Journal of Physics and Chemistry of Solids 75 (2014) 315–327

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs

Review

A comprehensive overview on the structure and comparison of magnetic properties of nanocrystalline synthesized by a thermal treatment method

Mahmoud Goodarz Naseri [a,*], M.K. Halimah [b], Arash Dehzangi [c], Ahmad Kamalianfar [d], Elias B. Saion [b], Burhanuddin Y. Majlis [c]

[a] *Department of Physics, Faculty of Science, Malayer University, Malayer, Iran*
[b] *Department of Physics, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia*
[c] *Institute of Microengineering and Nanoelectronics (IMEN), Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia*
[d] *Department of Physics, Jahrom University, Jahrom, Iran*

ARTICLE INFO

Article history:
Received 14 November 2011
Received in revised form
22 October 2013
Accepted 7 November 2013
Available online 25 November 2013

Keywords:
A. Nanostructures
C. Infrared spectroscopy
C. Thermo-gravimetric analysis (TGA)
C. X-ray diffraction
D. Electron paramagnetic resonance (EPR)

ABSTRACT

This study reports the simple synthesis of MFe_2O_4 (where M=Zn, Mn and Co) nanostructures by a thermal treatment method, followed by calcination at various temperatures from 723 to 873 K. Poly(vinyl pyrrolidon) (PVP) was used as a capping agent to stabilize the particles and prevent them from agglomeration. The pyrolytic behaviors of the polymeric precursor were analyzed by use of simultaneous thermo-gravimetry analyses (TGA) and derivative thermo-gravimetry (DTG) analyses. The characterization studies were conducted by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Fourier transform infrared spectroscopy (FT-IR) confirmed the presence of metal oxide bands for all the calcined samples. Magnetic properties were demonstrated by a vibrating sample magnetometer (VSM), which displayed that the calcined samples exhibited different types of magnetic behavior. The present study also substantiated that magnetic properties of ferrite nanoparticles prepared by the thermal treatment method, from viewing microstructures of them, can be explained as the results of the two important factors: cation distribution and impurity phase of α-Fe_2O_3. These two factors are subcategory of the preparation method which is related to macrostructure of ferrite. Electron paramagnetic resonance (EPR) spectroscopy showed the existence of unpaired electrons $ZnFe_2O_4$ and $MnFe_2O_4$ nanoparticles while it did not exhibit resonance signal for $CoFe_2O_4$ nanoparticles.

Contents

---

[*] Corresponding author. Tel.: +60 142698153; fax: +60 3 89454454.
E-mail address: mahmoud.naseri55@gmail.com (M.G. Naseri).

0022-3697/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jpcs.2013.11.004

1. Introduction

Nanoscience and nanotechnology are involved in the manipulation of materials and the creation of structures and systems at the nanometer scale. As a result, nanomaterials have attracted much attention because of their surface effect (large surface-to-volume ratio) and quantum confinement effects (size-dependent properties). These factors affect their physical and chemical properties, which differ from the properties of their molecular and bulk counterparts. Nanoparticles with zero-dimensional nanostructures are generally classified according to their compositions, i.e., metal oxides, noble metals, transition metals, magnetic metals, and semiconductor nanomaterials or quantum dots. Like all nanostructures, magnetic metals nanoparticles are dependent on their size and shape. Currently, magnetic oxide nanoparticles are attracting significant interest due to their extensive applications, ranging from fundamental research to industrial use. Spinel nanocrystals are regarded as two of the most important inorganic nanomaterials because of their electronic, optical, electrical, magnetic, and catalytic properties. Spinel have the structure AB_2O_4 in which A and B display tetrahedral and octahedral cation sites, respectively, and O indicates the oxygen anion site. Metal spinel ferrite nanoparticles have the general molecular formula MFe_2O_4 (e.g., M=Ni, Zn, Mn, Co, or Mg), and they have a face-centered-cubic (fcc) close packing structure. Among the spinel ferrites compounds, zinc ferrite, manganese ferrite and cobalt ferrite have been studied extensively due to their different structures composed of normal, mixed and inverse spinel structures respectively and their high electromagnetic performance, excellent chemical stability, mechanical hardness, low coercivity, and moderate saturation magnetization, which make it a good contender for the application as soft magnets and low-loss materials at high frequencies [1–3]. These properties are dependent on the chemical composition and microstructural characteristics in which the particle size and shape might be controlled in the fabrication processes. In order to achieve materials that have the desired physical and chemical properties, the preparation of spinel ferrites nanocrystals through different routes has become an essential focus of the related research and development activities. Various fabrication methods to prepare spinel ferrites nanocrystals have been reported, e.g., citrate–gel methods [4], the ball-milling technique [5], co-precipitation [6], polymeric assisted route [7] the hydrothermal method [8], the reverse micelles process [9], and the micro-emulsion method [10]. Various precipitation agents have been used to produce specific size and shape spinel ferrites nanocrystals, e.g., metal hydroxide in the co-precipitation method, surfactant and ammonia in the reverse micelles process and various micro-emulsion methods, and organic matrices in the sol–gel method. Most of these methods have achieved particles of the required sizes and shapes, but they are difficult to employ on a large scale because of their expensive and complicated procedures, high reaction temperatures, long reaction times, toxic reagents and by-products, and their potential harm to the environment. In the present study, spinel ferrites nanocrystals with different structures were prepared from an aqueous solution containing metal nitrates, poly(vinyl pyrrolidon), and deionized water using a low temperature thermal treatment method, followed by grinding and calcination. No other chemicals were added to the solution. This method is environmentally friendly in that it neither uses nor produces toxic substances, and it offers the advantages of simplicity, low cost, and low reaction temperatures. The textural and morphological characteristics of the spinel ferrites nanocrystals we prepared were studied with various techniques to determine the influence of calcination temperature on the crystallization, morphology, and particle size distribution of the nanocrystals and to explore other parameters of interest.

