水热法制备超顺磁性铁氧体纳米微粒

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本文通过水热法制备了一系列铁氧体纳米微粒(MFe_2O_4, M = Zn, Ni, Co, Cu, Mn)，用XRD和TEM对产品进行了表征，产物为纯相、粒径均匀、团聚少的纳米粒子。磁性质测量表明它们具有超顺磁性质。另外，我们还对反应过程中溶液pH值对最终产物的影响进行了研究。

关键词: 铁氧体 水热法 超顺磁
分类号: O614.81⁺1

Hydrothermal Synthesis and Superparamagnetic Behaviors of a Series of Ferrite Nanoparticles

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Nanoparticles of a series of magnetic ferrites (MFe_2O_4, M = Zn, Ni, Co, Cu, Mn) were fabricated by hydrothermal precipitation route and studied by XRD, EDX, and TEM. XRD patterns show phase-pure products synthesized in this process, and TEM observations directly reveal the uniformly sized nanoparticles with little aggregation. Superparamagnetic behaviors of the synthesized samples were confirmed by magnetic characterization. In addition, influences of solution pH on the final products were also investigated in this study.

Keywords: ferrite hydrothermal superparamagnetism

Superparamagnetism as a unique feature of magneic nanocrystals is of great interest in basic science such as macroscopic quantum tunneling of spin states[1,2]. Superparamagnetic nanoparticles have great relevance to modern technologies including ferrofluid technology[3], contrast enhancement of magnetic resonance imaging(MRI)[4], and magnetocaloric refrigeration[5,6]. Also, the superparamagnetic nanoparticles are the lower limit for high density information storage. The fundamental studies on this subject are mostly concentrated on pure metal nanoparticles such as Fe, Co, and Ni[7-10]. For these metal nanoparticles, size is the only control to their superparamagnetic properties and superparamagnetic state usually exists in metal particles within a few size nanometers ranges. Besides, chemical instability is also an obstacle to broad applications of these metal superparamagnetic particles. Recently, metal oxides such as spinel ferrites have appeared to be another family of superparamagnetic materials and have been extensively studied. This class of materials show

收稿日期：2001-10-11。收修改稿日期：2001-12-25。
国家杰出青年科学基金资助项目(No. 20025102)。
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great advantages on the pure metals for the great tunability in their chemical composition and their chemical inertness towards oxygen[11~13].

Many methods for the preparation of ferrite powder have been reported in literature, such as solid state reaction[14], combustion synthesis[15], sol-gel[16], reverse micelle synthesis[17], coprecipitation and oxidation[18, 19], spray pyrolysis[20], flux and hydrothermal method[21~23]. Different from other methods, the hydrothermal synthesis requires neither extremely high processing temperature nor complicated operation procedures. In addition, no sophisticated equipments are needed in the hydrothermal process. For example, ferrites can be prepared via the hydrothermal method at a temperature of about 150℃, whereas the solid-state method requires a temperature of about 800℃[24]. Hydrothermal synthesis of several ferrites has been reported. However, to the best of our knowledge, no research on the superparamagnetism of the hydrothermally prepared products has been reported. It is known that the preparation route has critical influence on the magnetic behaviors of the resultant nanoparticles, thus it is of great significance to investigate the magnetic behaviors of a series of hydrothermally prepared ferrite nanoparticles.

We herein report the preparation of a series of ferrite nanoparticles by hydrothermal method and the physical characterization of them. The influence of the reaction pH on the final products was also considered in detail.

