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ORIGINAL ARTICLE

Influence of pH on properties of Mn–Zn ferrites synthesized from low-grade manganese ore

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Abstract Mn–Zn ferrite powders were produced from low-grade manganese ore (LMO) via the chemical co-precipitation method combined with the ceramic method, after the LMO was leached in sulfuric acid and the obtained solution was purified. The effect of the pH on the magnetic properties of Mn–Zn ferrite was investigated by the varying pH of the co-precipitation system. The crystal structure and phases of the samples were characterized by X-ray diffraction and infrared spectrum, respectively. The magnetic measurements were carried out on a vibrating sample magnetometer. The optimal sample was obtained with a saturation magnetization of 55.02 emu/g, a coercivity of 8.20 G and a remanent magnetization of 1.71 emu/g when pH is 7.5.

Keywords Low-grade manganese ore · Co-precipitation · Mn–Zn ferrite · Magnetic properties

1 Introduction

Mn–Zn ferrites are important electronic ceramic materials employed extensively in transformers, sensors, choke coils, magnetic recording heads, noise filters, information storage systems, medical diagnostic devices and biomedical devices, due to their high magnetic permeability, saturation magnetization, dielectric resistivity and relatively low eddy current losses (Hu et al. 2011; Rath et al. 1999; Kosak et al. 2004). The crystalline structure of Mn–Zn ferrite is similar to that of magnesia-alumina spinel ($MgAl_2O_4$). It is a soft magnetic material with a spinel structure and belongs to the cubic lattice (space group O_h^7—$Fd3m$), in which O^{2-} accumulates as an fcc structure and exists in a two-part symmetrical structure that is a tetrahedron and octahedron in A sites and B sites, respectively. Each lattice cell of Mn–Zn ferrites has 64 A sites and 32 B sites. In a normal spinel structure, divalent cations only occupy the A site and trivalent cations only occupy the B site, while Fe^{3+} occupies both the A site and the B site in $Mn_{1-x}Zn_xFe_2O_4$. This indicates that it is a mixed type spinel (Du Youwei 1996). Much attention has been paid to the preparation of spinel ferrites, as they are considered a crucial piece of technology. Presently, there are many means of preparing Mn–Zn ferrite, such as the ceramic method, the co-precipitation method, the sol–gel method, the hydrothermal method, the self-propagation high-temperature synthesis (SHS), etc. Among these processes, the co-precipitation method has been widely applied in the preparation of Mn–Zn ferrite particles of high purity and ultrafine size, as the particles benefit from its simple technology and its products with a performance of narrow diameter distribution, high chemical purity, and good disperse.

Spent battery (Xiao et al. 2009; Guoxi and Maixi 2005), sulfates of analytical grade (Xuan et al. 2007), nitrate (Wang et al. 2014; Limin et al. 2006) and hydrochloride (Cao et al. 2010) have currently been applied in the preparation of Mn–Zn ferrites. However, there has been no report on the synthesis of Mn–Zn ferrites from low-grade manganese ore (LMO). Due to the backward-developed ore-dressing technology in China and the low utilization ratio of LMO, the rich manganese ores are preferred in

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exploitation while a great number of low-grade ones end up abandoned. This has led to the waste of valuable manganese resources and a series of environmental problems. Hence, taking LMO as the raw materials of Mn–Zn ferrites will not only maximize the use of manganese resources, will greatly benefit the environment.

In this paper, Mn–Zn ferrite powders have been produced from LMO via the chemical co-precipitation method combined with the ceramic method, after leaching LMO in sulfuric acid and purifying the obtained solution. The aim is to study the effect of pH in co-precipitation systems on the properties of Mn–Zn ferrite powder.

2 Experiments

2.1 Preparation of Mn–Zn ferrite

The manganese ore samples were collected from Xiushan, Chongqin. The average composition is described in Table 1.

