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Enhanced magnetoresistance in nanocrystalline magnetite

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The magnetic and magnetotransport properties of nanoparticulate magnetite with different grain sizes are investigated using x-ray diffraction, microscopy, magnetometry, and magnetoresistance measurements. The magnetization varies significantly with grain size and is sensitive to preparation conditions. The reduction in saturation magnetization in coprecipitated particles is probably due to the surface spin disorder. Magnetoresistance of pressed powder compacts is significantly enhanced in material composed of small grain size magnetite particles prepared by coprecipitation. Useful magnetoresistance persists well above room temperature in sintered ceramic material. © 2003 American Institute of Physics. [DOI: 10.1063/1.1555371]

I. INTRODUCTION

Half-metallic ferromagnets CrO_2 ($T_C=395$ K), $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ ($T_C=360$ K) are not suitable for magneto-electronic applications in an extended temperature due to their low Curie temperature.^{1,2} Recently, the double perovskite $\text{Sr}_2\text{FeMoO}_6$ ($T_C=415$ K)³ with only one spin direction at Fermi level (E_F) attracted much interest, but the compound is moisture sensitive and quite unstable which makes it difficult to fabricate magnetic tunnel junctions. Magnetite is the half-metallic ferrimagnet⁴ with the highest Curie temperature ($T_C=860$ K). The magnetoresistance in nanocrystalline magnetite is of interest due to its potential application in magnetoresistive devices operating in an extended temperature range. Here, we report enhanced magnetoresistance in material composed of magnetite nanoparticles synthesized by chemical coprecipitation and compare it with that of samples produced by citrate decomposition or combustion synthesis.

II. EXPERIMENT

The magnetite nanoparticles were synthesized by coprecipitation of ferric (FeCl_3) and ferrous chloride (FeCl_2) salts in 1.5 M ammonium hydroxide (NH_4OH) solution following Massart's procedure.^{5,6} Stoichiometric quantities of FeCl_3 and FeCl_2 were dissolved in deoxygenated water and preheated to 40 °C in a water bath. NH_4OH (1.5 M) solution was continuously added under vigorous stirring until pH reached 9. The black precipitate was collected by a magnet and washed many times with deoxygenated water. The pellets were sintered at different temperatures (350–600 °C) in 5% H_2 /Ar for 2 h. Phase analysis was carried out using x-ray diffraction and transmission electron microscopy. Curie tem-

perature was determined by thermogravimetry and magnetoresistance measurements were performed using a linear four probe method with a MULTIMAG variable flux source in a magnetic field of up to 2 T. Most of the measurements are made on pressed powder compacts (powder magnetoresistance)⁷ (PMR) but in one case a ceramic was prepared for high temperature measurements. Magnetization measurements were carried out using a SQUID magnetometer.

III. RESULTS AND DISCUSSION

Figure 1 shows x-ray diffraction patterns confirming the formation of single phase Fe_3O_4 with lattice parameter $a_0=0.838(1)$ nm. The reflections are broad in the case of coprecipitated magnetite indicating a very fine particle size. This is confirmed by transmission electron micrographs of

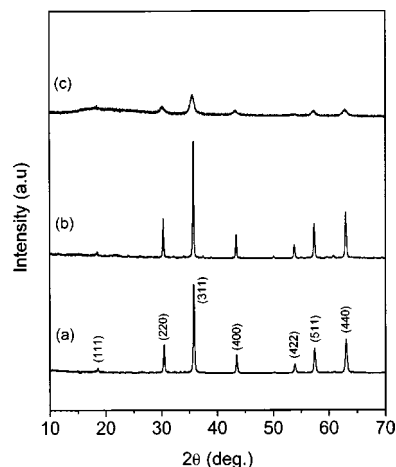


FIG. 1. X-ray diffraction patterns of polycrystalline magnetite synthesized by (a) citrate decomposition; (b) combustion; and (c) coprecipitation.