1 Experimental

A series of ferrites such as $ZnFe_2O_4$, $NiFe_2O_4$, $CoFe_2O_4$, $CuFe_2O_4$ and $MnFe_2O_4$ were prepared under hydrothermal conditions. Zinc acetate, sulfate of nickel, cobalt, copper or manganese were mixed with ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) under electromagnetic stirring. The mixture was then neutralized with 0.8mol · L^{-1} sodium hydroxide solution to a specific pH under vigorous stirring. The coprecipitation was formed and the resultant mixture was then transferred into a Teflon-lined autoclave with a stainless steel shell. The autoclave was kept in the temperature range 150~170℃ for more than 4.5 hours and then allowed to cool to room temperature naturally. The final product was washed with deionized water several times and dried under an infrared lamp for 6~8 hours. Powder X-ray diffraction (XRD) experiments of all the products were conducted on a Bruker D-8 Advance X-ray diffractometer with Cu $K\alpha$ radiation (λ = 1.5418 Å). The morphologies and sizes of the synthesized products are observed through a Hitachi-800 transmission electron microscopy (TEM) operated at 200kV.

2 Results and Discussion

Powder XRD results (Fig. 1) of the samples synthesized under various conditions clearly indicated that phase-pure ferrites were obtained in all cases except $MnFe_2O_4$, as listed in Table 1. Furthermore, EDX results were also given to demonstrate the purity of the products. The molar ratios of M/Fe (M = Zn, Ni, Co, Mn) were listed in Table 1. As expected, $NiFe_2O_4$ and $CoFe_2O_4$ show Ni∶Fe and Co∶ Fe equal to 1∶2, and $MnFe_2O_4$ sample has a Mn∶Fe ratio about 1∶3, in agreement with the XRD results in Fig. 1. However, although no visible XRD peaks of Fe_2O_3 exist in the XRD pattern of the $ZnFe_2O_4$ sample, the EDX show a Fe∶Zn ratio > 2, implying the existence of Fe-containing impurities, such as amorphous ferric oxide.

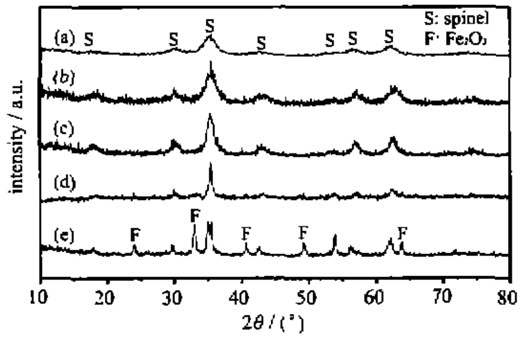

Fig. 1 XRD patterns of nanophase ferrites prepared via hydrothermal method

(a) zinc ferrite, (b) nickel ferrite, (c) cobalt ferrite, (d) copper ferrite, (e) manganese ferrite

The ferrites have small particle sizes, as indicated by the broad peaks in the XRD patterns. TEM images reveal uniformly sized particles with little aggregation

Table 1 Synthesis Conditions and Characterizations of Ferrites Formed via Hydrothermal Processing

synthesis condition	pH of starting suspension	existent phases	particle size	proper pH range	ratio of M/Fe
160℃ for 5 hours	8.0	$ZnFe_2O_4$	4nm	6.5 ~ 10	1:3
150℃ for 5 hours	7.5	$NiFe_2O_4$	5nm	6.5 ~ 8	1:2
160℃ for 6 hours	7.5	$CoFe_2O_4$	8nm	6.5 ~ 8	1:2
170℃ for 6 hours	7.5	$CuFe_2O_4$	16nm	6.5 ~ 8	—[a]
170℃ for 6 hours	7.5	$MnFe_2O_4$, Fe_2O_3	8.4nm	6.5 ~ 8	1:3

a: Quantification by EDX is not viable due to the interference from the TEM copper grid.

as illustrated in Fig. 2. The average particle sizes estimated from XRD half-peak widths using Scherrer formula are about 4nm, 5nm, 8nm, 16nm and 8.4nm for $ZnFe_2O_4$, $NiFe_2O_4$, $CoFe_2O_4$, $CuFe_2O_4$ and $MnFe_2O_4$ respectively, which are comparable with the TEM observations.

