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Journal of Magnetism and Magnetic Materials 272–276 (2004) e1155–e1156
journal of magnetism and magnetic materials
www.elsevier.com/locate/jmmm

Synthesis and magnetism of hematite and maghemite nanoparticles

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Abstract

Rod-shaped hematite and maghemite nanoparticles with diameters of 5 nm and lengths of 16 and 17 nm were synthesized by a newly designed sol–gel mediated reaction and their magnetic properties were investigated. The hematite nanorods showed ferromagnetic behavior from 5 to 300 K, while the maghemite nanorods exhibited superparamagnetic behavior with a blocking temperature at around 130 K.

PACS: 81.05.Ys; 81.05.−t

Keywords: Hematite; Maghemite; Nanorod; Ferromagnetic; Superparamagnetic

The size and shape controlled Fe_2O_3 nanoparticles has attracted a great attention in relation with their peculiar magnetic properties and device miniaturization. There have been some reports about Fe_2O_3 nanoparticles [1–5]. However, Fe_2O_3 nanorods with diameters below 10 nm were rarely reported [4]. The study has been further rare for discrete Fe_2O_3 nanorods with a single phase throughout the whole sample. To the authors' knowledge, there has been no report about the discrete hematite nanorods with diameters below 10 nm. Therefore, the synthesis of discrete and phase-controlled Fe_2O_3 nanorods is challenging and of important issue in relation with magnetic properties derived from shape anisotropy. Here we report a new synthetic method and magnetic properties of hematite and maghemite nanorods with average diameters of 5 nm and lengths of 16 and 17 nm.

We developed a novel and cheap synthetic procedure, which is a combination of sol–gel reaction [6] in reverse micelles and crystallization by reflux [7], for the preparation of hematite and maghemite nanorods. 1.30 g of $FeCl_3 \cdot 6H_2O$ dissolved in 0.43–0.95 ml of water was stirred with 9.17 ml of oleic acid and 150 ml of benzyl ether. About 3.07 g of propylene oxide was added to this solution. After 30 min of stirring, brown gel precipitates were formed, separated, and washed with 45 ml of ethanol 4 times using centrifugation. Then, the air-dried gel powder was refluxed in tetralin for 10 h, yielding a red (A) or brown (B) colloidal solution according to the hydrous state and refluxing condition (A from 168°C and air; B from 217°C and nitrogen). The colloidal particles were separated by magnetic decantation, washed with hexanes, and then dried.

For transmission electron microscopy (TEM) analysis, a drop of diluted nanoparticle solution in hexanes was put onto a carbon-coated copper grid and dried naturally. The X-ray diffraction (XRD) patterns of the particles were recorded using CuKα radiation. Mössbauer spectra were recorded at room temperature and 15 K using a constant acceleration Mössbauer spectrometer with a ^{57}Co in Rh matrix [8]. Magnetic properties were investigated with a superconducting quantum interference device (SQUID).

Fig. 1 shows the TEM images of the particles. The average diameter × length of the nanorods over 100 particles was 5×16 nm for A (with an exemption of smaller particles from oval to sphere) and 5×17 nm for B. The high-resolution TEM image analysis suggested a single crystalline hematite nanorod for A and maghemite nanorod for B (not shown here).

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0304-8853/$ - see front matter
doi:10.1016/j.jmmm.2003.12.201

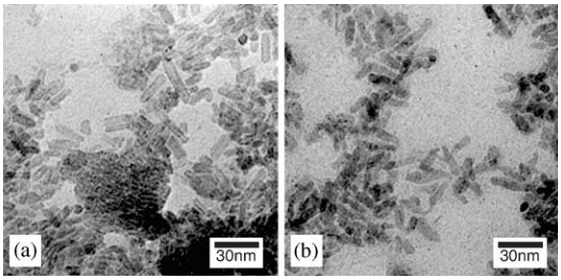

Fig. 1. TEM images of (A) hematite, and (B) maghemite nanorods.

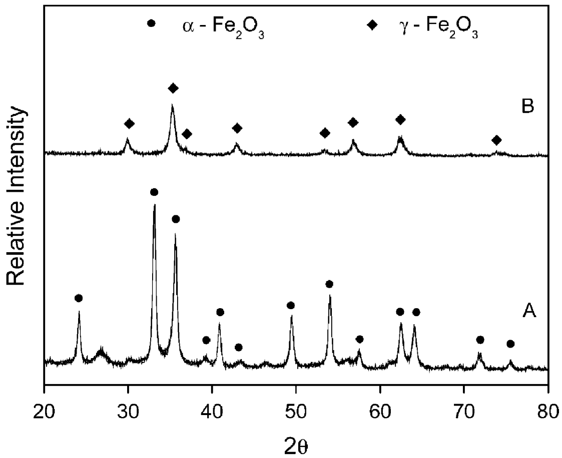

Fig. 2. XRD patterns of (A) hematite, and (B) maghemite nanorods.

Fig. 2 shows the XRD patterns of the nanoparticles. The peak positions and intensities of samples A and B matched very well with those of standard hematite and maghemite, respectively.

The Mössbauer spectrum of hematite nanoparticles at room temperature consisted of a set of two-line pattern (25.5%) and a set of six-line patterns (74.5%). The latter pattern is a ferromagnetic phase originated from hematite nanorods and the former, a superparamagnetic phase is considered as a contribution from smaller nanoparticles close to sphere. The set of two-line pattern transformed to another set of six-line pattern at 15 K, representing a ferromagnetic transition. At present, we need further study to investigate the maghemite nanoparticles. However, there was no ferrous (Fe^{2+}) ion in sample A and in a mixed phase sample prepared by the same method. Therefore, sample B is considered as maghemite even though maghemite and magnetite (Fe_3O_4) show similar XRD patterns [7].

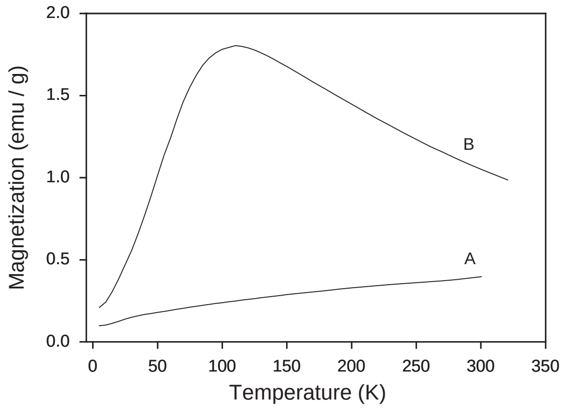

Fig. 3. Magnetization vs. temperature for (A) hematite, and (B) maghemite nanorods with zero-field cooling at the applied field of 100 Oe.

Fig. 3 shows the magnetization vs. temperature curve of the nanoparticles recorded by a SQUID magnetometer. The magnetization of hematite nanorods shows a constantly increasing trend with the temperature up to 300 K, representing a ferromagnetic property. This trend of hematite nanorods is contrasted with that of roughly spherical hematite nanoparticles, which show superparamagnetic behavior [1]. The coercivity and remnance of hematite nanorods at room temperature were 53 Oe and 0.28 emu/g, respectively. On the other hand, maghemite nanorods behaved as superparamagnetic at room temperature: they did not exhibit a significant hysteresis (not shown here). The magnetization vs. temperature curve of maghemite nanorods shows a blocking temperature at around 130 K, which is much higher than that [3] of maghemite nonospheres with the similar diameter.

We thank Dr. J.-P. Ahn for TEM and Prof. C.S. Kim for Mössbauer data.

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