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Polyol synthesis and magnetic study of Mn_3O_4 nanocrystals of tunable size

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ABSTRACT

Nanosized manganese oxide particles were prepared by the so-called polyol process. The average diameter of the particles was controlled by the growth time. X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photon spectroscopy (XPS) show that the particles are well crystallized, pure, stoichiometric Mn_3O_4 single crystals of uniform size ranging from about 5 to 12 nm. The variation of their dc-magnetization, M, as a function of the magnetic field, H, and temperature, T, clearly corresponds to ferromagnetic ordering at low temperature, with a Curie temperature slightly higher than 40 K. The evidence for superparamagnetism in these particles, due to their very small size, has been discussed in the light of their $M(H)$ and $M(T)$ for zero-field-cooled (ZFC) and field-cooled (FC) plots.

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1. Introduction

Manganese oxides are very interesting materials in many domains: catalysis, batteries, electrochromism and magnetism are among their fields of application. The reduction of their particle size down to a few nanometers can greatly affect their chemical and physical properties and improve their potential for these applications. Consequently, the formation of Mn_3O_4 nanoparticles has attracted much attention over the last years. Several *chimie douce* methods (synthesis temperature below 250 °C) have been developed to produce such particles [1–16]. Nanometer-sized particles were produced by decomposition of organometallic or more generally inorganic salt compounds in amine solvents using conventional [1–4] or microwave [5] heating. Nanospheres and nanocubes were prepared by a two-phase (toluene and water) route [6]. Nanorods were obtained in a mixture of dimethylformamide (DMF) and water by the Oswald maturation process after 3 months [7] or nanoparticles in pure DMF after 24 h at 140 °C [8]. The production of nanoparticles has been reported in water upon addition of NaOH [9–10] or with $NaNO_3$ as an oxidant in a basic medium [11]. Particles have also been obtained by hydrolysis in alcohol solvents [12–15]. Finally, the synthesis of very monodisperse 4–5 nm nanocubes, which self-assemble into large-scale walls after reaction at 60 °C for 24 h in NaOH/ethanol, was reported [16].

The magnetic behavior of these Mn_3O_4 nanoparticles was sometimes described. In most cases, the authors present the particles as superparamagnets below a blocking temperature of 33–40 K [1,5–7,16]. For instance, Du et al. [17] observed an irreversibility between the field-cooled (FC) and zero-field-cooled (ZFC) thermal variation of the dc-magnetic susceptibility χ at low temperature for 100 nm-diameter rods up to 15–20 μm long. The ZFC–$\chi(T)$ curve exhibits a maximum while FC-$\chi(T)$ increases continuously to reach a kind of plateau at low temperature. Based on these experimental results and without any further evidence, they claimed that the rods exhibited superparamagnetic behavior. In a comment, Zysler and Winkler [18] refuted this assertion and estimated that the maximum diameter of Mn_3O_4 particles should be about 7 nm for superparamagnetism to be observed below the Curie temperature, T_C. Wang et al. [16] observed the same irreversibility between the FC– and ZFC–dc-$\chi(T)$ curves for an assembly of 4.5 nm nanocubes. They considered that the temperature maximum of the ZFC–$\chi(T)$ curve corresponds to the transition between the blocked ferromagnetic state (below) and the unblocked superparamagnetic state (above). Moreover, the authors observed a dependence of the transition temperature on the applied field and interpreted it as a consequence of the superparamagnetic character of the as-produced nanocubes, without discussing the possibility of collective macro-spin-glass behavior between strongly interacting magnetic objects. Jiao et al. [3] observed a frequency dependence of the in-phase (χ') and out-of-phase (χ'') components of the thermal variation of the ac-magnetic susceptibility of arrays of 7.8 nm particles. The $\chi'(T)$ and $\chi''(T)$ curves exhibited a maximum. The temperature of the maximum (T_{max}) for each component increased with increase in frequency. This was attributed to spin-glass behavior of strongly interacting superparamagnets. Winkler et al. [9] studied the magnetic properties of 15 nm-sized particles as a function of their

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dilution in a polymer, polyvinyl–pyrrolidone (PVP), attempting to vary the interparticle interaction strength. They showed that the transition temperature does not change with the applied field. They claimed that such a particle size is higher than the critical diameter $2R_c'$ below which Mn_3O_4 particles should exhibit superparamagnetic behavior in the single domain regime below the Curie temperature, T_C. Namely, particles bigger than 7 nm do not suffer from the magnetic relaxation process resulting from thermal effect and existence of energy barriers separating the different equilibrium states of the system. This energy barrier is usually related to the particle size and to the effective anisotropy energy constant [19]. As a result, the magnetization of these particles is always blocked below the Curie temperature, while it would become blocked only below a temperature T_B ($<T_C$) for particles smaller than 7 nm. At T_B, the experimental time window is equal to the relaxation time τ characteristic of the particles. For an assembly of non-interacting particles, the relaxation time is generally assumed to be given by the Néel–Brown expression [20]. A number of studies have considered the temperature dependence of the magnetization of nanoparticles as an experimental probe of superparamagnetism, and have determined T_B at the maximum of the ZFC–dc-$\chi(T)$ curve measured at low magnetic field. The facts are rather more complex since the thermal variation of the magnetization of particles less than $2R_c'$ in size depends on the effects of finite size on zero-temperature spin ordering, magnetic excitation and relaxation, interparticle interaction, surface disorder, etc. Thus a complete magnetic study must be performed on Mn_3O_4 nanoparticles of different sizes before any conclusion can be reached.

