Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Journal of Solid State Chemistry 179 (2006) 1225–1229
JOURNAL OF SOLID STATE CHEMISTRY
www.elsevier.com/locate/jssc

Low temperature synthesis of Mn_3O_4 polyhedral nanocrystals and magnetic study

Li-Xia Yang[a,b], Ying-Jie Zhu[a,*], Hua Tong[a,b], Wei-Wei Wang[a,b], Guo-Feng Cheng[c]

[a]*State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, PR China*
[b]*Graduate School of Chinese Academy of Sciences, PR China*
[c]*Analysis & Testing Center for Inorganic Materials, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, PR China*

Received 30 November 2005; received in revised form 4 January 2006; accepted 16 January 2006
Available online 21 February 2006

Abstract

Manganese oxide (hausmannite) polyhedral nanocrystals were prepared by a microwave-assisted solution-based method using $Mn(CH_3COO)_2$ and $(CH_2)_6N_4$ at 80 °C. The as-prepared Mn_3O_4 nanocrystals were characterized by means of X-ray diffraction, field-emission transmission electron microscopy, field-emission scanning electron microscopy and Raman spectrum. Mn_3O_4 polyhedral nanocrystals prepared by microwave heating at 80 °C for 60 min were of cubic and rhombohedral shapes with the edge lengths in the range of 15–40 nm. Mn_3O_4 nanocrystals grew following the Ostwald ripening mechanism with increasing reaction time. High-resolution transmission electron microscopy and selected area electron diffraction confirm that the as-obtained polyhedral nanocrystals were single-crystalline. The magnetic behavior of Mn_3O_4 nanocrystals was studied. Mn_3O_4 nanocrystals show an obvious ferromagnetic behavior at low temperatures. The magnetic behavior of Mn_3O_4 nanocrystals was sensitive to crystal size. Ferromagnetic onset temperatures (T_c) of samples 1 and 3 are 40.6 and 41.1 K, respectively, lower than that observed for bulk Mn_3O_4 (42 K).
© 2006 Elsevier Inc. All rights reserved.

Keywords: Mn_3O_4; Nanocrystal; Chemical synthesis; Magnetic property

1. Introduction

Considerable research has recently focused on the synthesis of uniformly sized and shape-controlled nanoparticles of manganese oxides due to their potential applications in catalysis, high-density magnetic storage media, ion exchange, molecular adsorption and electronics [1–4], and hence on the study of physical and chemical properties related with the specific morphology. Among them, Mn_3O_4 (hausmannite) is known to be an efficient catalyst in some processes, such as the decomposition of waste gas NO_x, selective reduction of nitrobenzene or oxidation of methane and carbon monoxide [5–11]. Moreover, Mn_3O_4 is also used to produce soft magnetic materials such as manganese zinc ferrite [12]. Lithiation of Mn_3O_4 for synthesis of intercalation compounds such as lithium manganese oxides as electrode materials for rechargeable lithium batteries is now attracting a growing interest [13–15].

One of the keys to realization of these applications lies in synthesizing high-quality nanoparticles and thus studying the relationship between characteristics, size and morphology. This prompts scientists to continuously develop new physical and chemical preparation methods. Up to now, different methods have been developed to produce nanomaterials. Among them, solution-based methods have been recognized as an effective way in tailoring the morphology and properties of nanomaterials. In general, Mn_3O_4 powders were prepared by heating manganese oxides (e.g., MnO_2 and Mn_2O_3, etc.) or manganese hydroxides, oxyhydroxide, carbonate, nitrate and sulfate at about 1000 °C in air [16–19]. However, the calcination methods have a tendency to form hard solid with coarse grains. Another conventional process to synthesize Mn_3O_4 powders was solvothermal method, which usually involves

---

[*] Corresponding author. Fax: +86 21 52413122.
E-mail address: y.j.zhu@mail.sic.ac.cn (Y.-J. Zhu).

0022-4596/$ - see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2006.01.033

an organic solvent at higher reaction temperatures or for a long period of time [19,20]. More recently, Park et al. have reported the synthesis of monodisperse, size-controlled Mn_3O_4 nanoparticles by thermal decomposition of a single precursor $Mn(CH_3COO)_2$ in oleyamine under an inert atmosphere at 150–250 °C [21]. Ultrasonic irradiation was also used to synthesize Mn_3O_4 nanocrystallites employing the aqueous solution of manganese acetate without the addition of alkali [22]. Vázquez-Olmos et al. reported the synthesis of Mn_3O_4 nanorods using manganese acetate in a mixed solvents of *N,N′*-dimethylformamide and water at room temperature for 3 months [23]. Currently, developing a simple, low-temperature solution chemical synthetic method for shape-controlled Mn_3O_4 nanomaterials with a narrow size distribution is of great importance.

