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Reduced surface effects in weakly interacting ZrO_2 coated $MnFe_2O_4$ nanoparticles

F. Zeb[a], M. Ishaque[a], K. Nadeem[a,*], M. Kamran[a], H. Krenn[b], D.V. Szabo[c,d], U. Brossmann[e], I. Letofsky-Papst[f]

[a] Nanoscience and Technology Laboratory, International Islamic University, Islamabad 44000, Pakistan
[b] Institute of Physics, Karl-Franzens University, Universitätsplatz 5, A-8010 Graz, Austria
[c] Institute for Applied Materials, Karlsruhe Institute of Technology (KIT), D-76344 Eggenstein-Leopoldshafen, Germany
[d] Karlsruhe Nano Micro Facility (KNMF), Karlsruhe Institute of Technology (KIT), D-76344 Eggenstein-Leopoldshafen, Germany
[e] Institute of Materials Physics, University of Technology Graz, A-8010 Graz, Austria
[f] Institute for Electron Microscopy, University of Technology Graz, Steyrergasse 17, A-8010 Graz, Austria

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ABSTRACT

Surface effects in zirconium dioxide (ZrO_2) coated manganese ferrite ($MnFe_2O_4$) nanoparticles have been studied by using dc and ac magnetization. The average crystallite size of $MnFe_2O_4$ and ZrO_2 phase was about 9 and 4 nm, respectively as determined by Debye-Scherrer's formula. TEM images revealed that the nanoparticles are spherical in shape with less agglomeration. Selected area electron diffraction analysis shows two different crystalline species such as nanoparticle's core $MnFe_2O_4$ and coating ZrO_2, which was in agreement with the XRD analysis. Effective anisotropy constant ($K_{eff} = 3 \times 10^{04}$ erg/cm^3) as deduced from simulated ZFC/FC curves is close to bulk value ($K_{bulk} = 2.5 \times 10^{04}$ erg/cm^3) which is due to weak contribution of surface anisotropy. Saturation magnetization showed an increasing trend at low temperatures (more pronounced below 50 K) which is again due to reduced surface spins disorder. Temperature dependent coercivity revealed a sharp increase at 5 K, which is due to the surface spins freezing. The Arrhenius law fit to frequency shift of T_B in ac susceptibility revealed weak interparticle interactions. The nanoparticles showed slow spin relaxation in ZFC protocol which signify the presence of disorder in our nanoparticles, however the value of shape parameter β lies outside the spin-glass regime. In summary, non-magnetic ZrO_2 coating on these fine $MnFe_2O_4$ nanoparticles reduces their surface energy, magnetic interparticle interactions and surface effects, which are not sufficient to establish a spin-glass behaviour.

1. Introduction

Among the ferrimagnetic spinel ferrites, manganese ferrite ($MnFe_2O_4$) is one of the soft ferrite with promising applications due to their $Fe3_+$ large resistivity, permeability, high saturation magnetization, small coercivity and moderate magnetocrystalline anisotropy. Soft ferrites are best candidates for applications such as microwave devices, transformer cores, ferro-fluids and telecommunication [1–4]. According to the cationic distribution, manganese ferrite ($MnFe_2O_4$) has partially inverse spinel structure [5,6]. At nanoscale, $MnFe_2O_4$ shows reduced magnetization as compared to bulk due to reduced bonds and frustration of the exchange coupling between ferrimagnetically coupled spins near the surface of the individual nanoparticle. This surface disorder sometimes becomes strong enough to produce surface spin-glass behavior in ferrite nanoparticles [7,8].

In addition to surface spin-glass, magnetic nanoparticles also exhibit superparamagnetism which is usually manifested by the existence of blocking temperature. Thermal energy and magneto-crystalline anisotropy energy are the competing mechanism for superparamagnetism. This phenomenon is usually observed in small-sized nanoparticles, where thermal energy exceeds the magneto-crystalline energy barrier that flips the spins more frequently. In nanoparticles, blocking and spin-glass transition temperatures are usually overlapped [9], which makes them difficult to distinguishable. However by using indirect experimental evidences, now it is well established to distinguish between superparamagnetism and spin-glass behavior in magnetic nanoparticles [10]. Ferrite magnetic nanoparticles also contribute random interparticle dipolar interactions which can also lead to spin-glass behavior

* Corresponding author.
E-mail address: kashif.nadeem@iiu.edu.pk (K. Nadeem).

