Journal of Magnetism and Magnetic Materials 409 (2016) 6–9

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

A study of the mechanism of microwave-assisted ball milling preparing $ZnFe_2O_4$

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ARTICLE INFO

Article history:
Received 17 December 2015
Received in revised form
1 February 2016
Accepted 20 February 2016
Available online 23 February 2016

Keywords:
Microwave-assisted ball milling
$ZnFe_2O_4$
Dispersion
Pre-ball milling
Pre-microwave irradiation
Reaction rate

ABSTRACT

In this paper, well dispersed $ZnFe_2O_4$ nano-particles with high magnetization saturation of 82.23 emu/g were first synthesized by microwave assisted ball milling and then the influences of pre-treatments and microwave powers to the progress were studied. It was found that under the both function of crack effect induced by ball milling and rotary motion induced by microwave the synthesized ferrtie nano-particles were well dispersed that is much different from the powders synthesized by normal high energy ball milling. The pre-treatment of ball milling can only enhance the reaction rate in the first several hours but the pre-irradiation of microwave can enhance the hole reaction rate. Further more, it was also been found that with increasing the microwave power, the more raw materials will converted into zinc ferrite in the first 5 h. 5 h latter the microwave power of 720 W is high enough for the coupling effect of microwave and ball milling with stirrer rotation speed of 256 rpm.

1. Introduction

As a important kind of ferromagnetic material, spinel ferrite shows perfect characters room temperature ferromagnetism in dielectric, diamagnetic, and wide band semiconductors have been a topic of intense research during the last few years [1,2]. As one of the most important spinel ferrite $ZnFe_2O_4$ have been widely studied and there emerged many excellent methods such as combustion [3], micro-emulsion [4], co-precipitation [5], sol–gel [6], hydro-thermal [7], mechanical milling [8] and so on for preparing it at low temperature.

It always takes hundreds of hours to synthesis spinel ferrite by normal high energy ball milling. In order to decrease the reaction time, the authors developed a new method of microwave assisted ball milling recently and some kind of spinel ferrite have been directly synthesized in much less than 100 h with out any following heat treatment [9–11]. Compared with conventional processes, microwave-assisted ball milling is a simple and environment friendly way for producing high magnetic property spinel ferrite.

In this paper, microwave assisted ball milling is applied to synthesis $ZnFe_2O_4$ and then the dispersion of the synthesized particles as well as that prepared by normal high energy ball milling were studied comparatively. In order to further reduce the reaction time and save energy, the influence of pre-treatment (ball milling and microwave irradiation) as well as microwave power to the reaction rate is studied.

2. Experiment

The raw materials for microwave assisted ball milling are ZnO (hexagonal phase, P63mc, ICSD#29272) and Fe (hexagonal, p63/mmc, ICSD#631723) powders with molar ratio of 1:2. There are several experiments designed: a. Microwave assisted ball milling (MVBM); b. The raw materials were first disposed by ball milling for one hour without microwave irradiation and then treated by microwave assisted ball milling (BM+MVBM); c. The raw materials were first irradiated by microwave without ball milling for one hour and then treated by microwave assisted ball milling (MV+MVBM); d. Microwave assisted ball milling with microwave power respectively set as 960 W, 720 W, 360 W and 120 W. In all the experiments above special stainless steel balls of 3 mm in diameter were used as the milling balls. The rotation speeds of the stirrer during the ball milling process were all 256 rpm. The microwave power applied to the materials was 1200 W if there was no special illustration. The experiment details of microwave assisted ball milling can be found elsewhere [2]. The phase constitutions and their percentages in the samples were identified by X-ray diffraction (XRD) and the magnetic properties were

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http://dx.doi.org/10.1016/j.jmmm.2016.02.066
0304-8853/

characterized by vibrating sample magnetometer (VSM). The mass percentage of zinc ferrite is estimated by semi-quantitative XRD analysis [12].

3. Results and discussion

Fig. 1 shows the XRD pattern of the product synthesized by microwave assisted ball milling for 30 h. Retrieved refinement reveals that the production is spinel ferrite, space group Fd-3m for $ZnFe_2O_4$. It can be observed that there is no other peak existed but the diffraction peaks belongs to $ZnFe_2O_4$, showing that all the raw materials of ZnO and Fe powder have converted to the zinc ferrite completely. The X-ray pattern displaying sharp and well-resolved diffraction peaks proves that the products are in good crystallinity. Although the (311) is the strongest peak, it is not suitable enough according to the width of it, because the (311) peak is neighbor with (222) diffraction peak, the two peaks is too close to distinguish each other in the pattern. Therefor, we selected (220) and (511) peaks for calculating the size of synthesized zinc ferrite particles. From the XRD pattern we found that the peak FWHM of (220) is 0.350 degree and that of (511) is 0.341. If it is assumed that the crystals are mono-domain and free of strain, the crystalline size of the synthesized $ZnFe_2O_4$ particles is estimated to be about 23.24 nm and 26.19 nm respectively using scherrer's equation, $d=0.89\lambda/(\beta^*\cos(\theta))$.

The magnetic property of the $ZnFe_2O_4$ synthesized by microwave-assisted ball milling in 30 h was characterized by VSM at room temperature, and the hysteresis loop is presented in Fig. 2. It could be observed that the saturation magnetization of the prepared $ZnFe_2O_4$ reaches 82.23 emu/g and it is much higher than that as reported synthesized by many of other methods, such as high-energy ball-milling (30 emu/g) [13], surfactant assisted hydro-thermal method (12.0 emu/g) [14], ultrasonic cavitation assisted solvothermal technique (24.32 emu/g) [15], advanced combustion route (60 emu/g) [16] and so on.

