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Simple Synthesis, Structural and Magnetic Properties of $Zn_{0.2}Co_{0.4}Mn_{0.4}Fe_2O_4$ System

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Abstract

$Zn_{0.2}Co_{0.4}Mn_{0.4}Fe_2O_4$ system was prepared by using glycine assisted combustion method. Characterizations of different composites are systematically investigated with various analytical techniques. X-Ray Diffraction (XRD) pattern and Fourier- Transform Infrared Spectroscopy (FTIR) indicate the growth of well crystalline $Zn_{0.2}Co_{0.4}Mn_{0.4}Fe_2O_4$ nanoparticles with a cubic spinel structure. The magnetic properties namely, Saturation Magnetization (M_s), Coercivity (H_c), and Remanent Magnetization (M_r) of the investigated system were determined. Finally, we can be concluded that $Zn_{0.2}Co_{0.4}Mn_{0.4}Fe_2O_4$ system showed attractive multifunctional features for magnetic applications.

Introduction

Ferrites are iron based materials; the dominant constituent of these materials is the iron element. Ferrite can be divided according to the divalent elements combined with iron within the ferrite structure into simple and mixed ferrites. Simple ferrite composed of one divalent transition metal which connected with the trivalent iron in the ferrite frame. While the mixed ferrite consisted of two or more divalent transition metal that boned with iron cations inside the ferrite environment. So, there are significant differences between the physical and chemical properties of the simple ferrite and that of the mixed ferrite. These differences could be attributed to the difference in the effect of presence of one or more transition elements on the different properties of ferrites. In addition, the precursors and concentrations of the divalent element have various effects on the different properties, especially in the mixed ferrites.

Principle investigator in this project has an excellent experience in green synthesis for simple and mixed ferrites by using combustion method depending on the glycine as chemical fuel. Deraz *et al.* reported to preparation of $ZnFe_2O_4$, $CoFe_2O_4$ and $MnFe_2O_4$ as simple ferrites [1-3]. On other hand, $Zn_{0.5}Co_{0.5}Fe_2O_4$ and $Zn_{0.5}Mn_{0.5}Fe_2O_4$ have been prepared by using glycine assisted auto-combustion [4,5].

Deraz 's group studied the structural, morphological and magnetic properties and found that these properties were much better than those of ferrites prepared by other traditional methods. The Glycine-Nitrate Process (GNP) [1,6] is one of an auto-combustion method for synthesis of ceramic oxides. This method has different advantages over other low-temperature methods as following: (i) this route resulted in the combusted product in a short time period with the main advantages included energy and time savings. In other words, this method is

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a particularly simple, safe and rapid fabrication process. Based on the previous advantages, the auto-combustion method can be used to synthesize homogeneous, high-purity, crystalline oxide ceramic powders including ultrafine ferrite powders with a broad range of particle sizes.

In fact, the Ferrite nanoparticles have been prepared by various methods, including sol-gel, hydrothermal, co-precipitation, and thermal decomposition methods [7-11]. In our quest to prepare nanometric that has industrial applications, the economic and environmental dimension was very important. At the same time, in order to preserve the environment and reduce the cost, a search for a natural product used as fuel to obtain nanometric materials having an economic dimension such as ferrites. This natural product was egg white because of its multiple advantages [12]. The use of egg white simplified the economical synthesis of nanocrystalline ceramic particles. Indeed, egg white has gelling, foaming and emulsifying characteristics [13-15]. However, egg white used as a binder gel for shaping material especially bulk and ceramics due to its solubility in water and its ability to associate with metal ions in solutions [16,17]. In order to emphasize the importance of using natural materials in the preparation of ceramic materials, we will deal with the process of preparing the same materials in the traditional way, which is called the ceramic method.

The main goal of this study was fabrication of porous spinel Mixed Quarterly Transition Ferrite (MQTMF) Nanoparticles (NPs) as electrode material for high performance super capacitors due to their novel properties and technological applications especially when the size of the particles approaches to nanometer scale. In addition, the magnetic materials, such as ferrites, have explored a wide range of applications and thus are replacing conventional materials.

