

# Microwave synthesis and magnetic properties of polycrystalline Mn-Zn ferrites powder

HAOWEN REN, YUANDONG PENG\*

State Key Laboratory of Powder Metallurgy, Central South University, Changsha, 410083, P.R. China

Microwave synthesis of  $(\text{Mn}_{0.5}\text{Zn}_{0.5})\text{Fe}_2\text{O}_4$  ferrite powder prepared at temperature from 890°C to 1010°C with the same 30min soaking time is reported. The relationship between soaking temperature and magnetic properties has been studied. Microwave synthesis utilizes ferrite's inherent absorption characteristic which result in rapid heating rate. XRD analysis indicates that the synthesized powder is dominated by Mn-Zn ferrite. Heating-temperature curve of microwave synthesis method reveals that the synthesis reactions start at 520°C, in accordance with the DTA/TG data. VSM figures show that we got maximum saturated magnetization and residual magnetization at 1010°C. Coercive field have its minimum value at 980°C, deducing this phenomenon results from grain size.

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## 1. Introduction

Mn-Zn ferrite has been employed widely to transformers, electromagnetic interference [1], magnetic heads [2], etc, since it has relatively higher permeabilities and lower magnetic losses at high frequencies. Several methods have applied to synthesize Mn-Zn ferrite, including conventional ceramic process, high-energy ball milling [3], co-precipitation method [4], hydrothermal method [5], sol-gel method [6], Self-propagating High-temperature Synthesis (SHS) [7] and pulsed laser deposition [8] etc. Conventional ceramic process has apparent defects, like relatively longer reaction time, costly to maintain a high temperature, lower reaction rate and uneven heating among surface and interior. Chemical methods like co-precipitation, hydrothermal and sol-gel method are able to produce small particle ferrite, however, in low productivity. In order to overcome these disadvantages, new synthesis method is necessary to be explored.

Applying microwave heating to ceramics synthesis, called Microwave Synthesis (MS), has received a great amount of attentions during the past years. Ceramics have high dielectric constant, which makes them capable of absorbing microwave energy and turns it into thermal energy. Compared to conventional methods [9], microwave energy heating has couples of advantages such as high thermal efficiency, steady increased heating rate, uniform heating and less costs. Additionally, the temperature of medium used in microwave heating adjustment process has no lag, no hot inertia, and it can quickly start and stop [10].

In this work the microwave synthesis process is

evaluated for the synthesis of polycrystalline Mn-Zn ferrite powders. The relationship between synthesis temperature and magnetic properties has been studied.

## 2. Experimental

### 2.1. Synthesis of $(\text{Mn}_{0.5}\text{Zn}_{0.5})\text{Fe}_2\text{O}_4$ ferrite

The raw materials used in experiment are  $\text{Fe}_2\text{O}_3$ ,  $\text{MnO}_2$  and  $\text{ZnO}$ , both are analytically pure reagents. To precisely synthesize Mn-Zn ferrite, the mass ratio of three materials should be  $\text{Fe}_2\text{O}_3:\text{MnO}_2:\text{ZnO}=66.9:17.3:15.8$ , according to the chemical formula  $(\text{Mn}_{0.5}\text{Zn}_{0.5})\text{Fe}_2\text{O}_4$ . After be weighed and loaded, the raw materials (water was added to assist grinding as levigation) were thoroughly mixed by planetary activator for 120min at room temperature. The mixture was then transferred to a drying cabinet maintained at 100°C for 120 min. The obtained precursor was further grinded by mortar into dispersive dried particles. The diameter and height of initial loosely packed bed was 22 mm and 9 mm with mass of 30g per packed bed. Initial packed beds were compressed by compacting shape machine under 10MPa pressure.

Microwave heating device (MW-L0316 HAMiLab-V type, 6kW, 2.45GHz, multimode) was introduced to prepare the  $(\text{Mn}_{0.5}\text{Zn}_{0.5})\text{Fe}_2\text{O}_4$  ferrite. Temperature above 450°C is measured by infrared pyrometer (RaytekMM2MH, US) with an emissivity of 0.75. Temperature lower than 450°C cannot be detected, since the limitation of infrared pyrometer detected range. The compacts were placed in the center of alumina-fiber insulations with a small amount of SiC served as susceptor. Heating rate and soaking

temperature were manipulated through changing the input power of magnetron. The initial packed beds were separated into 5 groups and heated with the heating rate of approximately 20 °C /min from room temperature (20 °C) to 890 °C, 920 °C, 950 °C, 980 °C, 1010 °C respectively, and then each group was synthesized at 890 °C /30min, 920 °C /30min, 950 °C /30min, 980 °C /30min, 1010 °C /30min respectively in atmosphere. After that, synthesized materials were cooling with the furnace to room temperature. Finally, each group of the  $(\text{Mn}_{0.5}\text{Zn}_{0.5})\text{Fe}_2\text{O}_4$  ferrite were milled for 12 hours by planetary activator.

