研究简报

$MgFe_2O_4$ 纳米粉体的水热合成及其表征

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关键词: $MgFe_2O_4$; 水热法; 磁性材料
中图分类号: O614.22; O614.81+1 **文献标识码**: A **文章编号**: 1001-4861(2005)05-0697-04

Synthesis and Characterization of Nanosized $MgFe_2O_4$ Powders by Hydrothermal Method

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Abstract: $MgFe_2O_4$ nanoparticles were hydrothermally synthesized at 150 ℃ using iron nitrate [$Fe(NO_3)_3\cdot 9H_2O$], magnesium nitrate [$Mg(NO_3)_2\cdot 6H_2O$] and sodium hydroxide (NaOH) as starting materials by carefully controlling the reaction conditions. The influences of several factors such as presence or absence of Na^+, molar ratio of Fe^{3+}/Mg^{2+}, concentration of mental ions, temperature and reaction time on resultant products were investigated in the hydrothermal process. The sample was characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM), and its magnetic properties were measured using vibrating sample magnetometer (VSM).

Key words: $MgFe_2O_4$; hydrothermal method; magnetic materials

0 Introduction

In recent years, there has been a growing interest in the fabrication of nanoscale magnetic materials owing to their interesting properties and potential applications in data records and storage[1~3]. Magnesium ferrite ($MgFe_2O_4$) is a well-known spinel magnetic material and can be used as ferrimagnets, brown pigments and dehydrogenation catalysts. Moreover, these materials also have interesting humidity-sensing, oxygen-sensing and photoelectrical properties[4]. Machara et al.[5] have recently shown that Mg ferrite is more applicable in achieving local hyperthermia, which could be developed as a new therapy for tumors, when compared to other ferrites. Several methods have been reported in the literatures for the preparation of nanoscale $MgFe_2O_4$ particles, such as mechanical alloying[6], high-energy milling[7], co-precipitation[8], and microwave hydrothermal method[9].

Hydrothermal synthesis is capable of making fine particles at very low temperatures without any calcinations or milling steps[10]. Crystallization and morphology controlling of various ferrites under hydrothermal conditions have been investigated[11~14]. To the best of our knowledge, there has been no report on the synthesis of nanosized $MgFe_2O_4$ particles using simple hydrothermal route. We herein report the preparation of $MgFe_2O_4$ nanoparticles by hydrothermal method.

收稿日期:2004-09-06。收修改稿日期:2004-11-06。
国家自然科学基金资助项目(No.20125103,90206034)。
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1 Experimental

The starting materials for the present synthesis include iron nitrate [$Fe(NO_3)_3 \cdot 9H_2O$], magnesium nitrate [$Mg(NO_3)_2 \cdot 6H_2O$] and sodium hydroxide (NaOH). The hydrothermal synthesis was carried out in a 45 mL Teflon-lined stainless autoclave. The [$Fe(NO_3)_3 \cdot 9H_2O$] and [$Mg(NO_3)_3 \cdot 6H_2O$] were mixed and dissolved in distilled water, and then sodium hydroxide solution was added while stirring until the metal ion was precipitated entirely. The precipitate was washed by distilled water to remove sodium ions until the pH of the filtrate reached 7~8. The molar ratio of [$Fe(NO_3)_3 \cdot 9H_2O$] to [$Mg(NO_3)_2 \cdot 6H_2O$] was 2∶1, 1.5∶1 and 1∶1, the concentration of Mg^{2+} was 0.05 mol·L^{-1}. The slurry so obtained was hydrothermally treated at certain temperatures for 6, 12, 18 h, respectively. The products were washed several times with distilled water and absolute ethanol, and finally dried at 80 ℃ for 6 h.

The samples were characterized by XRD using Cu $K\alpha$ radiation (λ=0.154 18 nm) at a scanning rate of 0.05°·s^{-1} and in 2θ of 10°~70°. TEM images were taken with a Hitachi model H-800 transmission electron microscope, using an accelerating voltage of 200 kV. The magnetic properties were measured on a BHV-55 vibrating sample magnetometer at room temperature.

