

Magnetic properties of core-shell manganese-oxide nanoparticles fabricated by inert gas condensation technique

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ABSTRACT

Magnetic properties of Core-shell manganese oxide magnetic nanoparticles fabricated by Inert Gas Condensation (IGC) technique have been studied through measurements of the dc magnetization at different temperatures down to 5K. Microstructural analyses have shown that the particles with an average size distribution between 30 and 50 nanometer form random clusters and agglomerates. Antiferromagnetic-ferrimagnetic (AFM/FiM) and spin-canting effects are assumed to have taken place at different temperature regime in this rather complex matrix of core-shell /inverted core-shell manganese oxide nanoparticles. Some regions of metallic manganese formed due to rapid coalescence of Mn atoms from the melt are also identified. These metallic regions of clustered Mn atoms are surrounded by clusters of MnO nanoparticles.

Keywords: MnO, core-shell nanoparticles, exchange bias effect

1 INTRODUCTION

Recent studies on magnetic core-shell nanoparticles of different 3d transition metal elements in their oxide forms have drawn considerable interest among the researchers for their possible applications as nano-devices in magnetic storage media, catalysts, electrode materials, and in the field of medical sciences for its use in targeted drug delivery[1]. Manganese being one of the 3d-transition metal elements is in use in its bulk form in variety of applications for decades. However its use as an isolated or clustered core-shell nanoparticles are not known [2-4] until recent days. In this work we have investigated some of the important

magnetic properties of MnO nanoparticles in its core-shell and inverted core-shell structures. We have also made an attempt to understand the switching phenomenon of magnetic phases of the core and shell depending on the size of the core.

2 EXPERIMENTAL

Core-Shell nanoparticles have been fabricated in an inert gas condensation (IGC) chamber by resistive heating. Helium gas is used as the inert gas which is injected into the deposition chamber and is circulated by a roots blower to drag away the evaporating particles and be deposited onto the filter. A base pressure of 10^{-5} Torr is obtained using a rotary vacuum pump and a diffusion pump. The deposited oxidized nanoparticles of Mn are carefully brushed out of the filter surface for investigation in powder as well as in pellet form.

3 RESULTS AND DISCUSSION

Fig.1 shows the High Resolution Transmission Electron Microscopy (HRTEM) image of the as-deposited MnO core-shell nanoparticles. The figure shows chains of MnO clusters agglomerated over a few hundred nanometers. The image also indicates that the nanoparticles are assembled in irregular matrices and thus making the sample highly insulating. Some regions in the image are identified as un-oxidized metallic anti-ferromagnet which are screened from the other similar regions by the surrounding oxidized core-shells and hence

maintained the materials overall insulating nature.

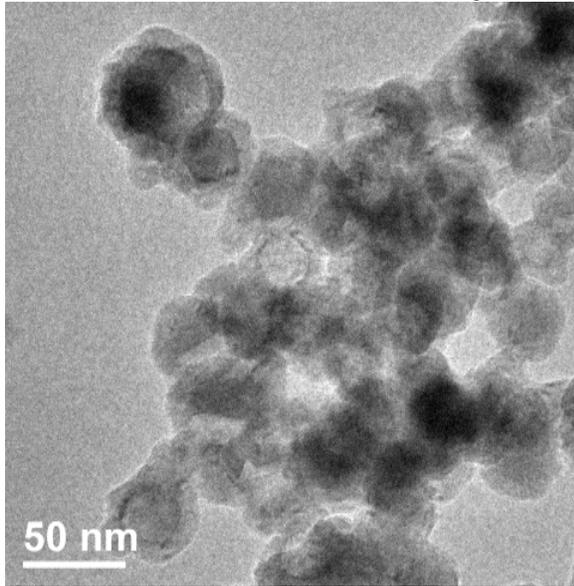


Fig. 1 High Resolution TEM (HRTEM) image of MnO core-shell nanoparticles

HRTEM image shows there are possible states of anti-ferromagnetic Mn_2O_3 cores surrounded by Mn_3O_4 ferrimagnetic shells, and vice versa (inverted core-shell) depending on the core size of the oxidized nanoparticles. This corresponds to the earlier observation on these particle system fabricated in a different technique[5]. It is an well observed phenomenon that in this type of particles system exchange bias effect