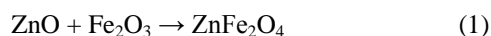
## 2.2. Characterization

A part of raw mixture was sent to process the DTA and TG (Pyris Diamond TG/DTA type, produced by Perkin-Elmer). X-ray diffraction (XRD, model: D8 Discover) was employed to determine the synthesis samples' composition, and, in turn, a vibrating sample magnetometer (VSM, model: Lake shore 7410) was used for measuring the magnetic properties. The milled particle powder was observed and analyzed by laser particle size analyzer and SEM.

## 3. Results and discussion

### 3.1 The microwave synthesis process

Fig. 1 shows output and temperature depends on synthesis time. From Fig. 1, as can be seen the microwave synthesis cost just 80 min to reaction termination. However, conventional ceramic synthesis, which normally requires relatively higher synthesis temperatures (900–1000 °C) and longer synthesis time (over three hours), waste more energy and time than MS. So Microwave heating can dramatically reduce the treatment time for solid-phase reaction. Plenty experimental investigations over the past few decades established that overall process of chemical reactions can be enhanced by using microwave heating [11-13]. A series of solid phase reactions appears during the synthesis which results in the phases of MnZn ferrite. The reaction steps are as follows [14]:



In this process, chemical reactions occur after microwave energies convert to thermal energy. Research has shown that the activation energy of CuO reduction in microwave heating at the maximum point of E-field (E-field heating) decrease to 2/3 of what it is in conventional one and the activation energy in microwave heating at the maximum point of H-field (H-field heating) also decrease to 1/3, compared to that in conventional one [15]. These processes are called as “microwave

non-thermal effect”. Using non-thermal microwave effects is a promising processing, in that it is absolutely different from the process in conventional heating. The results suggest that the energy for reaction is supplied not only by the thermal energy (heat) but also by the non-thermal energy.

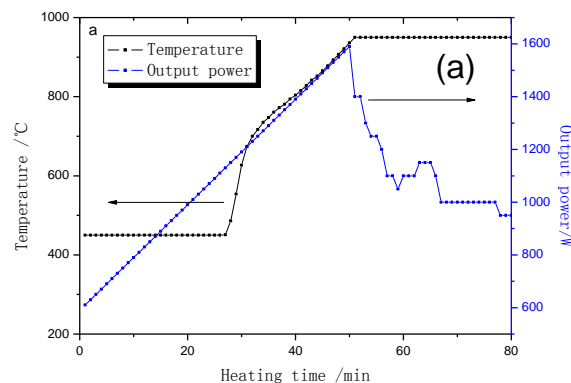
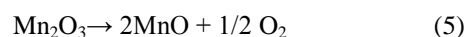
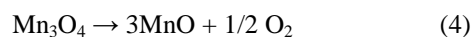
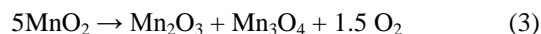


Fig. 1. Heating time vs. temperature and output power curves for  $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  ferrite synthesized by microwave method at 980 °C. (Temperature lower than 450 °C cannot be detected by temperature sensor).

Fig. 1 shows that the slope of temperature changed conspicuously at 700°C, corresponding to the alteration in TG figure in Fig. 2. There are three main factors attribute to the change of temperature: the heat generated by synthesis process, the energy loss caused by the extra oxygen releasing and the degree of thermal run-away. From Fig. 2, we observed that synthesis reaction started at 520 °C, and then finished at 700 °C, deduced by the weight loss. Since we used the  $\text{MnO}_2$  as raw materials, there are some intermediate reactions took place, resulted from the thermal decomposition of  $\text{MnO}_2$ , before the ultimate chemical reaction according to [16]:



The transformation of Mn ions produced excess unstable  $\text{O}^{2-}$  ions and resulted in release of  $\text{O}_2$  and then weight loss. The end of synthesis reaction equals to the end of weight loss. From 450 °C to 520 °C, increasingly raising output power resulted in the increasing heating rate. From 520 °C to 700 °C, the beginning of chemical reaction resulted in rapid heating rate. However, with the finish of reaction, exothermic process decreased which resulted in the deceleration of heating rate at the end of reaction. Above 700 °C, the increasing thermal run-away, in direct proportion to temperature, is compensated by the increase

of output power, thus resulted in constant heating rate.