Further experiments have been conducted at different pH to understand its influence on the physical characteristics of the resultant ferrite powders. It was found that all the ferrites could be synthesized in the pH ranges as listed in table 1. Proper control of the pH is crucial for synthesizing phase-pure ferrites. For ex-

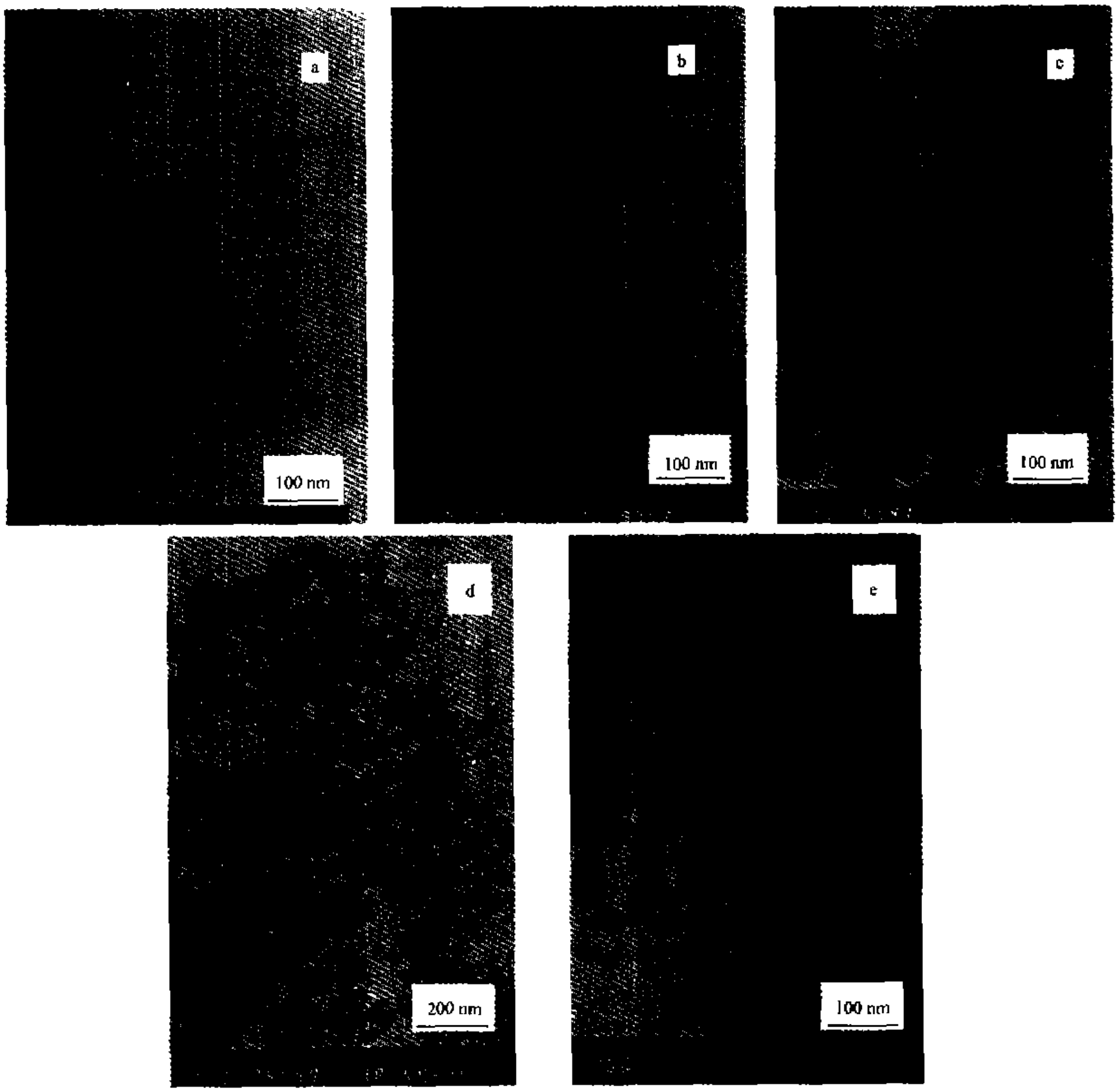

Fig. 2 TEM micrographs of nanophase ferrites prepared via hydrothermal method

(a) zinc ferrite, (b) nickel ferrite, (c) cobalt ferrite, (d) copper ferrite, and (e) manganese ferrite ample, in the preparation of $ZnFe_2O_4$, pH> 12 will lead to some impurities such as Fe_2O_3.

