

Research Article

Preparation and Magnetic Properties of ZnFe₂O₄ Nanotubes

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Ordered ZnFe₂O₄ nanotube arrays with the average outer diameter of 100 nm were prepared in porous anodic aluminum oxide template using an improved sol-gel approach. The morphology was studied by transmission electron and field emission scanning electron microscope. X-ray diffraction result shows that the nanotubes were polycrystalline in structure. The magnetic properties of the prepared ZnFe₂O₄ nanotubes were also studied. The results show that the sample shows typical superparamagnetism at room temperature and obvious ferromagnetism below blocking temperature.

1. Introduction

Spinel ferrites belong to a kind of magnetic materials that can be used in many areas, such as magnetic devices and switching devices [1–3]. Zinc ferrite (ZnFe₂O₄) is of interest not only to basic research in magnetism, but also has great potential in technological application, such as magnetic materials [4–10], gas sensors [11], catalysts [12], photocatalysts [13], and absorbent materials [14–18], described by the formula (A)[B]₂O₄. Spinel ferrites, which possess the cubic structure, are the (A) and [B] that indicate tetrahedral and octahedral cation sites in a face-centered cubic anion (oxygen) sublattice, respectively. Bulk ZnFe₂O₄ has a normal spinel structure with Zn²⁺ ions in the A-site and Fe³⁺ ions in the B-sites. For bulk Zn-ferrite prepared by the conventional ceramic method, the inversion parameter δ equals zero (normal spinel). However, in contrast to bulk compound, the nanocrystalline ZnFe₂O₄ system always shows up as a mixed spinel in which Zn²⁺ and Fe³⁺ ions are distributed over the A and B-sites. This cationic rearrangement leads to the formation of two magnetic sublattices, which is responsible for the enhanced magnetization displayed when compared with normal ZnFe₂O₄ [19–21]. It is known that the bulk ZnFe₂O₄ is a paramagnet at room temperature, however, magnetic order has been observed in its nanoparticles at room temperature [22–28], and similar reports of magnetic properties in ZnFe₂O₄ ferrite thin films [29–33].

Up to now, only a few groups reported the preparation of ZnFe₂O₄ nanotubes [34, 35]. There are a few reports of magnetic properties for ZnFe₂O₄ nanotubes. Thus, the synthesis and magnetic study of ZnFe₂O₄ nanotubes should be of substantial interest from both fundamental and applied perspective. Herein, we synthesized ZnFe₂O₄ nanotube arrays by an improved sol-gel template method. The structure and morphology of the ZnFe₂O₄ nanotubes were characterized and its magnetic properties were studied. Our results show that the sample has superparamagnetism at room temperature, and ferromagnetic below T_B .

2. Experimental

Anodic aluminum oxide (AAO) templates with a pore diameter of about 100 nm were prepared by anodic oxidation of 99.99% pure Al foil in oxalic acid (1.2 M) under two-step anodizing process [36]. The precursor solution was prepared as follows. Fe(NO₃)₃ and Zn(NO₃)₂ with a molar ratio of 2 : 1 were dissolved in distilled water to form 0.045 M aqueous solution of nitrate. An amount of citric acid equal to NO₃⁻ was dissolved in the mixture solution as a surfactant. The pH value of the solution was adjusted to near 7 by adding ammonia, and then an amount of urea as complexing agent was added into the solution, the molar ratio of NO₃⁻ and urea was 1 : 10. All chemicals were of analytical grade and used without further purification. The AAO templates

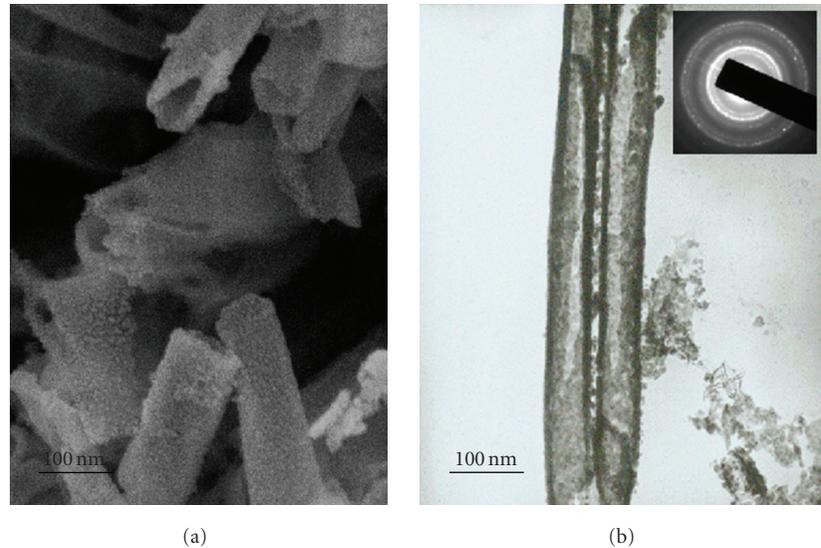


FIGURE 1: (a) SEM (b) TEM and SAED pattern images of the ZnFe_2O_4 nanotubes.