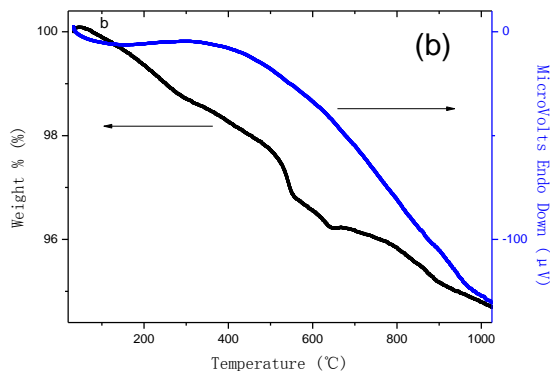


Fig. 2. Thermogravimetric and differential thermal curves for  $Mn_{0.5}Zn_{0.5}Fe_2O_4$  ferrites.

Through the information above, microwave synthesis ferrite has couples of advantages. Firstly, through microwave synthesis method, all substance contained in initial packed bed are able to absorb the microwaves and self-generate heat [17], in that microwave can penetrate into the body of materials, so the interior substance's temperature, unlike conventional heating method, is normally equal to what it is on surface. Thus, it heat samples uniformly. Moreover, compared to other methods, its soaking time is much shorter. Additionally, extremely high speed of heating rate can be achieved by microwave synthesis. Low synthesis temperature and short soaking time minimize the loss of zinc during synthesizing so that the magnets has a stable composition [18]. All these advantages are cores for Mn-Zn ferrite to be fabricated industrially. Using microwave synthesis as an industrial application is low-energy consuming and high productivity.

### 3.2. Microstructure and magnetic properties of the $(Mn_{0.5}Zn_{0.5})Fe_2O_4$ powder

The color of initial tablets are mostly iron brown with few reddish on upper surface. The reddish color is caused by the structure of microwave devices, in that upper surface is close to the pore of the temperature detector. It results in a quicker rate of radiation, and then higher thermal run-away, which leads to an incomplete reaction on upper surface. Additionally, the color becomes darker with the increase of synthesized temperature. The SEM and diffraction patterns for sample synthesizing at 920°C are depicted in Fig. 3. Packed tablets are grinded for 12 hour, and the average particle size of granulated powder is approximately 0.98 $\mu m$ . The average grain size can be measured from the broadening effect of the most intense peak, employing the Debye-Scherrer formula [19] from

the (311) peak of XRD patterns in Fig. 4. The results are presented in Table 1. The crystalline grains have a narrow range of size from 36nm to 44 nm. The smallest average grain size has been found at 980 °C, relevant to better magnetic properties under this temperature, caused by higher synthesis rate. The grain size is larger than that synthesized by hydrothermal method (10-30 nm)[20], but smaller than that synthesized by high-energy ball milling (50nm) [21]. XRD figure of samples show that the sample synthesized at 980 °C own a higher  $(Mn_{0.5}Zn_{0.5})Fe_2O_4$  synthesis rate, deduced by higher characteristic peak of  $(Mn_{0.5}Zn_{0.5})Fe_2O_4$  and lower characteristic peak of  $Fe_2O_3$ .

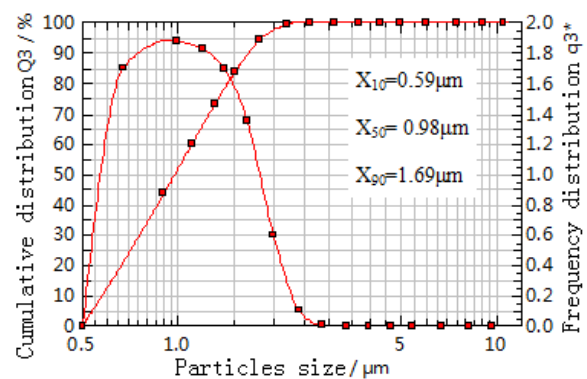
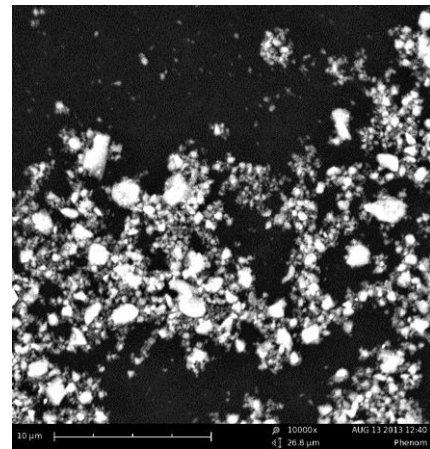


Fig. 3. SEM and size distribution of  $Mn_{0.5}Zn_{0.5}Fe_2O_4$  powder milled for 12 hour after synthesizing at 920 °C.