After dealt in the grinder, the sample was put in a 250 ml three-necked flask. Then, sulfuric acid of 30 % concentration was added with a liquid/solid ratio of three, heated at constant temperature with a water bath and stirred with a magnetic stirrer (180 r/min) at 85–90 °C (Xie et al. 2012). The manganese sulfate solution was obtained after the slurry was filtrated with waste heat. Its pH was adjusted to 5.4 with a 10 mol/L sodium hydroxide solution at 50 °C. Barium sulfide was added to remove Pb^{2+} and any other heavy metal ions, then appropriate amounts of sodium fluoride were added to remove Ca^{2+}, Mg^{2+} and other impurity ions (Peng et al. 2008). One hour later, the solution was filtered. In order to prepare $Mn_{0.27}Zn_{0.23}FeO_2$, the suitable amounts of analytically pure ferrous sulfate and zinc sulfate were added to the filtrate, in order to adjust the Fe and Zn concentrations. Then, the mixed metallic solution was added to the stirred autoclave to react with ammonium bicarbonate for 3 h and its pH was adjusted to 6.5–8.5 with aqua ammonia. The co-precipitated product was transferred to the flask and treated with natural aging for 12 h at room temperature. The precursor powder was obtained after the precipitate was filtered, washed and baked under 100 °C for 24 h.

During the preparation of the precursor with the co-precipitation method samples of different properties can be prepared by varying the pH of the solution. In this paper,

five samples were prepared via adjusting the pH of the co-precipitated solution to 6.5, 7.0, 7.5, 8.0 and 8.5, while other conditions were kept unchanged. The samples were marked as sample A, B, C, D and E accordingly, and their structure and magnetic properties were characterized respectively.

2.2 Characterizion of Mn–Zn ferrite

The content of the element in the samples is measured by a X-ray energy dispersive spectrometer (EDS). The crystalline phase identification of the sample is examined by powder X-ray diffraction (XRD) (Bruker Advance D8) as well as infrared spectrum (IR). The saturation magnetization and coercivity of the samples are carried out on a vibrating sample magnetometer (VSM) (LDJ-9500).

3 Results and discussions

3.1 Influence of pH on the content of element in sample

The content of the element in the samples are measured by EDS. The results listed in Table 2 show that, when the pH is below 7.0, the zinc content increases with the pH; however when the pH is between 7.0 and 8.5, the zinc content decreases from 12.33 to 3.89 %. Obviously, zinc content reaches a maximum value of 12.33 % when the pH is 7.0, which almost is the same as the one in designed sample ($Mn_{0.27}Zn_{0.23}FeO_2$). This indicates that a low pH value is needed for the precipitation of Zn^{2+} in an NH_4HCO_3–$NH_3\cdot H_2O$ system and that Zn^{2+} can completely precipitate at a pH value of 7.0. When the pH increases (when higher than 7.0), the zinc reacts with the ammonia to form soluble $Zn(NH_3)^{2+}$, resulting in zinc loss in the sample. This agrees with the conclusion drawn by Junxi (2005) and Zhang et al. (2003).

Table 2 Composition of zinc in samples (wt%)

	A	B	C	D	E
pH	6.5	7.0	7.5	8.0	8.5
Zn	11.58	12.33	10.46	9.87	3.89

Table 1 Chemical composition of low-grade manganese ore (wt%)

Mn	SiO$_2$	Fe$_2$O$_3$	CaO	MgO	Al$_2$O$_3$	K$_2$O	P	S	Others
12.31	37.94	3.08	7.88	3.99	2.21	2.14	0.25	3.13	27.07

3.2 X-ray diffraction analysis of samples

The XRD determination of the structures present in the samples A, B, C, D and E are carried out on a Bruker Advance D8 X-ray diffractometer with CuKα radiation (λ = 0.154 nm) at 40 kV and 30 mA. The scan rate is 4°/min for values of 20°–70°. The XRD patterns for the as-prepared samples are shown in Fig. 1. It is thought that the mean crystallite size can be determined by the Scherrer formula, when it is less than 100 nm in theory of XRD.

$$d = k\lambda/\beta \cos \theta \tag{1}$$

where d denotes mean crystallite diameter, λ X-ray wavelength, θ Bragg angle and β the half width of the relevant diffraction reflection.

