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Preparation and Characterization of Manganese-Zinc Ferrites by a Solvothermal Method

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Abstract: Manganese-zinc ferrites (Mn-Zn ferrites) nanocomposites were prepared by a solvothermal method and characterized by X-ray Diffraction，scanning electronic microscope and vibrating sample magnetometer. Effects of different factors, including the ratio of Mn^{2+} to Zn^{2+}, the temperature and time of solvothermal reaction on the magnetic properties and microstructures of Mn-Zn ferrites were investigated. Results demonstrate that with the rising of reaction time, the particle size becomes bigger and more stable, and the saturation magnetization of the Mn-Zn ferrites nanocomposites increases; when the temperature are 160 and 180 °C, no Mn-Zn ferrites are formed for the temperatures are too low, and the formation temperature of Mn-Zn ferrites spherical particles is 200 °C; rising of Mn^{2+} concentration can not change the morphology of Mn-Zn ferrites, but will contribute to increasing of the saturation magnetization and decreasing of the coercivity of products obtained.

Key words: Mn-Zn ferrites; solvothermal method; magnetic property; microstructures; morphology

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Since produced in 1935 by Snock, ferrite magnetic material has become a promising non-metallic magnetic material in high-frequency weak current areas due to its larger resistivity and higher dielectric properties than that of metals, and its high-frequency magnetic permeability[1-5]. Moreover，ferrite has a higher machining performance, easier to be compressed and molded, better chemical stability and lower cost. Therefore, it plays a very significant role in research and development of magnetic materials [6-10]. It is extensively applied in wired communications, wireless communications, radio, television, and aerospace technology, and is used as the inductor components and transformers in other electronic technologies [11-15].

Mn-Zn ferrite is a kind of soft magnetic ferrite with high saturation magnetization and low resistivity. Mn-Zn ferrite can be produced by many processes including thermal decomposition, chemical co-precipitation, electrolytic precipitation, spraying, self-propagating high-temperature synthesis, a sol-gel method. While Mn-Zn ferrites obtained by dry methods, like mixture of oxides [16,17], show poor composition controllability, larger particle size, and impurities. The wet chemical methods can produce ultrafine and homogeneous powders with great controllability of particle sizes, and best magnetic performance. Several wet chemical methods were used to synthesize ultrafine Mn-Zn ferrites powders, such as the citrate precursor method [18-20], autocombustion route[21,22], hydrothermal route[23-25], sol-gel method [26,27] and solvothermal method [2-5].

In general, solvothermal synthesis offers many advantages over other methods, for example, it is simple, and the products can be obtained at a relatively low temperature with high crystallinity. What's more, the chemical composition can be accurately controlled, and homogeneous nano powders can be prepared, so the particle shape and size can be controlled and it is capable to control crystal growth and adequate to prepare samples in a large scale. S. Yáñez-Vilar [28] reported a

solvothermal method using alcohol as both a solvent and a ligand to produce nanoparticles of $MnFe_2O_4$ with sizes ranging from 5 nm to 10 nm; Q. Zhang produced monodisperse Mn-Zn ferrite ($Mn_{1-x}Zn_xFe_2O_4$) nanospheres via a simple solvothermal method and studied the dependence of magnetic properties of $Mn_{1-x}Zn_xFe_2O_4$ nanospheres on the composition content *x* of Zn [29]; W. Yan synthesized monodisperse Ni-Zn ferrites ($Ni_xZn_{1-x}Fe_2O_4$) microspheres via the solvothermal method and the maximum magnetic saturation value of the $Ni_{0.2}Zn_{0.8}Fe_2O_4$ microspheres can reach 60.6 A·m²/kg [30].

In this paper, a one-pot solvothermal method was used to produce Mn-Zn ferrites. Meanwhile, the effects of synthesis conditions on the morphologies and magnetic properties of Mn-Zn ferrites were systematically studied. Results demonstrate that it is easy to control the synthesis conditions to produce products with uniform particle size and good magnetic properties by the solvothermal method.

1 Experiment

All materials used in our experiments were analytically pure and used without further purifying. The morphologies and structures of the products were determined by X-ray diffraction (XRD, DX2700, China) with Cu Kα radiation and scanning electronic microscope (SEM, TM3000, Japan)，and its magnetic properties were studied by vibrating sample magnetometer (VSM, LakeShore7407, American).