takes place along the interface regions between AFM and FiM spin structures causing a shift of the hysteresis loop along the field axis. While the bulk of the core and shell remain unaffected and maintain their intrinsic magnetic phases, it's the spins close to the interface of the core and the shell that show exchange coupling resulting in a shift in the hysteresis loop. A schematic spin structures along the interface are reported in [6]. From our measurements we observed such effects as the sample is studied at different temperatures down to 5K. It may be worth mentioning here that a shift in hysteresis in either positive or negative side of the field axis is an indicator of exchange bias effect.

Fig.2 M-H hysteresis curves of MnO core-shell nanoparticles at room temperature and at 5K. The curves show a ferromagnetic nature over a certain field regime. Fig 3(a) and (b) show the field cooled (FC) and zero field cooled (ZFC) magnetization curves of the MnO core-shell nanoparticles. The ZFC curve shows a peak around 42K which is assumed to be the blocking temperature. The FC curve shows a maximum of the temperature derivative of M around 47K which is the Curie temperature T_c of the ferrimagnetic shell.

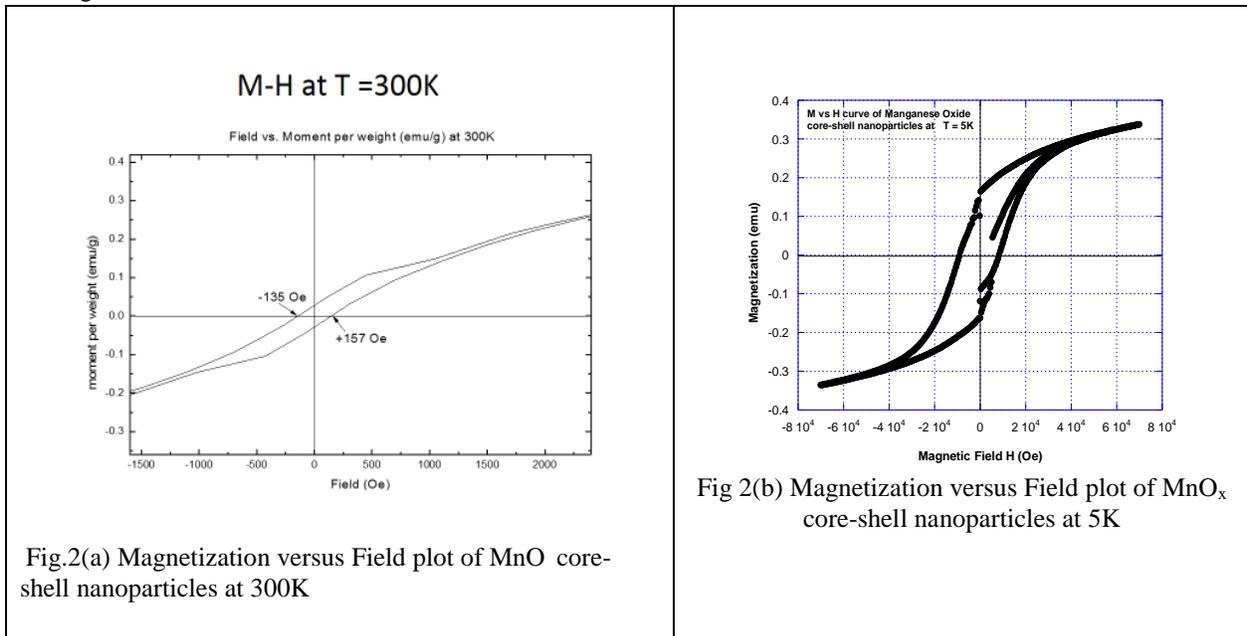


Fig.2(a) Magnetization versus Field plot of MnO core-shell nanoparticles at 300K

Fig 2(b) Magnetization versus Field plot of MnO_x core-shell nanoparticles at 5K

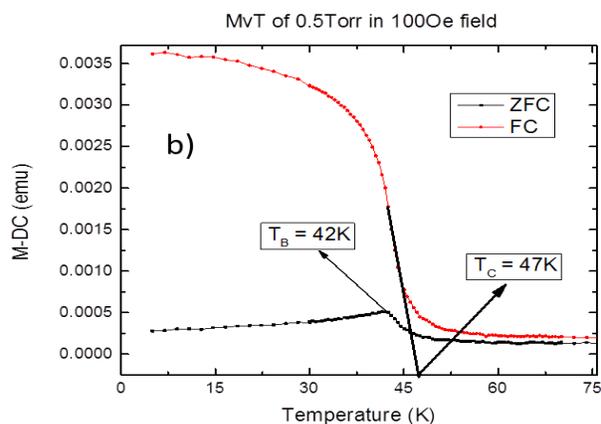
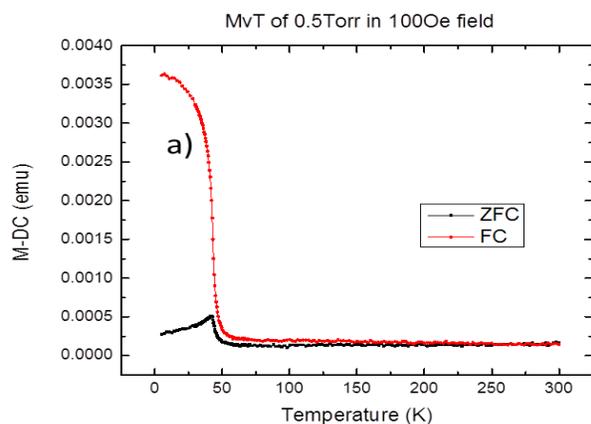


Fig.3 Field cooled (FC) and Zero field cooled (ZFC) curves of MnO core-shell nanoparticles. As measured fig.(a), and enlarged for determining T_B and T_C , fig.(b)

4 CONCLUSION

