Oe).

3. Results and discussion

3.1 HZFO synthesized via a hydrothermal route

In this study, ZFO specimens were prepared using the Fe/Zn atomic ratio of 2:1, a stoichiometric composition, in the starting materials. Fig. 1 shows the XRD patterns of as-synthesized HZFO specimens with different T_h . Typical peak information from

ZFO without any other impurity peaks is revealed in the three XRD patterns, indicating their single-phase spinel ZFO structure (PDF#22-1012) in the space group $Fd-3m$.

The results of FTIR can help to confirm the formation of spinel structure and give some information of chemical bond. Fig. 2 gives the FTIR spectra of HZFO specimens. The characteristic absorption bands at around 450 cm^{-1} and 575 cm^{-1} can be ascribed to the bending or stretching vibrations of $A-O_4$ and $B-O_6$ in spinels, which is consistent with the results in previous reports [10, 20], suggesting the formation of spinel structure.

Using the XRD patterns in Fig. 1 and the famous Scherrer equation [16], the average crystallite size (D) was calculated to be 7.3, 7.4 and 8.2 nm for specimens HZFO-160, HZFO-180 and HZFO-200, respectively. It can be concluded that the crystallites grew faster at a higher T_h . This can be confirmed by the typical FESEM and TEM images of HZFO specimens shown in Fig. 3 and Fig. 4, respectively. Seen from Fig. 3, the HZFO specimens consist of many aggregated small particles. When seen from Fig. 4, all the HZFO specimens are composed of small nanoparticles mainly less than 10 nm, which is consistent with the values of D obtained using the Scherrer equation. The obvious increase of D in HZFO-200 (Fig. 4c) due to the higher T_h can also be found if compared with that of HZFO-160 (Fig. 4a) and HZFO-180 (Fig. 4b). What should be pointed out is that as shown in Fig. 3c, the specimen synthesized at $T_h = 200^\circ\text{C}$ (HZFO-200) exhibits a more compact aggregation, which may be due to the higher saturation magnetization (M_s) discussed later.

The typical EDS mapping images of a selected area in the typical specimen HZFO-200 are given in Fig. 5. For the metal elements, only count from Zn and Fe can be found in the measured area. Moreover, the count is uniformly distributed in the mapping images, implying that the compositional distributions of Zn and Fe in the specimen are uniform.

3.2 CZFO-750 prepared via a ceramic route

In order to compare the magnetic properties with HZFO, the CZFO-750 specimen was prepared via a ceramic route. Fig. 6a shows the XRD pattern of CZFO-750. The pattern also reveals the typical peak information of spinel ZFO (PDF#22-1012) in the space group $Fd-3m$. However, the peaks became visibly narrower compared with those in Fig. 1. This can be ascribed to the crystallite growth after sintering at the high temperature of 750°C. Note that the typical FESEM image of CZFO-750 illustrated in Fig. 6b confirms this result. Most of the crystallites grew up to a size of about 200 nm, far beyond the limited size of 100 nm that can be calculated by using the Scherrer equation. Fig. 6c gives the typical EDS mapping images in the selected area of CZFO-750 to prove the uniformity of metal elements. Obviously, the count from both Zn and Fe are uniformly distributed in the selected area just like that in Fig. 5, also indicating the uniformity of chemical composition in CZFO-750.

3.3 Magnetic properties

The magnetism of spinels is associated with the difference of magnetic moments between A and B sites [9]. According to the cation distribution in lattice sites described above for a normal spinel ferrite, the magnetic moment in a ZFO molecular formula can be calculated as:

$$|M_A - (M_{B\uparrow} - M_{B\downarrow})| = |0\mu_B - (5\mu_B - 5\mu_B)| = 0\mu_B \quad (1)$$

Where M_A and M_B present the magnetic moment in A and B sites, respectively. Therefore, generally, the normal spinel ferrite should exhibit zero magnetic moment.

The RT magnetic hysteresis loops of HZFO specimens are illustrated in Fig.7. According to the Ref. [18] combined with D obtained from the results of XRD and TEM, the negligible coercivity (H_c) and remanent magnetism (M_r) together with unsaturated magnetization at relatively high magnetic field could help to confirm the superparamagnetism of our HZFO nanoparticles. However, the superparamagnetism of HZFO nanoparticles is not the emphasis in this study, and will be discussed in another report systematically. Therefore, the dependence of magnetization (M) on the temperature (T) under the zero field cooling (ZFC) and field cooling (FC) that can confirm the existence of superparamagnetism is not given here.