Further, ferrite nanoparticles are commercially important for several applications such as in electromagnetic devices operating at radio frequencies where the Super Paramagnetic [SPM] properties have a strong influence in enhancing their quality of applications [18]. Therefore, in this project, we have started the preparation process and determination of the magnetic properties that will have a significant impact in different applications. Ferrite materials are recognized as more important and essential for the further development of electronics than before, and it is believed that the production of ferrites will increase year by year as their applications become more diverse. Chakrabarti et al. [19] studied the magnetic properties of nanocrystalline $Ni_{0.2}Zn_{0.6}Cu_{0.2}Fe_2O_4$ prepared using a chemical route method, and they reported that below 80 K, the nanoparticles exhibit super paramagnetism, and the saturation magnetization increases with increasing particle size. Seong et al. [20] investigated the structural and electrical properties of Cu-substituted Ni-Zn ferrites, and they have reported that the alternating current [ac] conductivity increases with increasing temperature of the sample and frequency of the applied field.

In this study, we will report on a comparative study of structural and magnetic characteristics of Mixed Quarterly Transition Metal Ferrites (MQTMF) such as $Zn_{0.2}Co_{0.4}Mn_{0.4}Fe_2O_4$ prepared by glycine assisted combustion route.

Materials and techniques

All the reagents were of analytical grade and used without further purification, ferric nitrate, $Fe(NO_3)_2.9H_2O$, manganese nitrate, $Mn(NO_3)_2.4H_2O$, cobalt nitrate $Co(NO_3)_2.6H_2O$, Zinc nitrate, $Zn(NO_3)_2.6H_2O$. And glycine, NH_2CH_2COOH.

Preparation of pure MQTMF nanoparticles

Pure MQTMF solid was prepared by adding glycine (4 mol) to mixture of transition metal nitrates with vigorous stirring at room temperature to obtain a well-dissolved solution as sol. Then, the sol was evaporated by heating on a hot plate at 80°C with vigorous stirring until a gel of precursor was obtained. When a container temperature was reached to 300 °C for quarter hour, a great deal of foams produced and spark appeared at one corner which spread through the mass, yielding a voluminous and fluffy product. The dried products were crushed into powder using a mortar and pestle. In this study, the ratios of the glycine: zinc nitrate: cobalt nitrate: manganese nitrate: ferric nitrate were 3: 0.59495: 1.164136: 1.00404: 8.08 g, respectively.

Characterization Techniques

An X-ray diffraction measurement of various mixed solids was carried out using a BRUKER D8 advance diffractometer (Germany). The patterns were run with Cu K_α radiation at 40 kV and 40 mA with scanning speed in 2θ of 2 ° min^{-1}. The crystallite size of the as synthesized solids was based on X-ray diffraction line broadening and calculated by using Scherrer equation.

$$d = \frac{B\lambda}{\beta \cos\theta} \qquad (1)$$

where d is the average crystallite size of the phase under investigation, B is the Scherrer constant (0.89), λ is the wave length of X-ray beam used, β is the Full-Width Half Maximum (FWHM) of diffraction and θ is the Bragg's angle.

An infrared transmission spectrum of various solids was determined using Perkin-Elmer Spectrophotometer (type 1430). The IR spectra were determined from 4000 to 400 cm^{-1}. Two mg of each solid sample were mixed with 200 mg of vacuum-dried IR-grade KBr. The mixture was dispersed by grinding for 3 min in a vibratory ball mill and placed in a steel die 13 mm in diameter and subjected to a pressure of 12 tons. The sample disks were placed in the holder of the double grating IR spectrometer.

A vibrating sample magnetometer (VSM; 9600-1 LDJ, USA) has been used to measure the magnetic properties of the examined solids at room temperature in a measured maximum field of 20 kOe. The Saturation Magnetization (M_s), Remanence Magnetization (M_r), Coercivity (H_c), Squareness (M_r/M_s), and Anisotropy Constant (K_a) have been evaluated using the hysteresis loops obtained.

Results and discussion

XRD analysis

Effects of glycine as a fuel on various structural properties of the as synthesized ferrite were estimated. XRD analysis was used to determine the nature and the crystallite size of phases present in the as prepared solid. **Figure 1** shows XRD pattern of the prepared sample. Inspection of this figure revealed that the synthesized sample composed of cubic spinel mixed zinc, cobalt, and manganese ferrites according to JCPDS Files (900-2490, 434-4128 and 152-8317) indicating the solid state reaction between the reacting oxides containing ZnO, CoO, Mn_2O_3 and Fe_2O_3. Stimulation of such reaction was observed due to high the release heat energy from autocombustion of the glycine and nitrates. Because of all diffraction lines coincide with that observed in the prepared solids, we speculate that the fi-

nal product is ($Zn_{0.2}Co_{0.4}Mn_{0.4}Fe_2O_4$) depending on the diffraction lines of the individual ferrites are overlap and the ratios of elements used. An X-ray data enabled us to determine the structural parameters such as the crystallite size (d), lattice constant (a) and unit cell volume (V) of cubic spinel structure for the produced ferrite crystallites. The estimated values of various structural parameters are, 43 nm, 0.845nm and 0.6033 nm^3, respectively.

