



A novel synthesis method for manganese ferrite nanopowders: The effect of manganese salt as inorganic additive in electrosynthesis cell

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Abstract

Manganese ferrite nanoparticles were electro-crystallized in an electrochemical cell containing two iron electrodes, and an electrolyte solution of sodium sulfate, sodium butanoate, and manganese sulfate hydrate. The samples were characterized by X-ray diffraction, electron microscopy, magnetometry, and Mössbauer spectroscopy methods. The crystal structure of the samples was studied using X-ray diffraction. Based on obtained results we found that the manganese ferrite nanoparticles are formed in the electrochemical cell containing 0.001 M manganese sulfate hydrate. Also, the formation of a paramagnetic secondary phase in the sample without manganese is suppressed by adding manganese salt in the electrochemical cell. The nanoparticle size, shape, and morphology were characterized using electron microscopy. Magnetization curves show that all samples are magnetically soft and their specific magnetization ranges from $15 \text{ A m}^2 \text{ kg}^{-1}$ to $75 \text{ A m}^2 \text{ kg}^{-1}$, depending on the growth conditions. Room temperature Mössbauer spectra confirm the formation of nonstoichiometric spinel ferrite of magnetite or manganese ferrite, again depending on the growth conditions. Based on Mössbauer analysis, reduction in the population of octahedral sites provides direct evidence for the presence of the manganese ions substitution in the octahedral sites.

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1. Introduction

In the last decade, magnetic nanomaterials have attracted great attention because of their special properties which are different in comparison with their corresponding bulk structures. Recently, magnetic oxide nanoparticles have attracted significant interest due to their extensive applications ranging from fundamental research to industrial applications [1]. It is well known that magnetic nanoparticles are suitable for many industrial, and biological applications such as controlled drug delivery, hyperthermia-based therapy [2], immuno-recognition and detection [3], biosensors [4], cell separation and detection [5], anti-cancer treatment [6], imaging [7], tissue engineering and regenerative medicine [8], and wastewater treatment [9]. Polycrystalline spinel ferrites are the subject of many research works due to their physical and chemical properties [1,10–14].

Spinel ferrite is one of the most important and applicable magnetic oxides, where oxygen has fcc close packing and M^{2+} and Fe^{3+} ions occupy either tetrahedral (A) or octahedral (B) sites [1]. The spinel ferrite is a potential candidate for understanding and controlling the magnetic properties of nanocrystals at the atomic level. Furthermore, they can be used in different biological and industrial areas such as biosensing, drug delivery, ferrofluids, electronic and information storage devices, and MRI technology [1,11]. Manganese ferrite nanoparticles have found great interest because of their remarkable soft-magnetic properties accompanied by good chemical stability and mechanical hardness. These nanoparticles have higher magnetization than magnetite nanoparticles and other metal doped iron oxide nanoparticles such as CoO , Fe_2O_3 and $\text{NiO}\cdot\text{Fe}_2\text{O}_3$ [12]. Recently, manganese ferrite nanoparticles received increased attention for their application as negative contrast agents in magnetic resonance imaging (MRI) [12,13]. The magnetic properties of manganese ferrite nanoparticles strongly correlated to their atomic level structure and arise from the

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distribution of cations in the tetrahedral and octahedral sites. Therefore, the study of the cation distribution in the ferrite nanoparticles is essential to understand and control the magnetic properties of ferrites [13]. The synthesis of ferrite nanoparticles has been studied during the last decades. Several techniques, including coprecipitation, microemulsion, solid state reaction, ball milling, hydrothermal, thermal decomposition, reverse micelle synthesis, and other methods have been used to prepare ferrite nanoparticles [1,14]. In this paper, manganese ferrite nanoparticles were grown using a simple, fast, and inexpensive electro-crystallization method, for the first time. One of the best advantages of this new synthetic route is that an inert atmosphere is not necessary to avoid the unexpected chemical reaction during the synthesis process. Also, unlike the other synthesis methods, there is no need to anneal the products for formation of the crystal structure.

2. Materials and method

2.1. Materials

Iron sheet (purity 99.5%) was supplied by Advent Research Materials Ltd. Sodium sulfate anhydrous supplied by BDH limited Poole England. Sodium butanoate, sodium sulfate anhydrous, and manganese (II) sulfate hydrate were purchased from Sigma-Aldrich Co.