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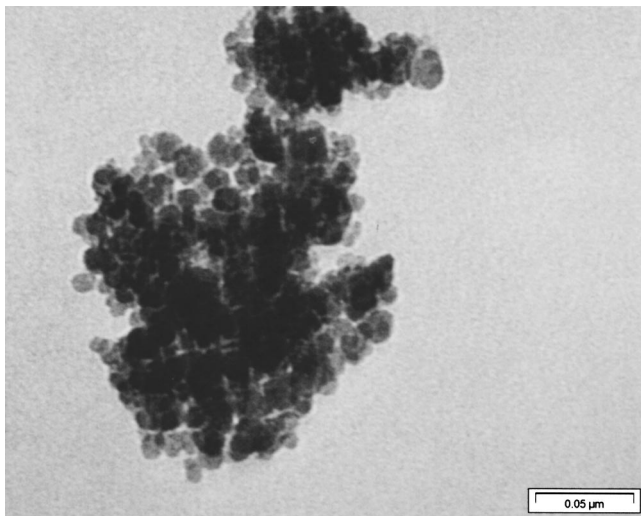


FIG. 2. Transmission electron micrographs of magnetite prepared by coprecipitation showing the nanometer size particles.

coprecipitated magnetite particles shown in Fig. 2. The particles are nearly spherical and practically monodisperse with a size (d_g) of 10 ± 2 nm. This is increased to 30 nm after sintering in 5% H_2/Ar at $450^\circ C$ for 2 h. The particle size is sensitive to preparation conditions (Table I). Thermogravimetric scans in a magnetic field gradient shows a Curie temperature transition around 850 K. The structural and magnetic properties are summarized in Table I.

Figure 3 compares the saturation magnetization of magnetite particles prepared by citrate decomposition, combustion, and coprecipitation methods. The saturation magnetization, at 5 K, of coprecipitated samples is $3.0\mu_B/f.u.$ much less than the value of $4.0\mu_B/f.u.$ anticipated for a half-metallic ferrimagnetic configuration of Fe^{3+} and Fe^{2+} ions. The magnetization is unsaturated even at 5 T. On the other hand, the saturation magnetization values reach almost $4.0\mu_B/f.u.$ for citrate decomposition and combustion synthesized samples. The reduction and lack of saturation could be attributed to the particle size effect, surface spin disorder, and probably the presence of antiphase boundaries.⁸

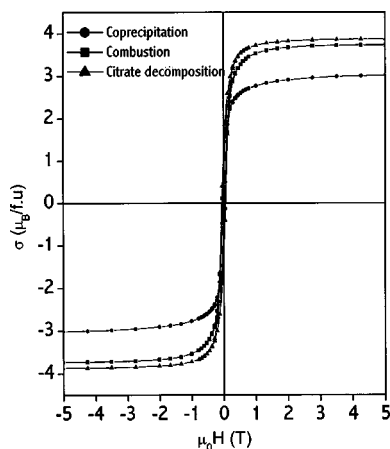


FIG. 3. Magnetization plots of magnetite synthesized by citrate decomposition, combustion, and coprecipitation.

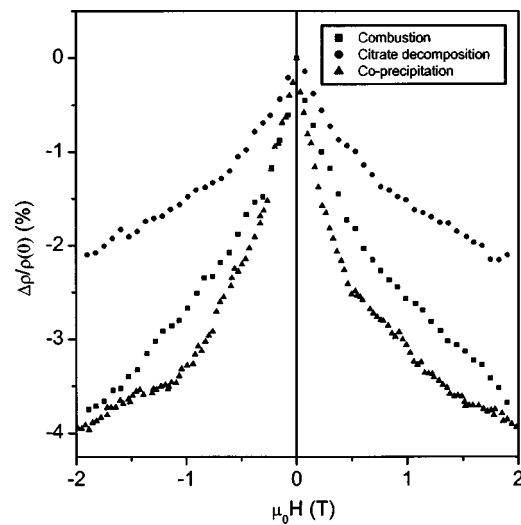


FIG. 4. Magnetoresistance of magnetite synthesized by citrate decomposition, combustion, and coprecipitation.

The room temperature magnetoresistance [$\Delta\rho/\rho(0)$] measured on pressed pellets of all three types of magnetite particles are compared in Fig. 4. The MR ratio in samples prepared by combustion and coprecipitation is greater than that of samples prepared by citrate decomposition. The MR ratio is slightly higher in coprecipitated samples. The room temperature magnetoresistance of coprecipitated nanoparticles reaches 3.8% in a 2 T field.

