

Microwave assisted low temperature synthesis of MnZn ferrite nanoparticles

Lai Zhenyu · Xu Guangliang · Zheng Yalin

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Abstract MnZnFe₂O₄ ferrite nanoparticles were prepared by co-precipitation method using a microwave heating system at temperature of 100 °C. X-ray diffraction reveals the samples as prepared are pure ferrite nanocrystalline phase, transmission electron microscopy image analysis shows particles are in agglomeration state with an average size of about 10 nm, furthermore, crystal size of samples are increased with longer microwave heating.

Keywords MnZn ferrite · Nanoparticles · Microwave heating

Introduction

Ferrites with the spinel structure form a group of technologically important materials [1]. There are many methods for the preparation of ferrites, including conventional ceramic method (solid state reaction) [2, 3], co-precipitation method [4–6], hydrothermal method [7–9], high-energy ball milling method [10–12], micro-emulsion method [13–15], self-propagating high-temperature method [16] and sol–gel method [17]. Among these methods, co-precipitation method appears to have attracted much attention for preparing ferrites nanoparticles. But particles prepared by co-precipitation method require heat treatment to get better crystalline, so the process need long time

consuming with bad quality control and easy chemical contamination. For these reasons, we previously introduce ball-milling hydrothermal method [18] and microwave-hydrothermal [19–21] to reduce the processing time and energy cost, and finally we found the crystallization of the spinel ferrites was promoted by the increase in reaction temperature and time. Microwave-assisted process is often found to be rapid, and has a potential to enhance the crystallization kinetics of reaction process. In this paper, MnZn ferrites nanoparticles were prepared by microwave assisted co-precipitation method. The formation of nanoparticles depends on microwave heating and conventional heating were carried out. The crystal structure of ferrites and microscopy were measured by XRD and TEM.

Experimental details

Reagent grade Fe(NO₃)₃·9H₂O(WAKO Chem. Co., Tokyo, Japan), Zn(NO₃)₂·6H₂O(WAKO Chem. Co., Tokyo, Japan), Mn(NO₃)₂·6H₂O(WAKO Chem. Co., Tokyo, Japan) were used as the starting materials, NaOH(WAKO Chem. Co., Tokyo, Japan) was used as a precipitator. The starting solutions with 0.25 Mol/L metal nitrates were poured into a tetrafluoronetoxil vessel, then, the mixture was subjected to precipitation with a 4 Mol/L NaOH solution maintaining pH = 10 under vigorous stirring about 30 min. After that, the vessel was heat up to 100 °C with microwave oven(2.45 GHz, 800 W) or conventional heating(oven, 1,000 W). Each sample was cooled to the room temperature after heat treatment, filtered, washed with distilled water several times until pH = 7 could be

L. Zhenyu (✉) · X. Guangliang · Z. Yalin
Key Laboratory of Advanced Building Materials of Sichuan Province, Southwest university of Science and Technology, Mianyang, Sichuan 621010, P.R. China
e-mail: laizy74@163.com

reached. All samples were dried at 80 °C for 24 h and kept in desiccators before characterization.

X-ray diffractograms were recorded in the 2 theta range of 10–80° on Mac Science, Model Mx 3VA diffractometer using CuK α radiation ($\lambda = 1.54056\text{\AA}$). TG-DTA data were traced by using a thermal analyzer (STA 449C, NETZSCH, Germany). The transmission electron microscopy (TEM) of the nanoparticles was done by JEM 100CX (Japan Electron Optics Laboratory, Japan).

Results and discussion

XRD patterns of the samples with formula of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ synthesized under different time are shown in Fig. 1, which shows, all the diffraction peaks of samples could be the spinel phases with microwave heating up to 5 min. Figure 1a shows XRD pattern of powders without any heating method, only minor ferrite can be detected, when microwave heating was prolonged to 5 min, 10 min, 15 min, 20 min, 30 min, according to the peaks intensity of XRD patterns, crystalline of synthesized nanoparticles was improved.

Figure 2 shows XRD patterns of synthesized powders using conventional heating. In the XRD pattern of the powders after heating at 100 °C for 3 h, the crystal structure was detected. As heating time increased to 6 h, in Fig. 2b, better growth ferrite nanoparticles can be gotten.