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known as super spin-glass. Kodama *et al.* [11] proposed a surface spin-glass freezing model which are based on surface disorder arises due to the existence of broken bonds and as a result it reduced the saturation magnetization (M_S) of the nanoparticles. Lartigue *et al.* [12] reported the existence of super-spin glass behavior in Fe_3O_4 nanoparticles, but an enhancement of M_S is observed, which arises from both inter-particle dipolar and exchange coupling. Gao *et al.* [13] synthesized $MnFe_2O_4$ nanoparticles by the thermal decomposition method and reported surface spin-glass like state. Ghosh *et al.* [14] studied the PVA capped Fe_3O_4 nanoparticles and reported spin glass type transition at 125 K.

It is desirable to reduce the interparticle interactions to study the surface effects in ferrite nanoparticles. Suitable non-magnetic surface coating can be useful in reducing the interparticle interactions and agglomeration. Non-magnetic surface coating can also reduce the surface energy of the ferrite nanoparticles and surface disorder can be minimised. Aslibeiki *et al.* [15] synthesized $MnFe_2O_4$ nanoparticles by using different contents of tri-ethylene glycol and found that polymer coating can enhance the M_S value by reducing the surface spins disorder and lower the blocking temperature with remarkable shift. Rashid *et al.* [16] reported that the ZrO_2 coated $MgFe_2O_4$ nanoparticles are useful for hyperthermia applications. Girija *et al.* [17] reported that ZrO_2 coating prevents the aggregation among Fe nanoparticles. However, some non-magnetic coating can enhance the surface effects as reported by Larumbe *et al.* [18] in SiO_2 coated $NiFe_2O_4$ nanoparticles.

In this work, we have preferred non-magnetic ZrO_2 as a coating material to reduce the agglomeration, interparticle interactions and surface disorder. ZrO_2 is one of the material that exhibits remarkable properties such as high melting point, low thermal conductivity at room temperature, excellent chemical and corrosion resistance, high refractive index, large band gap, high dielectric constant, and bio-compatibility. Its stability at room temperature makes it stable against agglomeration and surface disorder. It can also restrict the growth of nanoparticles as observed by Xu *et al.* [19] in ZrO_2 coated FePt nanoparticles.

2. Experimental

$MnFe_2O_4$ nanoparticles coated with ZrO_2 and protected by poly methyl methacrylate (PMMA) were prepared by microwave plasma synthesis [20,21]. Fig. 1 shows the schematic diagram for the preparation of these nanoparticles by using microwave plasma synthesis method. For synthesis of ZrO_2 coated nanoparticles, a 2.45 GHz microwave equipment with commercial components as microwave generator, magnetron, isolator, directional coupler and tri-stub-tuner (Muegge, Reichelsheim, Germany), and specially designed cavities, using the rotating TE_{11}-mode in consecutive arrangement were used. The diameter of the used quartz glass reaction tube was 28 mm. The length of the plasma zone was 12 cm, which approximately corresponds to one wavelength λ of the 2.45 GHz microwaves.

1 g of solid $Mn_2(CO)_{10}$ and 2.1 g of liquid $Fe(CO)_5$ were mixed, yielding 2 ml of liquid precursor, fed with a rate of 20 ml/h using a syringe pump, evaporated at 160 °C and transported with 0.2 lpm Ar carrier gas into the reaction system just before the plasma zone, where formation of the core nanoparticles occurs. In parallel, for the ZrO_2 coating 1.6 g of $ZrCl_4$ was used as the precursor, and evaporated at 280 °C outside the reaction zone. The preheated precursor gas was transported with 0.2 lpm Ar-carrier gas into the plasma zone for the formation of ZrO_2 coating. Plasma and reaction gas is a mixture of Ar/20% O_2 with a 7.5 lpm gas flow rate. The pressure in the system was set to 2 mbar by using two vacuum pumps. The microwave power was set to 2000 W, corresponding to reaction temperature around 350 °C. Electric charging of the particles induced by the plasma in combination with short residence time of only a few milliseconds and the low reaction temperatures prevent the formation of hard agglomerates during synthesis. The nanoparticles were collected via thermophoresis on a cold finger. This powder was subsequently scraped off with a razor blade. The structural characterization of powder samples recorded with radiation Cu-Kα (λ = 0.154 nm) (Bruker D8 Advance instrument) at room temperature. Transmission electron microscopy (TEM) was used for nanoparticle's imaging. The magnetic properties were done by using a superconducting quantum interference device (SQUID)-magnetometer (Quantum Design, MPMS-XL-7).