were immersed in the precursor solution for the desired time at 80°C . When the solution was heated, the pH value of the solution increased because of urea undergoing hydrolysis above 60°C , the OH^- combined with Fe^{3+} , and Zn^{2+} formed negatively charged $\text{Fe}_2\text{Zn}[(\text{OH})_x](\text{H}_2\text{O})_y$ sol, which is similar to the previous report [37]. Meanwhile, the pore walls of the AAO were positively charged [38]. As coexistence of the charge interaction and the capillary action, it is reasonable that the nanotubes firstly formed near wall areas of the pores and then extended to the center area gradually. Subsequently, the AAO templates were taken out and placed into saturated HgCl_2 solution to separate templates from the Al substrate. After rinsing with distilled water, the precursor in templates was heat treated in a tube furnace at 600°C for 10 h in air, and the arrays of ZnFe_2O_4 nanotubes inside the AAO templates were obtained.

Field Emission Scanning Electron Microscope (FE-SEM) was performed by using a Hitachi S-4800 \times microscope operated at 10 kV. Structural and morphology data were collected by X-ray diffraction (XRD) using an X' Pertpro Philips diffractometer with $\text{Cu K}\alpha$ radiation and transmission electron microscope (TEM, Hitachi H-600), respectively. The magnetic properties were measured by a vibrating sample magnetometer (VSM, Lakeshore 7300) and Quantum Design MPMS magnetometer based on superconducting quantum interference device (SQUID).

3. Result and Discussion

Figure 1 shows the SEM, TEM images of ZnFe_2O_4 nanotubes with diameters of 100 nm. It is apparent that the ZnFe_2O_4 nanotubes have a uniform diameter. The mean outer diameter of these nanotubes is about 100 nm, corresponding to the diameter of channels in the AAO template. The thickness of tube wall is about 18 nm. The inset of Figure 1(b) shows the selective area electron diffraction (SAED) pattern of the ZnFe_2O_4 nanotubes. The SAED pattern indicates that

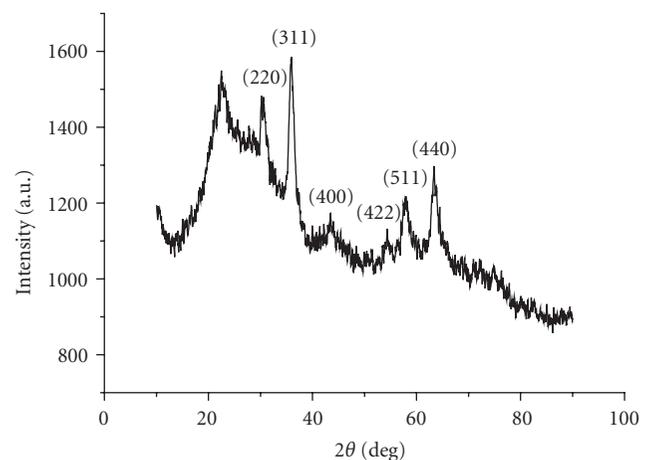


FIGURE 2: X-ray diffraction pattern of the ZnFe_2O_4 nanotubes annealed at 600°C .

the ZnFe_2O_4 nanotube is polycrystalline in structure. The pattern for the sample is well resolved in XRD patterns.

Figure 2 shows the X-ray diffraction pattern of the ZnFe_2O_4 nanotubes. The reflection peaks are clearly distinguishable. The main peaks correspond to a spinel-type lattice (Fd3m) with lattice parameter $a = 8.35 \text{ \AA}$. The lattice parameter a is smaller than that of bulk ($a = 8.443 \text{ \AA}$) because of crystallite size reduction plus lattice disorder. No other obvious reflections were detected indicating inexistence of a second crystal phase.