The preparation procedure of Mn-Zn ferrites was as follows: first, $FeCl_3 \cdot 9H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$ and $MnSO_4 \cdot H_2O$ were dispersed into 50 mL of ethylene glycol according to molar ratio of $Mn_xZn_{1-x}Fe_2O_4$ with $FeCl_3 \cdot 9H_2O$ fixed at 0.5 mmol, and the mixture was stirred until it was fully dissolved. Afterwards, 1.54 g NH_4COOH and 0.8 mL polyethylene glycol were added into the mixture, followed by stirring for another 30 min, and the color gradually turned to dark brown. The mixture was then transferred to a stainless steel autoclave and heated from 160 °C to 220 °C for 2~12 h. The black product was washed with ethanol several times and was dried at 80 °C in a drying oven [31]. In the so-called polyol process [32], the ethylene glycol served both as a reducing agent and as a solvent, while NaAc and PEG were used for electrostatic stabilization to prevent particles from agglomeration and as a protective agent.

2 Results and Discussion

2.1 Effects of reaction time on the products

Fig.1 shows the XRD patterns of products for different solvothermal time while the reaction temperature is 200 °C and value of *x*=0.5. When the time is 2 h, no peak corresponding to Mn-Zn ferrites is found. In other words, Mn-Zn ferrites crystals are not formed for the time is too short. As the time increases, until 5 h, Mn-Zn ferrites peaks are got. However the Mn-Zn ferrite phase contains an extra peak.
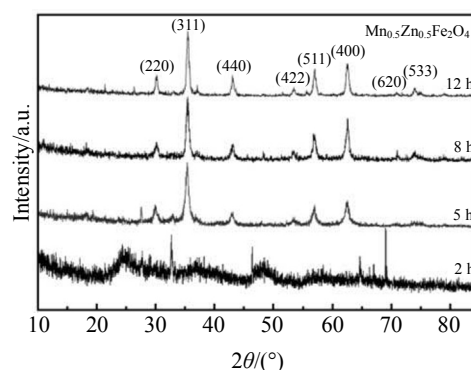

Fig.1   XRD patterns of products for different solvothermal time

When the time continues to increase to 8 h, a well-crystallized pure single $Mn_{0.5}Zn_{0.5}Fe_2O_4$ phase is formed. The crystallite size of the produced Mn-Zn ferrite phase for the most intense peak (311) is determined from the XRD data. It is demonstrated that at this time, the crystallinity of Mn-Zn ferrites is relatively higher. Continuing to increase the time from 8 h to 12 h, the crystallinity keeps stable.

Fig.2 shows the SEM images of products at different time. It is clear that there is an increase in particle size and particle number with the increasing of solvothermal time. No Mn-Zn ferrites spherical particles are formed when the time is 2 h indicating that 2 h is insufficient for the complete formation of the structure. With the time increasing until 5 h, a clear crystalline structure is observed, but the particle number is too little and particle sizes are not homogeneous. When the time continues to prolong, more and more particles are grown. The particle sizes become stable when the time is up to 8 h. Continuing to increase the time from 8 h to 12 h, the particle sizes illustrate no obvious differences. This is in accordance with Fig.1.
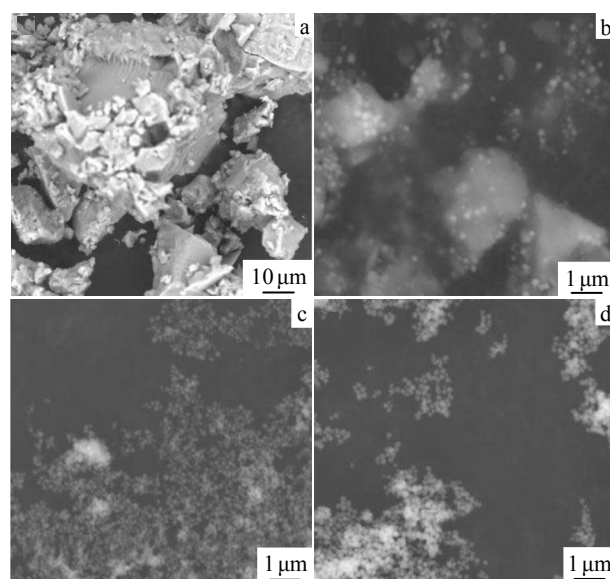

Fig.2   SEM images of products for different solvothermal time:
(a) 2 h, (b) 5 h, (c) 8 h, and (d) 12 h