The grain size of the sample is estimated by the strongest peak 311 in the XRD pattern, and the lattice parameters are obtained by analyzing the XRD data of the sample with JADE 5 software. The results presented in Table 3 show that the lattice parameters a, b and c agree with the equation a = b = c, indicating that the prepared sample belongs to cubic lattice. In addition, grain size of the sample increases from 32.7 to 45.4 nm in an irregular manner. The mean crystallite size is 40 nm with the increase of pH, showing that the change of grain size is insignificant in a low pH range of 6.5–8.5. As shown in Fig. 1, the position and relative intensity of the XRD peak agrees with Mn–Zn ferrite's standard pattern. No other impurity peak is detected, indicating that the prepared sample is spinel structure soft magnetic Mn–Zn ferrite. It is easy to conclude that single phase spinel structure soft magnetic Mn–Zn ferrite can be prepared by the chemical co-precipitation method, with a suitable pH range from 6.5 to 8.5, and, once leached in acid and purified, using LRO as raw material… And as presented in Fig. 1, the product transforms completely and displays reproducibility well.
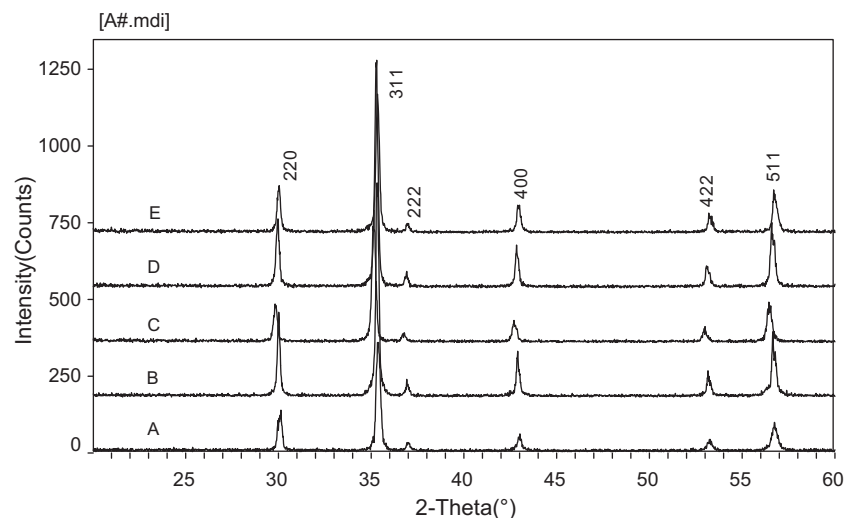
Table 3 Crystal lattice parameter and grain size of different samples

Sample number	Crystal lattice parameter			Grain size (nm)
	a	b	c	
A	8.397	8.397	8.397	32.7
B	8.433	8.433	8.433	44.1
C	8.460	8.460	8.460	40.1
D	8.441	8.441	8.441	45.4
E	8.425	8.425	8.425	38.8

3.3 FTIR spectrometric analysis of samples

The FT-IR spectra of samples A, B, C, D and E are presented in Fig. 2. As shown in Fig. 2, a strong peak appears at $3,464.49 \text{ cm}^{-1}$. This was caused by the stretching vibration of the hydroxyl ion, which resulted from a small amount of water, which had been absorbed from the air, in the production. The absorption peak appearing at $1,630 \text{ cm}^{-1}$ is attributed to the stretching vibration between Zn and O. Also, the absorption peaks present around 1,415 and $1,064 \text{ cm}^{-1}$ result from the asymmetric and symmetric stretching vibrations of the carbonate ion, respectively. All IR patterns have an absorption peak of large strength and width at $550–570 \text{ cm}^{-1}$, which is the intrinsic absorption peak of the spinel sublattice A site. However, the intrinsic absorption peak of the spinel sublattice B site appears around 410 cm^{-1} (Hemeda et al. 2001). This indicates that all the prepared samples are spinel Mn–Zn ferrites, agreeing with the conclusion made in 3.2.