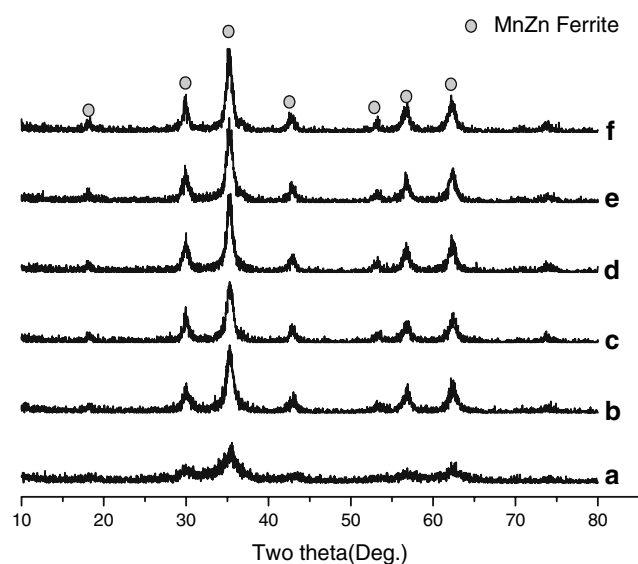


Fig. 1 XRD pattern of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles prepared by co-precipitation method using a microwave heating system: (a) room temperature; (b) 5 min; (c) 10 min; (d) 15 min; (e) 20 min; (f) 30 min

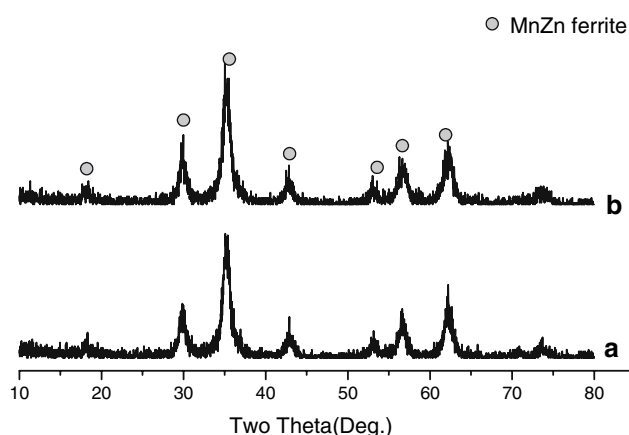


Fig. 2 XRD patterns of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles prepared by co-precipitation method using a conventional heating system: (b) 3 h; (c) 6 h

The XRD patterns of the products showed that highly crystalline MnZn ferrites was formed both under conventional heating condition (Fig. 1) and under microwave heating condition (Fig. 2). For determined the growth of nanoparticles of samples, average particle size for each sample was estimated using the Scherrer formula.

$$D = 0.89\lambda / \beta \cos\theta$$

where D is average crystallite size, λ is the X-ray wavelength used, β is the angular line width of half maximum intensity and θ is Bragg's angle in degrees. The instrument broadening has been estimated using well crystalline bulk Si. The values of particle size of samples prepared by microwave heating and conventional heating from the x-ray data are given in Fig. 3

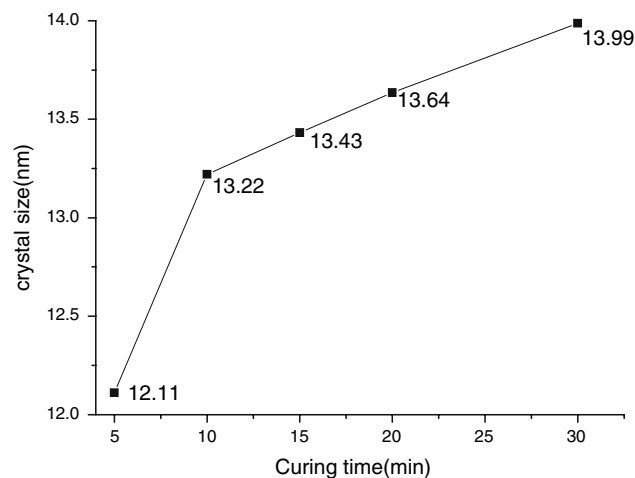


Fig. 3 Relationship between crystal size and heating time of $\text{MnZnFe}_2\text{O}_4$ nanoparticles prepared by microwave heating