Seen from Fig. 7, for the sake of discussion, the M at the maximum external field of $\pm 2388 \text{ kA}\cdot\text{m}^{-1}$ (30,000 Oe) was considered as the M_s . The calculated M_s of HZFO-160, HZFO-180 and HZFO-200 is 15.05, 22.19 and 24.56 emu/g, respectively, exhibiting a value much higher than zero. As is well-known, $\text{Zn}(\text{OH})_2$ is amphoteric, which can also be dissolved in the alkaline solution [21]. Therefore, for a hydrothermal method, Zn^{2+} is easy to lose in the aqueous solution during the synthesis.

As described above, theoretically, the molecular magnetic moment of normal ZFO should be zero. However, the Zn-deficiency in A sites could result in the occupancy of partial Fe ions in A sites, and consequently form the mixed spinel ZFO. According to the Yafet–Kittle configuration for spinels [15], this was sure to result in that the magnetic moment in A and B sites could not cancel each other out, which would enhance the molecular magnetic moment. As for the increasing trend of M_s with the increasing T_h , it should deal with the occupancy of Fe as well as the better crystallinity of specimens at higher T_h [22].

In order to prove the Zn-deficiency in HZFO specimens, the ICP results of both HZFO and CZFO-750 specimens are listed in Table 1. It can be seen that for HZFO specimens, the R_a is obviously higher than 2, the nominal composition in the starting materials. This is obviously related with the loss of Zn during the hydrothermal synthesis process as described above. However, the R_a of CZFO-750 is 1.984, which is very close to 2. As is well-known, Zn^{2+} ions are not easy to lose during a ceramic process.

The RT magnetic hysteresis loop of CZFO-750 is also given in Fig. 7. It can be seen that the M was not saturated at the maximum external field of about 2388 $kA \cdot m^{-1}$ (30,000 Oe) and was nearly proportional to the external magnetic field. Moreover, the M at the maximum external field of $\pm 2388 kA \cdot m^{-1}$ is lower than 4 emu/g, a very small value compared with that of the HZFO specimens.

In order to further interpret the difference in magnetism between HZFO and CZFO, the XPS spectra of two typical specimens HZFO-200 and CZFO-750 were

presented in Fig. 8 to show more information of ion occupancy in A and B sites, and the corresponding binding energies (BEs) are listed in Table 2. Seen from the Fig. 8 (a), the BEs of Zn 2p_{3/2} and Zn 2p_{1/2} in HZFO-200 is about 1021.06 and 1044.10 eV, respectively, just the typical BEs value of Zn²⁺ ions. However, both the Zn 2p_{3/2} and 2p_{1/2} peaks can be fitted to 2 peaks. The peaks at 1020.99, 1044.11 eV and 1021.68, 1045.04 eV can be ascribed to the tetrahedral (tet) A sites and the octahedral (oct) B sites, respectively. Generally, Zn²⁺ ions strongly prefer to occupy A sites, while they were also reported to occupy B sites [16, 17]. The similar results can be seen in Fig. 8 (b) of CZFO-750. Fig. 8 (c-f) shows the XPS spectra of Fe 2p, 3p and the corresponding satellite (sat) peaks. For the HZFO and CZFO specimens, all the Fe 2p and 3p peaks can be fitted to 2 peaks resulted from the Fe³⁺ ions in tetrahedral sites and octahedral sites (as shown in Table 2), respectively, which implies that Fe³⁺ ions occupy A sites as well as B sites. This is similar to the results in the previous reports [16, 17, 23].

