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Optical, electrical and magnetic properties of nanostructured Mn_3O_4 synthesized through a facile chemical route

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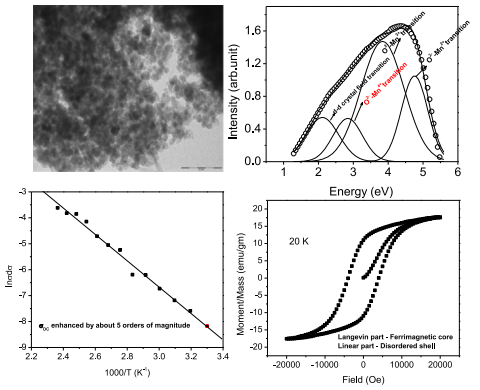
HIGHLIGHTS

- Synthesis of phase pure nanostructured Mn_3O_4 through a facile chemical route.
- Presence of Mn^{4+} ions established by Raman, UV–visible and X-ray photoelectron spectroscopy.
- Enhancement of DC conductivity by five orders of magnitude compared to that of single crystalline Mn_3O_4.
- Slight increase in Curie temperature due to the presence of a disordered surface.
- Magntization following the Langevin relation due to the ferromagnetic core and linear dependence due to disordered surface spins.

GRAPHICAL ABSTRACT

Cation vacancies lead to the presence of Mn^{4+} ions which alter the optical response, electrical conductivity and magnetic response of nanostructured Mn_3O_4.



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ABSTRACT

Nanostructured Mn_3O_4 sample with an average crystallite size of ~15 nm is synthesized via the reduction of potassium permanganate using hydrazine. The average particle size obtained from the Transmission Electron Microscopy analysis is in good agreement with the average crystallite size estimated from X-ray diffraction analysis. The presence of Mn^{4+} ions at the octahedral sites is inferred from the results of Raman, UV–visible absorption and X-ray photoelectron spectroscopy analyzes. DC electrical conductivity of the sample in the temperature range 313–423 K, is about five orders of magnitude larger than that reported for single crystalline Mn_3O_4 sample. The dominant conduction mechanism is identified to be of the polaronic hopping of holes between cations in the octahedral sites. The zero field cooled and field cooled magnetization of the sample is studied in the range 20–300 K. The Curie temperature for the sample is about 45 K, below which the sample is ferrimagnetic. A blocking temperature of 35 K is observed in the field cooled curve. It is observed that the sample shows hysteresis at temperatures below the Curie temperature with no saturation, even at an applied field (20 kOe). The presence of an ordered core and disordered surface of spin arrangements is observed from the magnetization studies. Above the Curie temperature, the sample shows linear dependence of magnetization on applied field with no hysteresis characteristic of paramagnetic phase.

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1. Introduction

Hausmannite, Mn_3O_4 is known to be one of the most stable oxides of manganese. It has normal spinel structure with a tetragonal distortion [1,2]. The structure of Mn_3O_4 can be expressed as $[Mn^{2+}(Mn^{3+})_2O_4]$ where the Mn^{2+} and Mn^{3+} ions, respectively, occupy the tetrahedral and octahedral sites. The tetragonal distortion is due to the Jahn–Teller effect owing to the presence of Mn^{3+} ions (d^4) in octahedral coordination [3,4]. The single crystalline Mn_3O_4 is reported to be ferrimagnetic below 42 K [5].

Mn_3O_4 is known to be widely used in the field of catalysis [6–9], as a starting material in the preparation of electrode materials for rechargeable batteries [9], to synthesis soft magnetic materials like manganese zinc ferrites [9–11] and in high density magnetic storage devices [6]. In addition, Mn_3O_4 is employed as an active material for electrochemical capacitors [6–8]. Mn_3O_4 is environmentally benign in nature which makes it a preferred choice for the above mentioned applications than many other transition metal oxides [12]. Another advantage is the lower cost of manganese salts, because the manganese ores are plenty enough in the earth′s crust [13]. Recently, many investigators have reported about the presence of Mn^{4+} ions in nanostructured Mn_3O_4, obtained from different synthesis techniques which could alter the optical, electrical and magnetic properties of the samples [14,15]. This paper reports the synthesis of nanostructured Mn_3O_4 through a facile chemical route and studies on the optical, electrical and magnetic properties.

2. Experimental

In the present study, all the chemicals used were of analytical grade, with no further purification. Controlled reduction of potassium permanganate, $KMnO_4$ (0.04 M) solution was carried out at room temperature using 80% weight of hydrazine, N_2H_5OH. The formed gel was allowed to settle for 12 h and separated by filtering. The precipitate was washed several times with distilled water and finally with ethanol. The obtained precipitate was dried in a hot air oven at 50 °C to get manganese oxide as a loose powder.