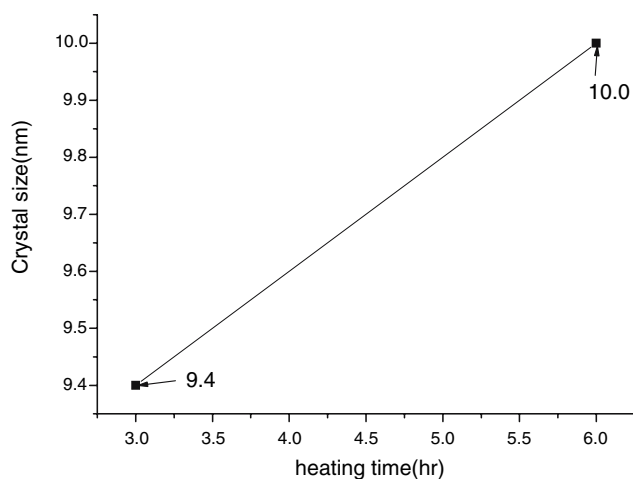


Fig. 4 Relationship between crystal size and heating time of $\text{MnZnFe}_2\text{O}_4$ nanoparticles prepared by conventional heating

and Fig. 4 respectively. Figures 3 and 4 indicate with longer time, the bigger crystal size of samples can be gotten because crystal normally grows upon heating time which is accordance with the kinetics of crystal growth. Figure 3 indicates crystal size of sample can be 12.11 nm after microwave heating for 5 min, but under conventional heating condition, crystal size can be 10.0 nm after 6 h heating (Fig. 4). The formation of ferrite phase within short time indicates the advantage of microwave heating. When the microwave is applied

in the system, microwave induces the rotation and migration of materials having dielectric property and molecular dipole moment. The microwave heating can enable to heat homogeneously both the core and the surface of materials because of the microwave energy transfers to the thermal energy by collision between rotating materials. Therefore, the generation of localized high temperatures in the presence of microwave, with energy transmitted directly to the reactants, the more energized molecules will form products more rapidly.

Figure 5 shows TEM images of MnZn ferrite nanoparticles prepared by microwave heating and conventional heating system. Nanoparticles are all in an agglomerated state and have spherical shape. The average particle size is about 10 nm, which is accordance with the result calculated by Scherrer formula. There is no significant difference between these two methods.

In order to confirm thermal properties of as prepared samples, TG was used to investigate weight loss of as prepared samples. Figure 6 shows the TG curve of $\text{MnZnFe}_2\text{O}_4$ nanoparticles prepared at 5 min and 20 min. The first step below 100 °C in the TG curve is induced by absorbed water of nanoparticles. The second step below 300 °C in the TG curve is induced by crystal water of spinel phase. TG curve shows the weight loss of sample prepared by microwave heating for 5 min is about 1.67 wt% and 2.92 wt% below 100 °C and 300 °C respectively, the weight loss of as