2 Results and discussion

The resultant products were strongly influenced by several factors such as the presence or absence of sodium, temperature, reaction time, molar ratio of Fe^{3+}/Mg^{2+} and the concentration. The synthesis of magnetic Mg ferrite at relatively low temperature is difficult. The results indicated that the presence of sodium ions had a negative effect on $MgFe_2O_4$ formation during hydrothermal treatment. The XRD result for powders synthesized at 150 ℃ for 12 h is shown in Fig.1. The $MgFe_2O_4$ phase was formed successfully at low temperature when the co-precipitation of hydroxides was washed to remove sodium ions before hydrothermal treatment. While sodium ions were present during hydrothermal treatment, α-Fe_2O_3 existed as the main phase and there was no $MgFe_2O_4$ phase. This observation may be related to the spinel structure. It has been reported that a small amount of sodium left in the slurry would obstruct to form the normal or mixed ferrite[15]. It is known that Fe^{3+} by itself prefers to occupy tetrahedral sites. It will manage to go in the ferrite structure even in the presence of a small amount of sodium. From the fact that Mg ferrite was not found when sodium was present in the system [Fig.1(a)], it is supposed that the presence of sodium ions affects the formation kinetics of Mg ferrite at the hydrothermal

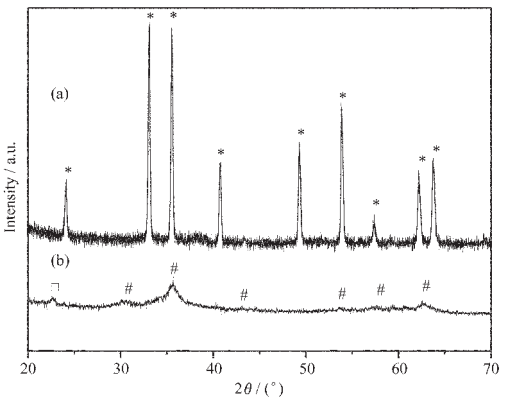

Fig.1 XRD patterns of the powders hydrothermally synthesized at 150 ℃ for 12 h
(a) Na left in the slurry,
(b) Na removed from the slurry
(*: Fe_2O_3, #: $MgFe_2O_4$, □: FeO(OH))

environment, resulting in formation of α-Fe_2O_3.

The yield of $MgFe_2O_4$ phase was also affected by temperature. The temperature effect on the phase formation of magnesium ferrite was investigated at 140~160 ℃ with Fe^{3+}/Mg^{2+} ratio and reaction time being fixed at 2∶1 and 12 h, respectively. Fig.2 shows the X-ray diffraction patterns of the magnesium ferrite pow-

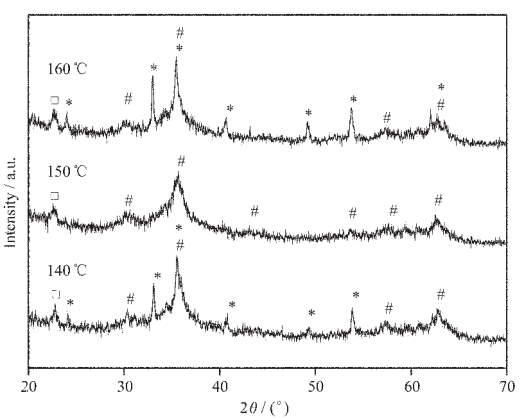

Fig.2 XRD patterns of the powders hydrothermally prepared at 140, 150 and 160 ℃, respectively
(*: Fe_2O_3, #: $MgFe_2O_4$, □: FeO(OH))

ders synthesized at different temperatures and Na^+ was removed from precursor before hydrothermal process. $MgFe_2O_4$ was formed with α-Fe_2O_3 as a minor phase at temperatures of 140 and 160 ℃. At 150 ℃, $MgFe_2O_4$ was observed as a main phase with trace amount of FeO(OH). This suggests that the temperature strongly affected the resultant phase formation. $MgFe_2O_4$ phase could be formed only in an extremely narrow temperature range around 150 ℃. However, other peaks are not obvious except for the strongest one, this may be due to the small particle size and poor crystallinity.

Phase evolution of this system under hydrothermal conditions was studied with variation in synthesis time for Fe^{3+}/Mg^{2+}=2:1 at 150 ℃. Fig.3 shows the result in the case of sodium ions being removed at each case. It is shown that the gained precursor is mainly amorphous in nature with a small amount of ferrite. After hydrothermal treatment for 6 h the $MgFe_2O_4$ phase has been formed. This suggests that the formation of Mg ferrite phase is very fast under the hydrothermal conditions in this investigation. With the increasing of reaction time, the peaks got narrower and sharper, manifesting the grain size increase and crystallinity improvement. However, no further changes were observed when the reaction time was longer than 18 h. The broad peaks imply the significant decrease of grain size. The grain sizes calculated using the Debye-Scherrer formula from the reflection of (311) is about 10 nm. The cubic lattice parameter is calculated as a=0.834 nm from the powder XRD pattern, slightly smaller than the lattice parameter of