Fig. 3 shows the magnetization curves measured at 290K for $ZnFe_2O_4$, $CoFe_2O_4$ and $NiFe_2O_4$. Slight hysteretic feature is observed from the magnetization curve of $CoFe_2O_4$(Fig. 3c), which indicates that the measurement was conducted at a temperature a little lower than or close to its blocking temperature[25-28]. Therefore, superparamagnetic behavior should not be expected. However, both $ZnFe_2O_4$ (Fig. 3a) and $NiFe_2O_4$ (Fig. 3b) nanoparticles exhibit superparamagnetic behaviors at 290K. The superparamagnetism of MFe_2O_4 (M = Zn, Co) at 290K is relevant with their extremely small sizes and low blocking temperatures. For $CoFe_2O_4$, the blocking temperature should be lowered if the particle size could be reduced further[26] since it will be easier for finer particles to be thermally activated to overcome the magnetic anisotropy. In a typical hydrothermal hydrolysis, particle size could be controlled by many operation parameters, e. g. the pH of the reaction media, proper selection of the co-existing ions, temperature and reaction period etc. The easy synthesis and size-control of superparamagnetic ferrites nanoparticles by hydrothermal hydrolysis will facilitate their production in large scale, and thus find more new applications. We are currently attempting to synthesize ferrites with different size distributions, and this will afford the possibility to investigate the size-dependent superparamagnetic behavior. The synthesized nanocrystalline ferrites are good candidates for the applications in ferrofluid technology, contrast enhancement of magnetic resonance imaging (MRI), and magnetocaloric refrigeration.

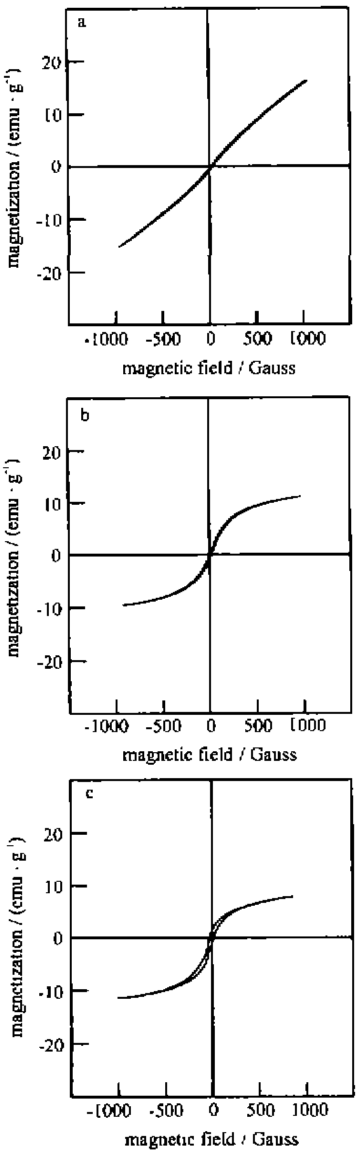

Fig. 3　Magnetization vs applied magnetic field for the ferrites (a) zinc ferrite, (b) nickel ferrite, (c) cobalt ferrite

3 Conclusions

Hydrothermal synthesis and magnetic characterization of a series of ferrite nanoparticles were performed. The proper synthesis conditions were discussed. The magnetic measurements showed that the prepared nanoparticles possessed good superparamagnetic behaviors. The successful syntheses of spinel ferrite nanoparticles will facilitate the exploration of potential superparamagnetic systems and the fine tuning of superparamagnetisms of existing materials.

Acknowledgements: We thank Dr. TANG Cheng-Chun for his help in conducting magnetic measurements. This work was supported by the NSFC (National Science Fund of China) though the National Outstanding Youth Science Fund.

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