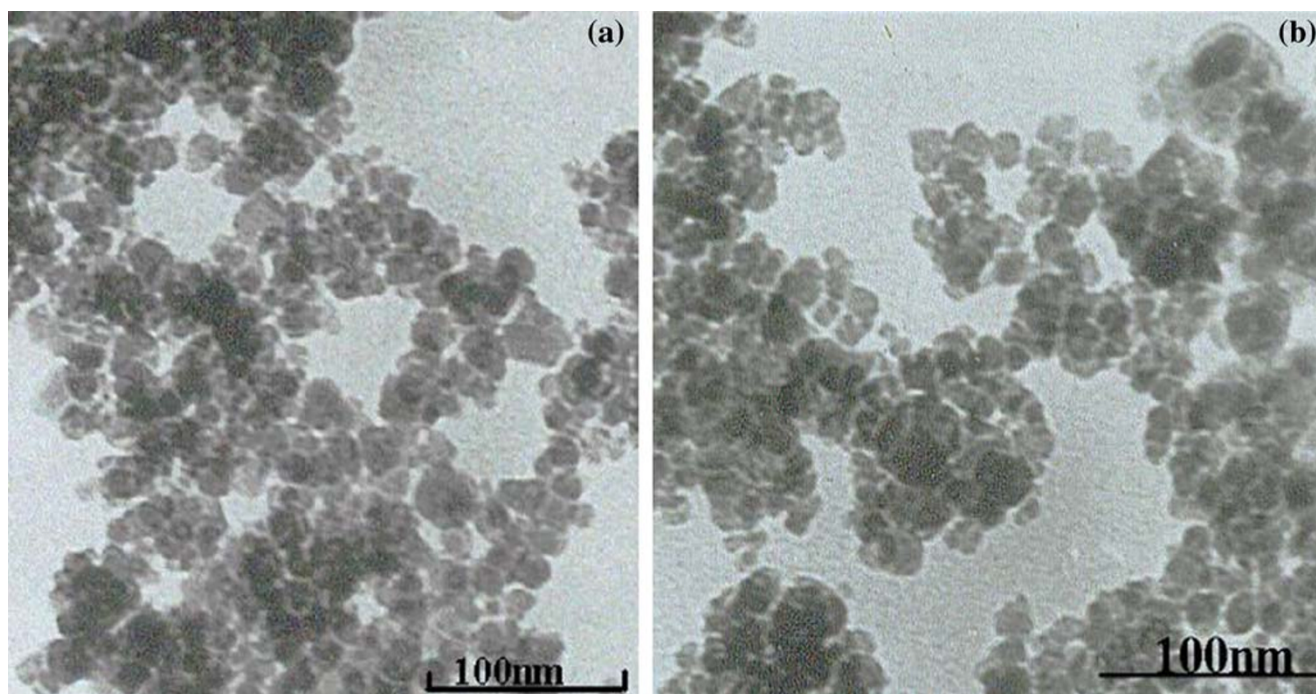
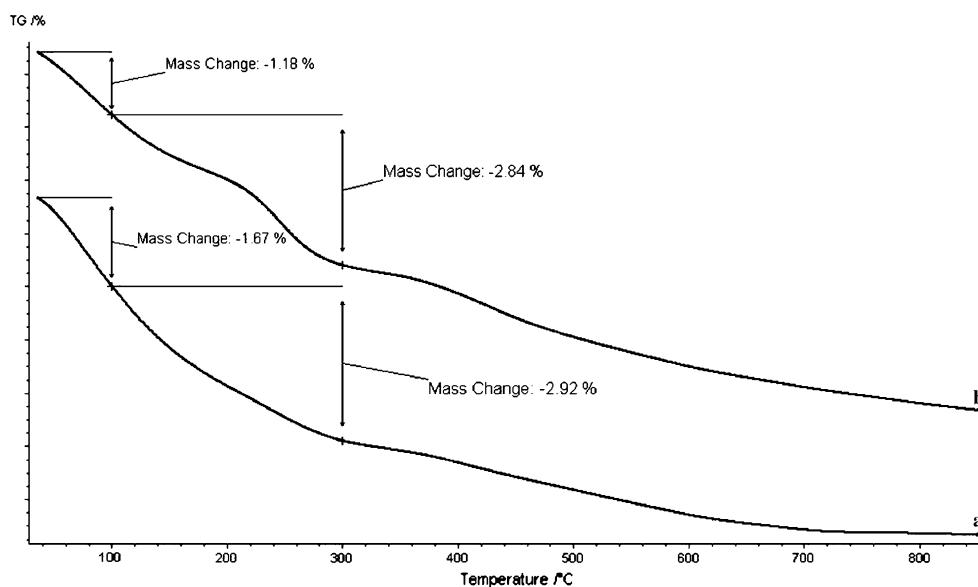


Fig. 5 Transmission electron microscopy picture of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles prepared by (a) microwave heating for 20 min; (b) conventional heating for 6 h

Fig. 6 DTG curves of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles as prepared at 5 min(a) and 20 min(b) ($10^\circ\text{C}/\text{min}$)



prepared sample at 20 min is about 1.18 wt% and 2.84 wt% below 100°C and 300°C respectively. With smaller size, nanoparticles of samples prepared at shorter time have higher surface activity with which can absorb more water than that of samples prepared at longer heating time. The content of crystal water of two samples has minor difference. The weight loss above 300°C is due to the residual nitrate matter in the sample. The weight of as received nanoparticles appears to be constant for temperature above 800°C .

Conclusions

$\text{MnZnFe}_2\text{O}_4$ nanoparticles have been successfully synthesized by microwave assisted low temperature synthesis method. Due to high heating efficiency, microwave can accelerate reaction. Particle size of nanoparticles is increased due to longer heating time. TEM shows nanoparticles are in agglomerated state and have spherical shape. These methods may be extended to synthesize other functional materials in the future.

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