Given the wide disparity of the results on the magnetic properties of Mn_3O_4 nanoparticles depending on their synthesis conditions, their size range or just the type of magnetic experiments carried out, the magnetic behavior of these nanomaterials must be clarified. Experimentally, the synthesis and manipulation of nanoparticles having well defined size, shape and material properties is of great importance. Consequently, we have used an original synthesis route, forced hydrolysis in a polyol, which gives well crystallized and very monodisperse particles with tunable size between 5 and 13 nm. This provides us with particles below and above the critical size corresponding to the superparamagnetic threshold roughly estimated by Winkler et al. [18].

2. Experimental section

2.1. Chemical synthesis

Manganese acetate tetrahydrate ($Mn(Ac)_2 \cdot 4(H_2O)$, 99%) and diethylene glycol (DEG, 99%) were purchased from Aldrich and Acros, respectively.

3.064 g of $Mn(Ac)_2 \cdot 4(H_2O)$, 125 mL of DEG and 10 mL of distilled water were heated rapidly to 100 °C in a three-necked 250 mL flask under vigorous stirring. The mixture was left for a given time before quenching in a water bath at room temperature. The brown powders were recovered by centrifuging and washing twice with ethanol before drying at 50 °C overnight.

Samples S1, S2 and S3 were obtained after 10 min, 30 min and 2 h, respectively. Another sample was obtained after 16 h. The yield increases with heating time.

2.2. Characterization techniques

X-ray diffraction (XRD) patterns were recorded on a Bruker D5000 diffractometer (reflexion geometry) with Cu-K_α radiation and equipped with a rear graphite monochromator and a high-sensitivity scintillation counter detector. Data collection range was from $2\theta = 10^\circ$ to 90° with a step size of 0.04° for all samples. Total counting time is indicated for each sample in the corresponding figure. Le Bail refinement [21,22] was carried out with Fullprof [23,24] to determine the size of the crystallites for each reaction time. A Thompson–Cox–Hasting pseudo-Voigt line-shape [25] was chosen in order to describe microstructural effects. Corrections were made for instrumental broadening.

Transmission electron microscopy (TEM) images were obtained on a JEOL-100-CX II microscope operating at 100 kV. The samples were dispersed in ethanol. One drop of this suspension was deposited on the carbon membrane of the microscope grid and the solvent was left to evaporate at room temperature.

XPS analyses were performed using a PHOIBOS 100 X-ray photoelectron spectrometer from SPECS GmbH (Berlin, Germany) with the Al K_α X-ray source ($h\nu = 1486.6$ eV) operating at 10^{-10} Torr or less. Spectra were recorded with a pass energy of 20 eV for the survey scan and 10 eV for the C1s, O1s and Mn2p regions. High-resolution XPS conditions were fixed: “fixed analyzer transmission” analysis mode, a 7×20 mm^2 entrance slit, leading to a resolution of 0.1 eV and an electron beam power of 250 W (12.5 kV and 20 mA). A take-off angle of 90° from the surface was employed and binding energies were calibrated against the C1s binding energy at 284.8 eV. Element peak intensities were corrected by Scofield factors; spectra were fitted using the Gelatine Casa XPS v.2.3.13 Software (Casa software Ltd., UK). Baselines are corrected by a Shirley function.

Magnetic measurements were performed on a Quantum Device MPMS-5S SQUID magnetometer. The thermal variation of the dc-magnetic susceptibility $\chi(T)$ was measured in the FC and ZFC modes between 2.5 and 320 K in magnetic fields, H, of 50, 200 and 1000 Oe. The ZFC-magnetization as a function of H, $M(H)$ curve, was obtained at $H = -50$ to 50 kOe, down to 5 K. The measurements were performed on the as-prepared powders diluted in alumina at a concentration of *ca.* 5% and slightly compacted in a plastic sampling tube, in order to reduce interparticle interactions and to prevent physical movement of the particles. The magnetization was calculated per gram of manganese oxide sample.

3. Results and discussion

The characterization of the three samples, S1 (synthesis time 5 min), S2 (30 min) and S3 (2 h) is presented in this article. All results on the characterization of the 16 h sample were similar to those for S3. Consequently, they are not presented here, and one can consider that the particles do not evolve beyond 2 h.

3.1. Structure and morphology

Samples were first characterized by XRD. The patterns for S1–S3 (Fig. 1) are all similar and present the characteristic peaks of the Mn_3O_4 hausmannite structure (PDF no. 00-024-0734). Inspection of the patterns leads to three main observations: (i) the intensities are rather poor, although the total counting time exceeds, for example, 90 h for S1. This is explained by the small quantity of product on the sample holder. (ii) There are weak, supplementary, non-indexed peaks at low angles, especially for S1 and S2. They are attributed to the use of adhesive tape to reduce the effective size of the sample holder. This angular domain ($2\theta < 22^\circ$) was excluded from all the refinement procedures. (iii) The broadening of the diffraction lines can be attributed to the fact that the crystallites are nanosized. It is obvious that the shorter the reaction time, the larger the peaks and, thus,

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