According to the results of XPS, both the HZFO and CZFO specimens formed the mixed spinel structure like (Zn_{1-x}²⁺Fe_x³⁺)[Fe_{2-x}³⁺Zn_x²⁺]O₄ during the preparation process. Consequently, the difference in magnetism should be ascribed to the arrangement of magnetic moments. According to the Yafet–Kittle configuration [15], for the Zn-deficient HZFO specimens whose R_a is larger than 2, in order to keep the balance of chemical valence, the specimens could prefer to form the magnetic structure of (Zn_{1-x}²⁺↓Fe_x³⁺)[[↑]Fe_{2-x+δ}³⁺Zn_x²⁺□_{3δ}⁻]O₄, where □ presents the vacancy with negative charge. However, for the CZFO specimen whose R_a is slightly smaller than 2,

the specimen could prefer to form the magnetic structure of $(\text{Zn}_{1-x}^{2+}\downarrow\text{Fe}_x^{3+})[\uparrow\text{Fe}_x^{3+}\uparrow\text{Fe}_{1-x}^{3+}\downarrow\text{Fe}_{1-x}^{3+}\text{Zn}_{x+\delta}^{2+}]\text{O}_4$. Similar to equation (1), theoretically, the molecular magnetic moment of the former is markedly larger than the latter.

From the discussion of magnetism, it is obvious that the Zn-deficiency affected the occupancy of Fe and the magnetism in ZFO.

4. Conclusions

Single-phase ZnFe_2O_4 specimens were obtained via a hydrothermal and a traditional ceramic method, respectively. The magnetization at assigned magnetic fields of the former specimens is obviously greater than that of the latter specimen. This can be ascribed to the loss of Zn ions in the aqueous solution during the hydrothermal process, which should result in the occupancy of some Fe ions in A sites of ZnFe_2O_4 to form the mixed spinel structure. Consequently, the magnetism could be tuned by the Zn-deficiency in the specimens synthesized via a hydrothermal route.

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Figure Captions

Fig. 1 XRD patterns of HZFO specimens obtained at different hydrothermal temperatures T_h .

Fig. 2 FTIR spectra of HZFO specimens obtained at different hydrothermal temperatures T_h .

Fig. 3 Typical FESEM images of HZFO specimens obtained at different hydrothermal temperatures T_h . (a) HZFO-160; (b) HZFO-180; (c) HZFO-200.

Fig. 4 Typical TEM images of HZFO nanopowders obtained at different hydrothermal temperatures T_h . (a) HZFO-160; (b) HZFO-180; (c) HZFO-200.

Fig. 5 EDS mapping results of a typical area in HZFO-200.

Fig. 6 The XRD pattern (a), the typical SEM image (b) and the EDS mapping images of a typical area (c) in CZFO-750.

Fig. 7 The room-temperature magnetic hysteresis loops of HZFO and CZFO-750 specimens.

Fig. 8 XPS spectra and the fitted curves of two typical specimens HZFO-200 (a, c, e) and CZFO-750 (b, d, f).

Tables

Table 1: The Fe/Zn atomic ratio (R_a) of ZFO measured by using ICP

Specimens	HZFO-160	HZFO-180	HZFO-200	CZFO-750
R_a	2.143	2.148	2.139	1.984

Table 2: The binding energy (BE, eV) of Zn, Fe ions in HZFO-200 and CZFO-750.

Specimens		HZFO-200			CZFO-750		
BE		Tet (A)	Oct (B)	Sat	Tet (A)	Oct (B)	Sat
Zn	2p 1/2	1044.11	1045.04		1044.15	1044.75	
	2p 3/2	1020.99	1021.68		1020.83	1021.70	
Fe	2p 1/2	726.52	724.37	732.06	727.04	724.65	732.43
	2p 3/2	712.66	710.70	719.32	712.46	710.68	719.47
	3p	56.64	55.64		57.13	55.76	

Figures

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Figures

Figure 1

XRD patterns of HZFO specimens obtained at different hydrothermal temperatures Th.

Figure 2

FTIR spectra of HZFO specimens obtained at different hydrothermal temperatures Th.

Figure 3

Typical FESEM images of HZFO specimens obtained at different hydrothermal temperatures Th. (a) HZFO-160; (b) HZFO-180; (c) HZFO-200.

Figure 4

Typical TEM images of HZFO nanopowders obtained at different hydrothermal temperatures Th. (a) HZFO-160; (b) HZFO-180; (c) HZFO-200.

Figure 5

EDS mapping results of a typical area in HZFO-200.

Figure 6

The XRD pattern (a), the typical SEM image (b) and the EDS mapping images of a typical area (c) in CZFO-750.

Figure 7

The room-temperature magnetic hysteresis loops of HZFO and CZFO-750 specimens.

Figure 8

XPS spectra and the fitted curves of two typical specimens HZFO-200 (a, c, e) and CZFO-750 (b, d, f).