Herein, we report a facile route to prepare Mn_3O_4 polyhedral nanocrystals at low temperature via an aqueous solution containing $Mn(CH_3COO)_2$ and hexamethylenetetramine, the magnetic properties of Mn_3O_4 polyhedral nanocrystals have also been investigated. This method involves no seeds, catalysts, or templates and may be scaled up to synthesize Mn_3O_4 polyhedral nanocrystals on a large scale at relatively low cost.

2. Experimental details

2.1. Materials

$Mn(CH_3COO)_2 \cdot 4H_2O$ and $(CH_2)_6N_4$ (hexamethylenetetramine, HMT) were of analytical grade and used as received without further purification. Deionized water was used in all reactions.

2.2. Preparation of Mn_3O_4 nanocrystals

In a typical procedure, $Mn(CH_3COO)_2 \cdot 4H_2O$ (1 g) and HMT (1 g) were dissolved in 20 ml deionized water in a round-bottomed flask. Then, the solution was heated by microwave at 80 °C for 10 min (sample 1), 40 min (sample 2) and 60 min (sample 3), respectively. The microwave oven used was a focused single-mode microwave synthesis system equipped with a magnetic stirring (Discover, CEM, USA). The brown products were collected by centrifugation, washed with deionized water and absolute ethanol several times, and dried in air at 60 °C.

2.3. Characterization

X-ray powder diffraction (XRD) was performed with a Rigaku D/max 2550 V X-ray diffractometer with high-intensity Cu$K\alpha$ radiation ($\lambda = 1.54178$ Å) and a graphite monochromator. The morphology was studied by a field emission scanning electron microscopy (FESEM, JEOL, JSM-6700F) and field emission transmission electron microscope (TEM, JEOL, JEM-2100F). The Raman spectrum was taken at room temperature in the range of 200–900 cm^{-1} using a Dilor LabRam-1B Raman Spectrometer equipped with a CCD camera and an optical microscope that provided a laser beam. A red line (632.81 nm) was taken as a back-scattering source. The laser power in front of the microscope was 0.75 mW. The time for spectral acquisition was 50 s and each spectrum was recorded three times. Magnetic property data were collected with a quantum design physical property measurement system (PPMS). The magnetizations as a function of temperature in the range of 10–80 K with the magnetic field of 100 Oe were measured. The hysteresis loops were obtained at 10 K in a magnetic field that varied from +7 to −7 T.

3. Results and discussion

The crystallinity and phase of the products were examined by XRD. Fig. 1 shows the XRD patterns of samples 1 and 3. All the reflections of sample 1 can be indexed to a single tetragonal phase of Mn_3O_4, which is in good agreement with the reported data (JCPDS, 24-0734). No peaks from other phases are observed, which indicates a high purity of the obtained Mn_3O_4 product through the reaction of $Mn(CH_3COO)_2$ with HMT in an aqueous solution at 80 °C for 10 min. XRD pattern of sample 3 is similar to that of sample 1, indicating that the product was still a single phase of tetragonal Mn_3O_4 when prolonging the reaction time to 60 min.

Fig. 2 exhibits the Raman spectrum of sample 3. Three peaks at 658.4, 374.7 and 318.9 cm^{-1} were observed, in agreement with reported values for Mn_3O_4 [24–26], which further supports the XRD result. The peak at 658.4 cm^{-1} is characteristic of Mn_3O_4 with a spinel structure, similar result from Mn_3O_4 nanowires synthesized via an inverse microemulsion method was also reported [27].

Fig. 3 shows the representative TEM and FESEM micrographs of samples 1, 2 and 3. The effect of preparation time was studied in order to obtain a better

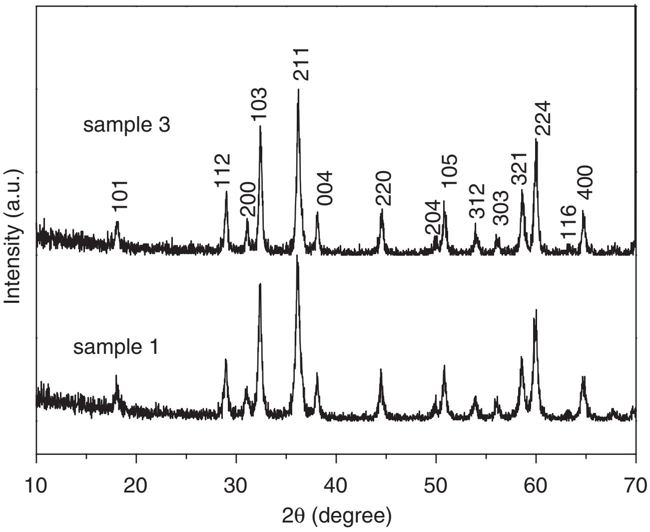

Fig. 1. XRD pattern of samples 1 and 3.

Download English Version:

https://daneshyari.com/en/article/1331887

Download Persian Version:

https://daneshyari.com/article/1331887

Daneshyari.com