The as-precipitated sample pellets were then sintered at different temperatures in the range $400\text{--}600^\circ C$ in H_2/Ar

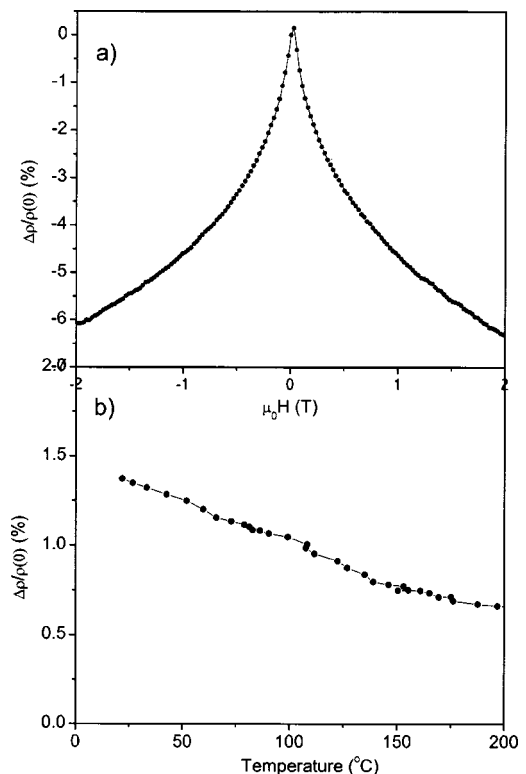


FIG. 5. (a) Magnetoresistance of coprecipitated magnetite upon sintering at $450^\circ C$ in Ar atmosphere and (b) temperature dependence of magnetoresistance.

TABLE I. Structural and magnetic properties of nanocrystalline magnetite ceramics.

Method	Type	d_g (nm)	σ_s (300 K) (μ_B /f.u.)	σ_s (5 K) (μ_B /f.u.)	ρ (RT) (m Ω m)	$\Delta\rho/\rho$ (%)	
						2.0 T	0.1 T
Decomposition	powder	31	3.6	3.9	4.2	2.1	0.3
Combustion	powder	33	3.7	3.9	1.6	3.6	0.8
Coprecipitation	powder	10	2.6	3.0	1.1×10^4	3.8	0.8
After sintering	ceramic	30	2.7	3.2	1.0	6.0	1.6

atmosphere for 3 h. The magnetoresistance increases from 3.8% to 6.0% in a 2 T and from 0.8% to 1.6% in 0.1 T upon sintering at optimum temperature 450 °C as shown in Fig. 5(a). Anisotropic magnetoresistance measurements performed in the MULTIMAG setup where the field is rotated in the plane of the film showed there is a variation of order 0.2%.

Magnetoresistance in polycrystalline magnetite is mainly due to spin-polarized hopping across grain boundaries. If the electron passes from one grain to the next in a single hop, and if there is no magnetic reconstruction near the boundary, the transmission T of a contact varies as $\cos^2(\theta_{ij}/2)$ where θ_{ij} is the misalignment of the ferromagnetic axes of the adjacent grains. Application of the magnetic field leads to alignment of magnetic moments of adjacent ferromagnetic grains, and increases the transmission. The magnetoresistance is $(1 - T)$. However, in a polycrystalline material, there are many conduction paths and the transport is dominated by the least resistance paths. These involve low resistance intergranular contacts which are likely to propagate exchange coupling from one grain to its neighbor. There is then no sharp change in magnetic orientation from one grain to the next but a domain wall allows for little magnetoresistance when the hopping distance is much less than the wall width.⁹ In fact it is the sintered sample, which has the lowest resistance, which shows the best MR (Table I). This suggests that there is actually little intergranular exchange coupling in this material.

The temperature dependence of magnetoresistance is shown in Fig. 5(b). It can be noted that magnetoresistance in our nanocrystalline Fe₃O₄ ceramics persists well above room temperature, with a MR ratio of 0.7% at 180 °C in 0.1 T magnetic field. For possible magnetoelectronic applications, it is important to maintain magnetoresistance well above room temperature. The sintered nanoparticulate material is potentially useful in this respect.

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