X-ray diffraction (XRD) pattern of the sample in the range $2\theta = 20°–70°$ was recorded using a Philips XPERT-PRO powder diffractometer employing Cu Kα radiation (1.54056 Å). Transmission Electron Microscopic (TEM) analysis was carried out using a Philips CM 200 Transmission Electron Microscope. Raman spectrum in the range 200–800 cm^{-1} was recorded with a Labram HR 800 micro Raman spectrometer using diode laser source ($\lambda = 784$ nm). Small quantity of the sample was dispersed in ethanol medium with the help of an ultrasonic bath, and the UV–visible absorption spectrum was recorded using a SHIMADZU UV-2550 double beam UV–visible spectrophotometer. The elemental analysis was performed using a VSW make X-ray photoelectron spectrometer (XPS) with AlKα source (1.48671 keV) under an operating pressure of 6×10^{-8} mbar. XPS survey scan was recorded in the energy range of 0–1400 eV. The Mn 2p and O1s peaks were recorded at slow scan rates in the range 635–675 eV and 520–545 eV, respectively. C 1s binding energy was used as an internal standard.

In order to study the dc electrical properties, the well ground sample was consolidated into a cylindrical pellet with a diameter of 13 mm and a thickness of about 1.5 mm with the help of a hydraulic press. The conducting silver epoxy was painted on the opposite circular faces to ensure good electrical contact. The electrical measurements were done in an evacuated (0.045 mbar) dielectric cell. Measurements were carried out in the temperature range of 313–423 K at an interval of 10 K and the temperature was maintained with an accuracy of ± 0.1 K. The voltage (V) was sourced in the range of 0–10 V and the current (I) was measured using a KEITHLEY 2400 source meter. From the slope of the V–I curve, the dc electrical conductivity, σ_{DC} was estimated.

The magnetic characterization of the sample was carried out using a Lakeshore 7410 Vibrating Sample Magnetometer (VSM). Temperature dependent magnetic properties of the sample was measured by recording the magnetization under the field cooled (FC) and zero field cooled (ZFC) conditions in the temperature range of 20–300 K under an applied magnetic field of 500 Oe. The magnetic hysteresis loop of the sample was recorded at different temperatures viz., 20, 30, 40, 50, 100, 150 and 303 K. Maximum field applied was 20 kOe.

3. Results and discussion

3.1. XRD and TEM analysis

The Fig. 1 shows the XRD pattern of the sample. All the peaks correspond to tetragonal Mn_3O_4 (JCPDS-ICDD pattern number 80-0382; space group $I4_1$). Thus the controlled reduction of $KMnO_4$ using hydrazine results in the synthesis of phase pure Mn_3O_4 at ordinary temperatures. The reaction can be summarized as

$$6KMnO_4 + 2N_2H_5OH \rightarrow 2Mn_3O_4 + 6KOH + 4NO_2\uparrow + 2O_2\uparrow + 3H_2\uparrow$$

The synthesis of Mn_2O_3 through the controlled reduction of $KMnO_4$ using hydrazine has been reported earlier [16]. In the present work, we have modified the relative concentration of the reactants and processing conditions so as to obtain single phase Mn_3O_4 [16]. Systematic investigation reveals that the ratio of reactants is crucial in determining the final product which could be Mn_3O_4, Mn_2O_3 or a mixture of both oxides.

The average crystallite size estimated from the five most intense XRD peaks using the Scherrer equation is 11.1 ± 0.8 nm [17,18]. The size estimation was done after applying correction for instrumental broadening. In the case of nanostructured samples, localized lattice strain (microstrain) could also contribute to the XRD line broadening [19]. The Williamson–Hall analysis was employed to separate the contribution of small size and microstrain to XRD line broadening [19,20]. This result in an average crystallite size of 15.5 ± 0.5 nm and an r.m.s microstrain of 2.72×10^{-3}.

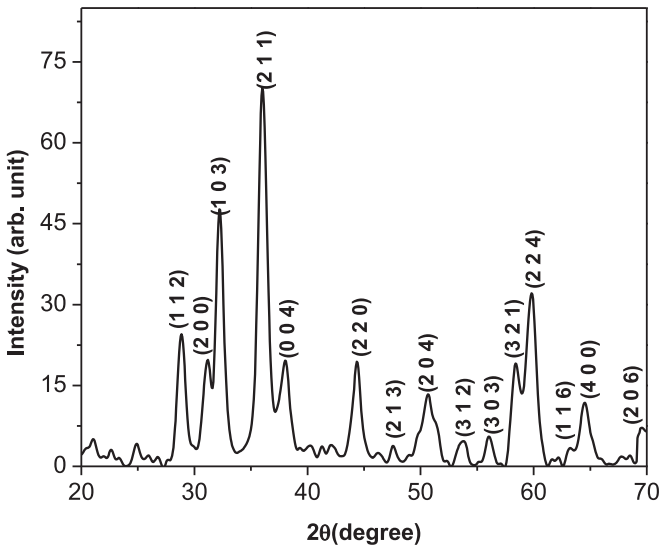

Fig. 1. XRD pattern of nanostructured Mn_3O_4.