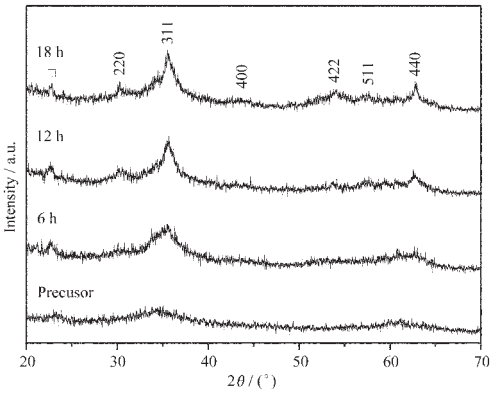

Fig.3 XRD patterns of as-synthesized precursor and powders obtained at 6, 12 and 18 h, respectively (□: FeO(OH))

bulk $MgFe_2O_4$, a=0.837 nm (JCPDS 73-2211).

The molar ratio of Fe^{3+}/Mg^{2+} and the concentration of the metal ions were also investigated. They had little contribution to the formation and crystallinity of $MgFe_2O_4$.

Fig.4(a) shows TEM micrograph of powders prepared by hydrothermal treatment at 150 ℃ for 12 h with the sodium removed from the slurry. The particles appear to be flake-shape. The selected area electron diffraction (SAED) pattern is shown in Fig.4(b). The pattern corresponds to that of a spinel phase. The particles are extremely small and the result agrees well with that calculated from XRD data. This indicates that hydrothermal technique could produce ultrafine and well-dispersed nanosized $MgFe_2O_4$ powders.

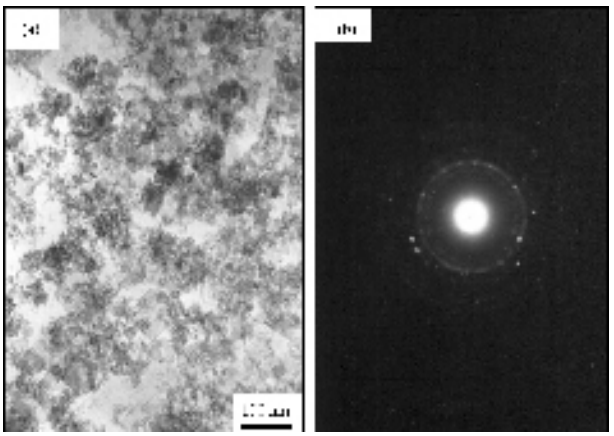

Fig.4 (a) TEM image of the sample prepared at 150 ℃, (b) SAED pattern of nanosized $MgFe_2O_4$ particles

Fig.5 depicts the hysteresis loop measured at room temperature over H=±15 000 Oe. Saturation of magnetization was not observed for the sample prepared at 150 ℃ even at a field of 15 000 Oe. The value of magnetization at room temperature under 15000 Oe field is found to be 11.14 emu·g^{-1}. And coercive force is 251.4 Oe, which is lower than that of bulk materials. The reason for these phenomena might be due to ultrafine feature of the powder. If the sample was annealed in air at 400 ℃ for four hours, the magnetization (30.47 emu·g^{-1}) increased significantly to slightly higher than that of $MgFe_2O_4$ produced by the conventional ceramic method (26.4 emu·g^{-1})[16]. But the coercive force (256.4 Oe) remains almost unchanged. The results of magnetization and coercive force in our investigation are different from those of samples prepared from the co-precipitation method,

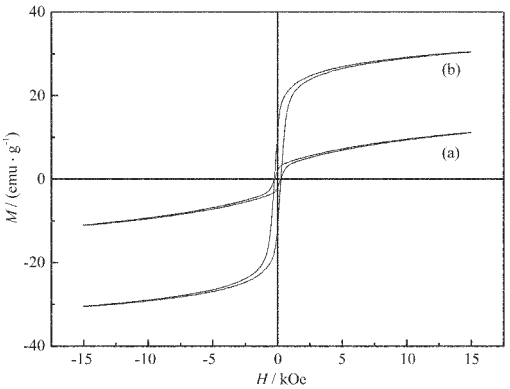

Fig.5 Hysteresis loops for the sample prepared at 150 ℃ (a) and then annealed at 400 ℃ (b) respectively

which are superparamagnetic at room temperature[8].

3 Conclusions

Nanoscale $MgFe_2O_4$ powder was successfully synthesized by using nitrate sources under hydrothermal conditions at temperature of 150 ℃. The formation of $MgFe_2O_4$ structure during hydrothermal treatment depends sensitively on several factors such as pH value (7~8) and temperature. $MgFe_2O_4$ could only be formed in an extremely narrow temperature range around 150 ℃ in our investigation. $MgFe_2O_4$ nanoparticles with flake-shape display soft magnetic behavior with an Ms of 11.14 emu·g^{-1}.

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