2.2. Methods

Manganese ferrite nanoparticles were synthesized using an electro-crystallization method. Two iron electrodes 1 cm² and 4 cm² were first polished mechanically with fine grain emery paper, and ultrasonically cleaned with ethanol and then dried. The electrodes were placed 1 cm apart each other in an electrolytic bath containing 0.25 M Na₂SO₄ and 0.04 M of sodium butanoate as stabilizer. In order to study the formation of manganese ferrite nanoparticles, different samples were synthesized by adding manganese (II) sulfate hydrate (MnSO₄·xH₂O) in the electrochemical cell. We have prepared four samples by varying the concentrations of manganese (II) sulfate hydrate from 0.001 M to 0.03 M. In order to understand the effect of this inorganic additive on the properties of products, one sample was prepared without MnSO₄·xH₂O salt as a reference sample. After applying an appropriate potential difference of 5 V, using a Solartron Instruments SI 1280B electrochemical measurement unit, water is reduced to hydrogen and hydroxyl anions at the cathode and the iron anode is oxidized to iron ions. Therefore, in the solution, manganese, iron and hydroxyl ions meet to react and form Mn_xFe_{3-x}O₄, depending on the manganese salt concentrations. The growth conditions affect the final composition of products. If the quantity of iron ions produced during the electrolysis process is high and the amount of manganese ions incorporated into the ferrite is not sufficient to fill the octahedral positions in the spinel structure, the product could be a mixture of particles with different nature. After 1800 s the obtained precipitates separated using an Nd-Fe-B permanent magnet and rinsed with copious amounts of deionised (DI) water. The crystal structure of the products was characterized using a Philips X'Pert PRO X-ray diffractometer,

using CuK α radiation ($\lambda=1.5405 \text{ \AA}$) generated at 40 kV and 40 mA. An FEI Titan high-resolution transmission electron microscope (HRTEM) and a Carl zeiss ultra plus scanning electron microscope (SEM) were employed to study the particle size, morphology, and nanostructure of the particles. Magnetic properties of samples were measured using a home-made vibrating sample magnetometer (VSM) with a 1.1 T permanent magnet flux source. Room temperature Mössbauer spectra in transmission geometry were recorded using a Co⁵⁷ source in Rh, for all samples.

3. Results and discussion

3.1. XRD results

Fig. 1(a) shows the X-ray diffraction (XRD) patterns of the reference sample prepared in the cell with no manganese salt and other samples prepared in the presence of manganese salt with different concentrations. In Fig. 1(b) one can see the XRD pattern and the Rietveld profile refinement, using the Fullprof program, for the electro-synthesized sample with 0.001 M of manganese salt. Based on XRD results we found that the crystallinity of the products is very sensitive to the variation of the manganese concentration. The sample synthesized without manganese salt has the cubic spinel crystal structure of magnetite. The lattice constant obtained from the XRD data for this sample is $\sim 8.374 \text{ \AA}$ which is in agreement with the reported value for magnetite (reference card code 01-088-0315). The small peak marked with an asterisk, observed in the XRD pattern of this sample, corresponds to organometallic complex phases formed between iron ions and butanoate seen in Mössbauer spectra [15]. As can be seen, this extra reflection is eliminated by adding manganese salt in the electrolyte solution. The XRD pattern of the sample synthesized with 0.001 M of MnSO₄·xH₂O correspond to the formation of cubic inverse spinel structure of manganese ferrite. The calculated lattice constant for this sample is $\sim 8.384 \text{ \AA}$ which is close to that reported for bulk crystalline manganese ferrite (reference card: 00-010-0319). In the case of sample synthesized with 0.007 M of manganese salt extra small peaks were observed in the XRD pattern. One small peak at $\sim 26.8^\circ$ is associated with cubic Mn₂O₃ (reference card: 00-002-0902 is presented in Fig. 1(c)). Furthermore, the XRD patterns of the samples prepared in the presence of MnSO₄·xH₂O with concentrations higher than 0.007 M, show a peak at $\sim 40.6^\circ$ which is correspond to cubic structure of Mn₂O₃ as impurity. According to our XRD data we found that the lattice parameter increases to $\sim 8.430 \text{ \AA}$ with increasing the manganese salt concentration up to 0.014 M and then decreases to $\sim 8.412 \text{ \AA}$. Different factors can affect on the unit cell parameters such as impurities and the crystal size. The relationship between unit cell parameters and nanomaterials size has been studied in many research works and both increasing and decreasing trends with size have been reported. The variation of unit cell volume with nanostructures size is related to strain,

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