Table 1. Grain size of  $(Mn_{0.5}Zn_{0.5})Fe_2O_4$  ferrites.

Samples	890°C	920 °C	950 °C	980 °C	1010 °C
d/nm	43.90	40.76	38.52	36.82	39.86

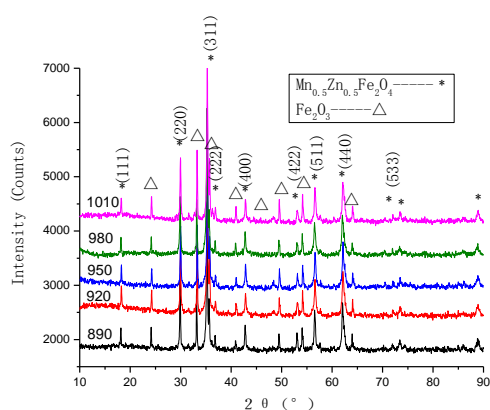


Fig. 4. The XRD patterns of  $(\text{Mn}_{0.5}\text{Zn}_{0.5})\text{Fe}_2\text{O}_4$ . The symbol (\*) marks the  $(\text{Mn}_{0.5}\text{Zn}_{0.5})\text{Fe}_2\text{O}_4$  diffraction peaks, ( $\Delta$ ) marks the  $\text{Fe}_2\text{O}_3$  diffraction peaks.

In this experiment, coercivities and magnetizations features of synthesized materials were characterized. The magnetization curves for the samples under different synthesis temperature were depicted in Fig. 5 by VSM. Magnetic properties are presented in Table 2. Study has shown that for iron based soft magnetic materials, the coercivity value decreases with the reducing of grain size, in that magnetic exchange coupling between the grains has significantly been enhanced [22]. Manaf [23] proposed that unequal distribution of grain sizes, caused by decrease of grain size, results in lower coercivity value. This theory in accordance with the experiment results that samples have the lowest level of coercivity 43.452G at the smallest average grain size of 36.82 nm at 980 °C. Saturation and residual magnetization of the synthesized samples had their maximum value of 24.836 emu/g and 3.022 emu/g respectively, both approached at temperature of 1010 °C.

It has known that there is no domain wall in the single-domain particles and magnetization mechanism is a domain rotation process. Additionally,  $H_c$  was in direct proportion to the size of single-domain particles [24–26]. Therefore,  $H_c$  gradually increased with the size of single-domain particles (below 980 °C). However, when the size arrived to the critical diameter of a single domain, the coercivity started decreasing because of the particles changed from single domain to a multi-domain structure.

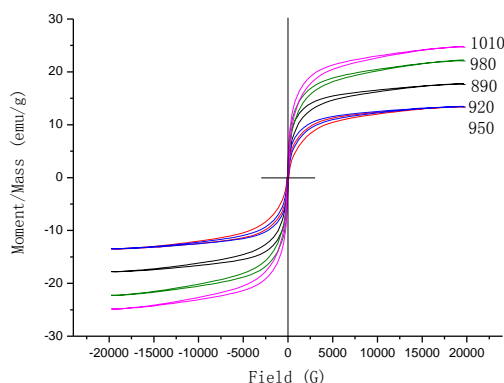


Fig. 5. Magnetic hysteresis loops of powders detected by VSM.

Table 2. Magnetic properties of powders detected by VSM.

Sample	Hci/(G)	Ms/(emu/g)	Mr/(emu/g)
890 °C	61.6	17.7	1.9
920 °C	69.9	13.4	1.6
950 °C	53.3	13.4	1.4
980 °C	43.4	22.2	2.4
1010 °C	54.8	24.8	3.0

#### 4. Conclusion

Microwave synthesis of  $(\text{Mn}_{0.5}\text{Zn}_{0.5})\text{Fe}_2\text{O}_4$  ferrite at temperature between 890 °C and 1010 °C were studied. XRD pattern shows a higher synthesis rate at 980 °C, with the smallest grain size and lower impurities of  $\text{Fe}_2\text{O}_3$ . Synthesized samples were dominated by target  $(\text{Mn}_{0.5}\text{Zn}_{0.5})\text{Fe}_2\text{O}_4$  ferrite. Powders have its smallest grain size at 980 °C, and coercivity decreased with the decrease of grain size, which led to samples synthesized at 980 °C have the lowest coercivity value. Magnetic properties of  $(\text{Mn}_{0.5}\text{Zn}_{0.5})\text{Fe}_2\text{O}_4$  ferrite synthesized by microwave synthesis method attain the standards of qualified soft magnetic materials. Meanwhile, the features and advantages of microwave synthesis are applicable to employ into industrial utilizations.

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\*Corresponding author: pengyuandong@csu.edu.cn