The results of zero-field-cooled (ZFC) and field-cooled (FC) measurements of magnetization as function of temperature for the ZnFe_2O_4 nanotubes are presented in Figure 3. In order to avoid the nonlinearity effect [6], these measurements were performed at a low field of 50 Oe. For antiferromagnetic materials, typical ZFC/FC curves show a sharp cusp at the Neel temperature. There is no such a cusp

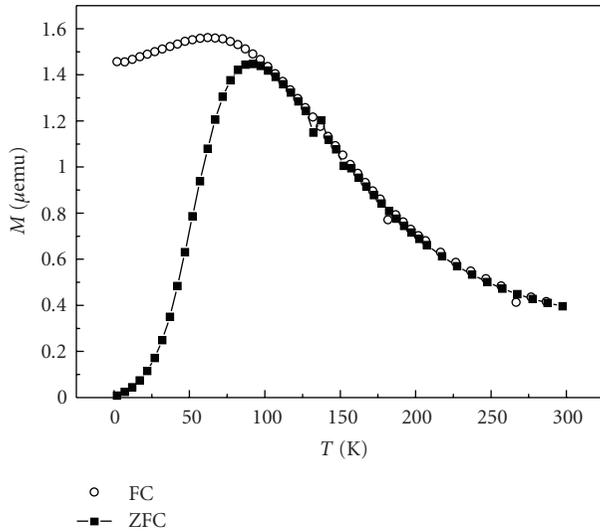


FIGURE 3: Field cooling (FC) and zero-field cooling (ZFC) magnetization curves for ZnFe_2O_4 nanotubes measured under a 50 Oe field.

in the present case. However, the ZFC curve shows a peak appearing at about 90 K. This behaviour of ZFC is typical of a superparamagnetic system. The blocking temperature (T_B) of 90 K is higher than the Néel temperature of 10 K for the bulk. This may indicate that the samples are indeed the mixed spinels with the Curie temperature at least higher than the observed blocking temperature. Below the blocking temperature, the ZFC and FC curves significantly diverge and the ZnFe_2O_4 nanotubes are in the ferrimagnetic state. Above T_B , the ZFC and FC curves coincide due to the fact that the nanotubes are at the superparamagnetic state.

Figure 4 shows the hysteresis loops measured at 10 K and 150 K. The temperatures are so chosen that one is well below and the other is above the blocking temperature (90 K) for the sample. The inset in Figure 4 is the magnified view of the $M-H$ curves. The loops at 10 K and 150 K are quite different. At 150 K, the coercivity is near to zero, which shows that the sample is completely superparamagnetic. This is well expected, as for a superparamagnetic system the coercivity is zero. But at 10 K the coercivity is as high as 1420 Oe, and the remanence is obvious. This clearly shows ferrimagnetic coupling due to the A–O–B superexchange interaction and hence existence of a significant amount of cation inversion. Cation distribution has changed from normal to mixed spinel type, that is, some Fe^{3+} ions occupy the tetrahedral A-sites and switch on the A–B superexchange interaction. Up to 30 kOe, the magnetization is far from being saturated and still increases with increasing magnetic field, due to the presence of a linear and reversible contribution. Such behaviour indicates the presence of a paramagnetic phase, as it has already pointed out by other authors [39].

4. Conclusion

In summary, we have prepared ZnFe_2O_4 nanotube arrays with a diameter of 100 nm by an improved sol-gel template

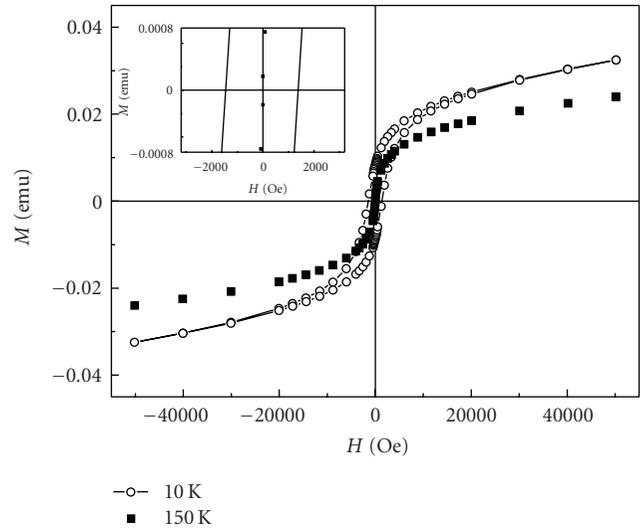


FIGURE 4: Magnetic hysteresis loops of the ZnFe_2O_4 nanotubes measured at different temperature.

method. The ZnFe_2O_4 nanotube has a uniform diameter with tube wall of about 18 nm. The sample shows typical T_B temperature of 90 K. When the measured temperature below T_B at 10 K, the coercivity is as high as 1420 Oe, and the remanence is obvious. These indicate that the nanocrystalline ZnFe_2O_4 system shows up as a mixed spinel.

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