2. Experimental

2.1. Materials

In this study, metal nitrate reagents, poly(vinyl pyrrolidon) (PVP), and deionized water were used as precursors. In addition, a capping agent to control the agglomeration of the particles and a solvent were used. Iron nitrate, $Fe(NO_3)_3 \cdot 9H_2O$, zinc nitrate, $Zn(NO_3)_2 \cdot 6H_2O$, manganese nitrate, $Mn(NO_3)_2 \cdot 6H_2O$ and cobalt nitrate, $Co(NO_3)_2 \cdot 6H_2O$, were purchased from Acros Organics with a purity exceeding 99%. PVP (MW=29,000) was purchased from Sigma Aldrich and was used without further purification. An aqueous solution of PVP was prepared by dissolving of polymer in 100 ml of deionized water at 363 K, before mixing 0.2 mmol iron nitrate and 0.1 mmol metal nitrate (Fe:M=2:1) into the polymer solution and constantly stirring for 2 h using a magnetic stirrer until a colorless, transparent solution was obtained. A glass electrode was used to determine the pH of the solution, which ranged 1–2. The mixed solution was poured into a glass Petri dish and heated at 353 K in an oven for 24 h to evaporate the water. The dried, orange, solid zinc ferrite that remained was crushed and ground in a mortar to form powder. The calcinations of the powders were conducted at 723, 773, 823, and 873 K for 3 h for the decomposition of organic compounds and the crystallization of the nanocrystals. (Note that 3 h was the minimum time that allowed the crystallization to be completed). The processing steps employed separately for the synthesis of each ferrite nanoparticles.

2.2. Characterization

The structure of the $ZnFe_2O_4$, $MnFe_2O_4$ and $CoFe_2O_4$ nanoparticles were characterized by the XRD technique using a Shimadzu diffract meter model XRD 6000 employing Cu K_α (0.154 nm) radiation to generate diffraction patterns from powder crystalline samples at ambient temperature in a 2θ range of 10–70°. The microstructure and particle size of the nanocrystals were determined from Transmission Electron Microscopy (TEM) images that were obtained by using a JEOL 2010F UHR version electron microscope at an accelerating voltage of 200 kV. FT-IR spectra were recorded using a PerkinElmer FT-IR model 1650 spectrometer. Before recording spectra, the samples were placed on a Universal ATR Sampling Accessory (diamond coated with CsI) and pressed, and then the spectra were recorded. Magnetization measurements were conducted using a vibrating sample magnetometer (VSM) (Lake Shore 4700) at room temperature with maximum magnetic field of 15 kOe.

3. Results and discussion

3.1. Thermal analyses of PVP

Fig. 1 shows the simultaneous thermo-gravimetry (TG) and derivative thermo-gravimetry analyses (DTG) of PVP. This thermogram showed that the PVP was thermally stable until 673 K and that the maximum decomposition rate occurred around 778 K. These results were supported by the FT-IR analysis (Section 3.3) that showed that the samples calcined at 873 K ($ZnFe_2O_4$, $MnFe_2O_4$) and at 773 K ($CoFe_2O_4$) did not show any absorption band belonging to PVP or nitrate anions. So, this confirmed that, at these temperatures, the magnetic nanoparticles were pure.

It is worth noting that several authors reported the thermal degradation of PVP exhibits only one mass loss [11–13].

3.2. Mechanism of interaction of PVP and metal ions in synthesize of metal ferrite nanoparticles

Interactions between the PVP capping agent [14] and metal ions are shown schematically in Fig. 2. We have shown the Metal (II)