We report the fabrication and magnetic studies of core-shell magnetic nanoparticles of Manganese oxide fabricated by Inert Gas Condensation (IGC) technique. This fabrication technique to yield different oxidation states of manganese forming ferromagnetic, antiferromagnetic, ferrimagnetic and spin-glass phases. We have observed that the IGC fabrication technique would yield particles of broad size distribution since its difficult to fine tune this system for fabrication of particles with a narrow size distribution. We have observed exchange bias phenomenon in this kind of particle system over an wide range of temperature. We also o that it is unlikely to fabricate particles of a narrow size distribution using IGC of particles is The material can be of huge technological interest in magnetic recording media, magnetic shielding and also in the field of medical sciences involved in targeted drug delivery. The complicated oxidation states of Manganese in this rather new core-shell form calls for further studies on this material. A significant exchange bias effect has been observed with the shift in hysteresis loops in the temperature range

$T_N < T < T_C$ where T_N is the Neel temperature of the antiferromagnetic core and T_c is the ferrimagnetic Curie temperature of the shell. This phenomenon is attributed to the net interfacial spin exchange interaction of the AFM/FiM core- shells and FiM/AFM inverted core-shell MnO nanoparticles.

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Reference

- [1] R.Skomsky, J.Phys.Condens.Matter 15,841 (2003)
- [2] X.L.Dong, Z.D.Zhang, Q.F.Xiao, X.G.Zhao, Y.C.Chuang, S.R.Jin, W.M.Sun, Z.J.Li, Z.X.Zheng, H.Yang, J.Mater.Sci.33, 1915 (1998)
- [3] X.L.Dong, J.D.Zhang, X.G.Zhao, Y.C.Chung, S.R.Jin, W.M.Sun, J.Mater.Res.14, 1782 (1999)
- [4] P.Z.Si, E.Brück, Z.D.Zhang, O.Tegus, W.S.Zhang, K.H.J.Buschow, J.C.P.Klaasee, Materials Research Bulletin 40,29-37,(2005)
- [5] German Salazar-Alvarez, Jordi Sort, Santiago Surinach, M.Dolors Baro and Josep Nogues, J.Am.Chem.Soc.,129,9102-9108,(2007)
- [6] Lopez-Ortega et.al.,J.Am.Chem.Soc.,132, 9398-9407,(2010)