Available online at www.sciencedirect.com
SCIENCE DIRECT®
Materials Research Bulletin 41 (2006) 647–654
Materials Research Bulletin
www.elsevier.com/locate/matresbu

Nanosize Mn_3O_4 (Hausmannite) by microwave irradiation method

S.K. Apte [a], S.D. Naik [a], R.S. Sonawane [a], B.B. Kale [a,*], Neela Pavaskar [b], A.B. Mandale [b], B.K. Das [a]

[a] *Centre for Materials for Electronics Technology (C-MET), Panchawati, Off Pashan Road, Pune 411008, Maharashtra, India*
[b] *National Chemical Laboratory, Homi Bhabha Road, Pune 411008, Maharashtra, India*

Received 4 April 2005; received in revised form 12 August 2005; accepted 31 August 2005
Available online 21 September 2005

Abstract

The present investigation reports, the novel synthesis of nanosize Mn_3O_4 powder with nanorods using microwaves and its physicochemical characterization. The nanosize Mn_3O_4 powder has been prepared using manganese nitrate as a precursor and effect of ethanolamine and ethylenediamine on particle morphology has been studied. The microwave irradiation has been carried out in the range 50–500 W and it was observed that formation of Mn_3O_4 takes place at 50 W. TEM analysis demonstrated nanosize Mn_3O_4 powder and nanorods with an average diameter of about 10 nm. The structural study by XRD indicates that these nano-powders have pure tetragonal phase. The phase pure samples were characterized using X-Ray Photoelectron Spectroscopy (XPS) for both Mn 2p and Mn 3s levels. The values of binding energies are consistent with the relative values reported in the literature. The metallic impurity levels have been characterized using Inductively Coupled Plasma-Optical Emission Spectrophotometer (ICP-OES).

Keywords: A. Oxides; A. Magnetic material; A. Nanostructures; B. Chemical synthesis; C. XRD

1. Introduction

Mn_3O_4 synthesis has gained significant attention due to its wide range applications, such as high-density magnetic storage media, catalysts, ion exchange, molecular adsorption, electrochemical materials, varistors and solar energy transformation [1–6]. Mn_3O_4 has also been widely used as a main source of ferrite [7], which have extensive applications in electronics and information technology. Nanometer-sized Mn_3O_4 powder with remarkably increased surface area and different morphology are expected to display better performance in all the above-mentioned aspects of applications. Synthesis of Mn_3O_4 by conventional high temperature and hydrothermal method is very well known in the literature [8–10]. But the conventional process leads to inconsistency in the product quality and is economically unviable. Currently, there is a trend toward devising simple, low temperature solution methods for nanomaterial preparation. Massive work has been reported by hydrothermal method at various temperatures and time [11–13]. This methodology leads to Mn_3O_4 formation through hydroxide followed by partial oxidation. It requires long reaction time i.e. from 48 to 72 h at different temperatures and pressure. There are reports on the synthesis of Mn_3O_4 by sol–gel

* Corresponding author. Tel.: +91 20 25899273; fax: +91 20 25898180.
E-mail address: kbbb1@yahoo.com (B.B. Kale).

0025-5408/$ – see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.materresbull.2005.08.028

method [14], which also covers uniform heating and programmed cooling. The sol–gel method has been found to be more expensive, time consuming and polluting. Microwave assisted synthesis is a novel method of synthesis [15] and it is a rapidly developing research area. In this system, an understanding of the microwave interaction with materials has been based on the concept of dielectric heating and the resonance absorption due to rotational excitation. Recently this technique has been extensively employed for variety of reactions including organic synthesis. As compared to conventional method, it is much faster, cleaner and economical. A variety of materials like carbide, nitride, sulfides [15,16] and complex oxides have been synthesized by microwave irradiation method. These materials are of industrial and technological importance. In view of this, we employed microwave irradiation method for the synthesis of nanosize Mn_3O_4.

The aim of the present work is to prepare nanosize Mn_3O_4 using microwave method and its physicochemical characterization. Mn_3O_4 obtained at different irradiation time has been characterized using SEM, TEM, XRD, XPS and ICP-OES. It is noteworthy that nanosize Mn_3O_4 synthesis using microwave irradiation method is hitherto unattempted.

2. Experimental procedure

A Microwave Digestion Unit, Microwave Labstation, MLS-1200, Mega by Milestone, GmbH, Germany was used for experimentation. Initially the digestion container was washed with distilled water and then calibrated for water pressure and temperature by using water to avoid backpressure. Manganese nitrate (45–50%), ethanolamine and ethylenediamine procured from M/s Aldrich were utilized for the experimental work. Twenty grams of manganese nitrate (Mn-content = 11%) was diluted with 40 ml distilled water and this solution was stirred for few minutes and then neutralized by using required stoichiometric amount of ethanolamine (EA) with continuous stirring. A light brown precipitate formed after the neutralization. The container was immediately press fitted and transferred to microwave digestion unit under programmed conditions. Initially 10 bar pressure and 1 min reaction time were set and irradiation was varied between 50 and 500 W. Then the second set of experiments was carried out at various time intervals, i.e. 1–5 min at 50 W. The pressure of the microwave reactor was set at 10 bar. Then the container was cooled and the precipitate formed was filtered, washed thoroughly with distilled water followed by ethanol. This precipitate was dried at 80 °C in an oven and subjected for further characterization. The similar procedure was followed for ethylenediamine (EDA)-mediated reaction.

The structural characterization was performed using X-Ray Diffractometer (XRD) model Philips PW-1729 Cu Kα radiation. The sample morphology and particle size were determined by Scanning Electron Microscope (SEM) Model XL-Philips, Dl-6650 and Transmission Electron Microscope (TEM) Model FEI TECNAI G^2 12. The surface of the manganese compound was characterized by X-Ray Photoelectron Spectroscopy (XPS) ESCA-3000 electron spectrometer from V.G. Microteck, UK with non-monochromatic Mg Kα radiation was used to excite the photoelectrons. The metallic impurities were identified by Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) Model Perkin-Elmer PLASMA-1000.

3. Results and discussion

In the present work, manganese nitrate was used to prepare Mn_3O_4 using microwave digestion system. The preliminary experiments (Table 1) were carried out to optimize the microwave conditions with respect to wattage and time. The microwave digestion reactor was set at 10 bar pressure, however, actual pressure occurred up to 0.8–1 bar in

Table 1
Weight percentage of MnO_2 in Mn_3O_4 processed at different microwave power levels at constant time

Precursor	Weight percentage of MnO_2 obtained at various microwave power levels						
	50 W	100 W	150 W	200 W	300 W	400 W	500 W
Mn nitrate + ethanolamine + distilled water	27.6 (M-39)	39.0 (M-41)	41.6 (M-43)	37.8 (M-45)	39.4 (M-47)	36.7 (M-49)	37.4 (M-37)
Mn nitrate + ethylenediamine + distilled water	34.7 (M-40)	41.56 (M-42)	37.7 (M-44)	43.7 (M-46)	38.6 (M-48)	36.9 (M-50)	37.9 (M-38)

Figures in parenthesis indicate the sample codes.