3.4 Magnetic properties of samples

The magnetic properties of the samples are carried out on a VSM, and the results are presented in Fig. 3. The magnetic
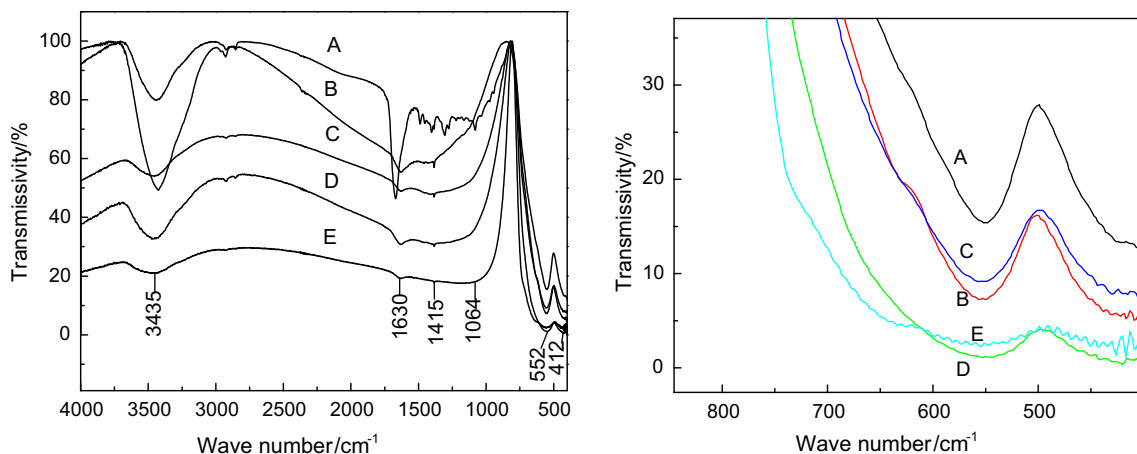
Fig. 1 XRD of Zn–Mn ferrite powder with different pH

Fig. 2 IR patterns of different samples

hysteresis curve of the samples show hysteresis, indicating that the samples exhibit good ferromagnetic behavior. This tallies well with the magnetic properties of Zn–Mn ferrite. The related parameters of magnetism by VSM listed in Table 4 show that the coercivity of Zn–Mn ferrite powder first decreases and then increases with the increase of pH, reaching its minimum at a pH of 7.5. As mentioned in Sect. 3.1, when at the stage of coprecipitation, the content of zinc in the samples first increases and then decreases with the increase of pH. Therefore, this was considered the main cause of that phenomenon. In fact, the coercivity of the magnetic material mainly depends on the material component and defect (impurity and stress). With a low enough zinc content it is easy to produce other phases that result in the increases of internal stress, and it leads, accordingly, to the increases of coercivity.

There are two sub lattices of the A site and the B site in spinel Mn–Zn ferrite (Wang et al. 2006), and its

**Table 4** Magnetic parameter of Mn–Zn ferrite powder synthesized under different pH

Sample number	Ms (emu/g^{-1})	Hc (G)	Mr(emu/g^{-1})
A	32.05	29.31	2.98
B	35.72	27.34	3.37
C	55.02	8.20	1.71
D	49.30	9.03	1.31
E	72.75	16.47	2.16

antiparallel coupling net magnetic moment (M) can be described by the following equation,

$$M = MB - MA \tag{2}$$

MB is the magnetic moment of the B lattice and MA is the magnetic moment of the A lattice. Zn^{2+} is a nonmagnetic ion, and merely occupies the A site. Therefore, when the content of zinc is excessive, Zn^{2+} occupies most of the A