The morphology and particle size of the ferrite were characterized by HRTEM. Fig. 3 shows the HRTEM and SAED patterns of the synthesized $ZnFe_2O_4$. From Fig. 3(a) we can see that the diameter of most particles are about 10–25 nm that is close to the average particle size estimated by XRD patterns. It is noteworthy that the synthesized particles are well dispersed. In fact, as we known, the powders produced by normal ball milling method

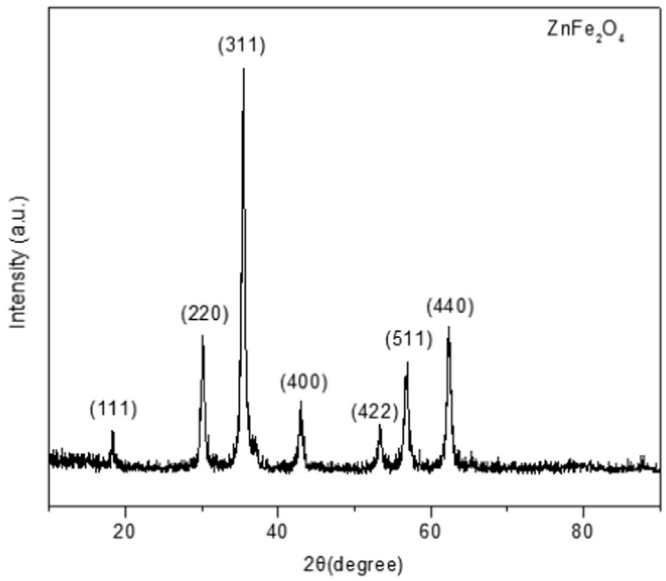

Fig. 1. XRD pattern of the powder produced by microwave assisted ball milling for 30 h.

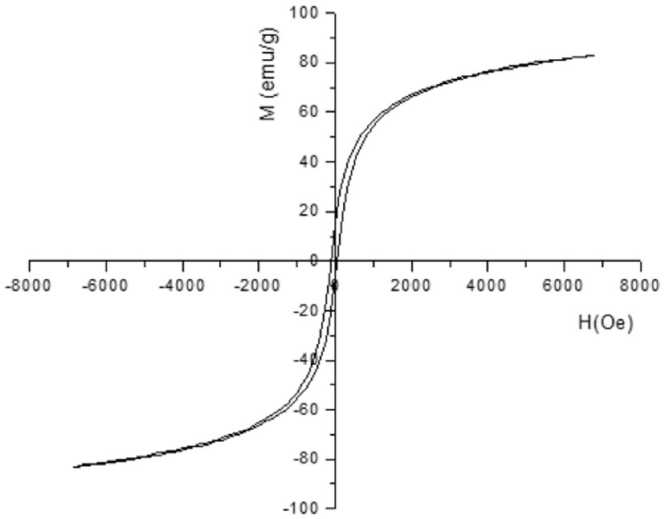

Fig. 2. The room temperature hysteretic loops of the synthesized ferrtie.

directly can not prevent the aggregation without the help of dispersing agent or any following heat treatment [19–21] and Fig. 4 shows the micrograph of the zinc ferrite powders synthesized by single high energy ball milling in 1000 h. In general ball milling process, the particles are cracked into smaller pieces and the smaller particles usually owe higher surface energy that makes them more easily to aggregate together. But in microwave assisted ball milling, on one way, the effect of ball milling crush the particles into smaller size, on the other way, microwave field can prevent the small particles aggregating. Because the microwave field is a union of magnetic field and electric field changing their direction at a frequency of 2.45 GHz. The electrons in milled particles are mostly distributed uneven and dipole moment induced. The particles with a induced dipole moment attempt to align themselves with the oscillating electric field of the microwave irradiation leading to shaking at a high frequency and aggregation is prevented. Fig. 3(b) is the SAED graph of the prepared particles and it can be observed that all the diffraction circles belong to spinel structure confirming that the product is $ZnFe_2O_4$, what is consistent to the result of XRD. The diffraction circles composed of lots of bright spots, suggesting that the particles are very small and with well ordered crystalline structure. The perfect crystalline is mainly induced by the high volume heating effect of microwave that make the atoms including that are in bridge arrange at a order.

3.1. Influence of pre-treatments

$ZnFe_2O_4$ percent versus microwave assisted ball milling time is showed in Fig. 5. In MV+MVBM experiment, all the raw materials converted into $ZnFe_2O_4$ completely in a short time of 25 h. From the curves we can see that the rate of zinc ferrite coming out in the experiment of MV+MVBM is always much higher comparing with that in MVBM experiment. It is the coupling of microwave and ball milling plays a major role in synthesis of the ferrite. In the pretreatment of microwave irradiation much microwave energy were stored in crystals that was contributed to the following ball milling so as to enhanced the coupling effect of microwave and ball milling [24]. From the curves we can also see that in the BM+MVBM experiment, the emerged $ZnFe_2O_4$ is about 22.1% that is much more than that in both MVBM experiment and MV+MVBM experiment in the first 5 h. It can also be observed that 5 h later, both in MVBM experiment and BM+MVBM experiment $ZnFe_2O_4$ emerged at the same rate that is lower than that in MV+MVBM experiment. It is the coupling of microwave and ball milling that