3. Results and discussion

Fig. 2(a) shows the X-ray diffraction (XRD) scan of ZrO_2 coated $MnFe_2O_4$ nanoparticles placed on aluminum substrate. In this pattern, aluminum substrate was used to support the sample for measurement whose peaks are represented by Miller indices (1 1 1), (2 0 0), (2 2 0) and (3 1 1) at scattering angles of 38.5°, 45°, 65° and 77°, respectively. The XRD peaks at ($\bar{1}$11), (2 1 1) and (3 0 2) correspond to monoclinic phase of ZrO_2 (m-ZrO_2). Peaks at (1 1 1) and (2 2 0) correspond to main cubic phase of ZrO_2 (c-ZrO_2). The diffraction peaks of $MnFe_2O_4$ fit perfectly with the standard data of the spinel $MnFe_2O_4$. Peaks at (2 2 0), (3 1 1), (4 0 0), (5 1 1), (4 4 0) and (5 3 3) are typical diffraction peaks of $MnFe_2O_4$ phase. Debye-Scherrer's formula is used for the calculation of average crystallite size as given below:

$$D = \frac{0.9\ \lambda}{\beta \cos\theta} \tag{1}$$

The average crystallite size of $MnFe_2O_4$ and ZrO_2 phase is about 9 and 4 nm, respectively. The average crystallite size is calculated after subtraction of instrumental broadening and error bar estimate ± 0.5–1 nm for ZrO_2 phase and ± 1–3 nm for the $MnFe_2O_4$ phase. Fig. 2(b) shows the selected area electron diffraction (SAED) of ZrO_2 coated $MnFe_2O_4$ nanoparticles as analyzed by using software "PASAD" [22]. The presence of sharp diffraction rings signify the crystalline nature of the nanoparticles. The PASAD evaluation of the SAED signify the presence of two different crystalline species such as $MnFe_2O_4$ (core of the nanoparticles) and ZrO_2 (coating material), which is in good agreement with the XRD findings. Fig. 2(c) and (d) represent the transmission electron microscopy (TEM) images of ZrO_2 coated $MnFe_2O_4$ nanoparticles at 50 and 20 nm scales, respectively. TEM images show that ZrO_2 coated $MnFe_2O_4$ nanoparticles are spherical in shape and less agglomerated. Arrow in Fig. 4(d) indicates the presence of ZrO_2 coating material.

Fig. 3 shows the experimental (blue circles) and simulated (red solid line) zero field cooled (ZFC)/field cooled (FC) magnetization curves of ZrO_2 coated $MnFe_2O_4$ nanoparticles in the temperature range 5–300 K under applied field of 100 Oe.

ZFC curve shows a broad peak at 100 K which represents the average blocking temperature (T_B) of the nanoparticles. The experimental FC curve ($FC_{EXP.}$) becomes flat at low temperatures (below 100 K) as compared to simulated FC curve (FC_{SIM}) which is due to the presence of interparticle interactions and/or surface spins disorder. Below T_B (ZFC), the nanoparticles spins are blocked along their random anisotropy axes and above T_B, the thermal energy is exceeded to anisotropy energy barrier and nanoparticles evolve in to the superparamagnetic state, which is also evident by the converging ZFC and FC curves above T_B [23]. For simulation (represented by red line in Fig. 3), we have adopted the Neel-Brown relaxation model by taking into account an uniaxial anisotropy [24,25]. The log-normal distribution function of particle volumes was used for corresponding to their respective blocking temperatures T_B is given as,

$$(T_B)dT_B = \frac{1}{\sqrt{2\pi\sigma_{T_B}^2}}\frac{1}{T_B} exp\left(-\frac{\ln^2 \frac{T_B}{\langle T_B\rangle}}{2\sigma_{T_B}^2}\right)dT_B \tag{2}$$

The relationship between average blocking temperature $\langle T_B\rangle$ and average particle volume $\langle V\rangle$ is given as:- $\langle V\rangle = \frac{\pi\langle d\rangle^3}{6}$ and $\langle T_B\rangle = \frac{k_{eff}}{k_B \ln(\frac{5m}{\tau_0})}\ \langle V\rangle$. Where d is the diameter of the nanoparticle and σ_{TB}