Fig. 3 VSM patterns of Mn–Zn ferrite powder synthesized under different pH

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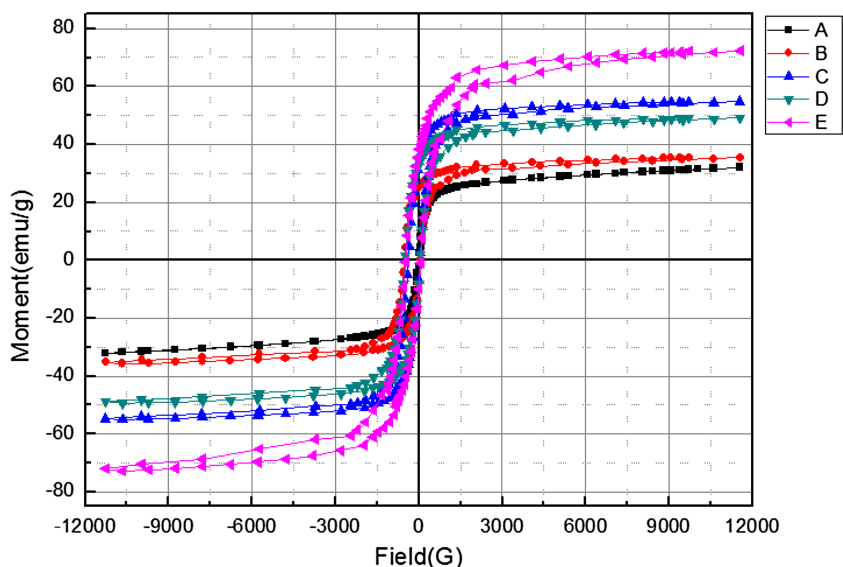
site. Accordingly, the number of magnetic ion Fe^{3+} is sharply reduced in the A site, resulting in the decrease of MA and a corresponding increase of M. This leads to the increase of coercivity required, outside the magnetic intensity, to get the magnetic moment reach zero.

Based on a higher saturation magnetization, it is good for soft magnetic material to have a coercivity as small as possible. Therefore, the optimum product is sample C, as the magnetic properties of prepared Mn–Zn ferrite are best when the pH of co-precipitation system is adjusted to 7.5.

However, many papers have reported that, when using the co-precipitation method, Mn–Zn ferrite exhibits the best magnetic properties (Li et al. 2009) and the zinc ion precipitation is the most complete when the solution is at a pH of 7.0 and NH_4HCO_3–$NH_3 \cdot H_2O$ is used as the precipitant. This does not agree with the conclusion drawn by this paper. However, it can be properly explained, as a different ratio of metal ions made different zinc content of Mn–Zn ferrite when the zinc ions completely precipitated. Hence, the pH required to achieve the best magnetic properties was different. Namely, in this paper, the zinc ion ratio was too high at the designed stoichiometry ratio of the initial raw metal and more experiments are essential for further research.

4 Conclusions

Mn–Zn soft magnetic ferrite nanoparticles with a mean crystallite size of 40 nm were prepared by means of the co-precipitation method and using LMO as the raw materials, after sulfuric acid leaching and purifying the obtained solution. This is not only a feasible method for reusing LMO and a technical proposal for reducing the production cost of Mn–Zn ferrite, but also has a positive impact on the environment. The effect of the co-precipitation solution pH on the properties of Mn–Zn ferrite has been studied. The brief conclusions are as follows. Spinel structure soft magnetic Mn–Zn ferrite can be prepared by the chemical co-precipitation method with a suitable pH range from 6.5 to 8.5 and a suitable stoichiometric addition of sulphate and, after acid leaching and impurity removing, using LRO as raw material. The zinc content of Zn–Mn ferrite powder simultaneously increased with the increase of pH when the pH was less than 7.0, and decreased with any further increase in pH. It reaches its maximum value 12.33 % at a pH of 7.0, which almost is the same as the one in designed sample ($Mn_{0.27}Zn_{0.23}FeO_2$). Its coercivity decreased with the increase of pH when it was below 7.5, but increased when the pH was higher than 7.5. As a result, the optimal sample could be obtained with a coercivity of 8.20 G, a saturation magnetization of 55.02 emu/g and a residual magnetization of 1.71 emu/g when pH was 7.5. The ratio of zinc in the designed sample is a little high, and in the future, further study is needed to obtain the best ratio.

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