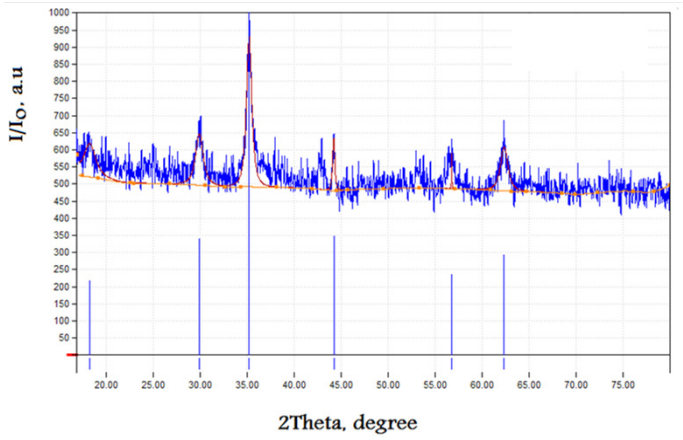

Figure 1: XRD pattern of the as synthesized ferrite.

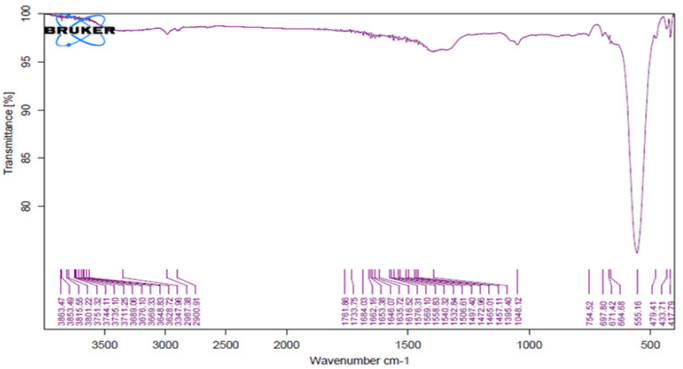

Figure 2: FTIR of the as synthesized ferrite.

FTIR analysis

FTIR analysis of the investigated sample was showed in **Figure 2.** Study of this figure revealed that: (i) Spectra of this sample displays different bands located at 3744-3042, 1652-1624, 1139-1115, 698-654, 577-520 and 459-414 cm^{-1}. These bands enabled us to identify of functional group and structure elucidation for the sample studied. (ii) The observed broad bands assigned at 3744-3042, 1652-1624 and 1139-1115 cm^{-1} of the as prepared ferrite could be attributed to the stretching and bending vibration of OH group of H_2O adsorbed on the ferrite surface and also KBr which blended with the sample during the measurement [12]. (iii) The spectra show sharp bands at 698-654, 577-520 and 459-414 cm^{-1}. These bands are corresponded to the spinel structure of $ZnCoMnFe_2O_4$. It is known that the characteristic bands of single and/or mixed oxides in the region of 1000 and 400 cm^{-1} are usually assigned to the vibration of metallic ions in the crystal lattice [1,4]. However, the spinel materials are known to exhibit two fundamentals IR active modes in the vibration spectra, which are high frequency band around 600 cm^{-1}at tetrahedral (A) site and low frequency band around 400 cm^{-1} at octahedral (B) site [21].

Finally, from the previous data confirm that porous spinel Mixed Quarterly Transition Ferrite (MQTMF) Nanoparticles (NPs) were prepared by using combustion synthesis based on glycine as fuel. XRD results show formation well crystalline $Zn_{0.2}Co_{0.4}Mn_{0.4}Fe_2O_4$ nanoparticles to use as electrode material for high performance super capacitors. FTIR data displays the two vibrations around 400 and 600 cm^{-1} that confirm presence of the characteristics bands for formation of spinel ferrite.

Magnetic properties

The magnetization ((M–H) curve of the investigated solid, at room temperature with applied magnetic field ±20 kOe using VSM is represented in Figure 3. The magnetic parameters, saturation magnetization (M_s), coercivity (H_c), and remanent magnetization (M_r) obtained from this curves were determined. The magnetization curve of this sample displays S - shape indicating both the Ferro magnetization and supper paramagnetization. The values of M_s, H_c, and M_r were found to be 29.776 emu/g, 19.490 Oe and 1.1140 emu/g, respectively. The change in concentration of the oxygen vacancies at the surface or interface of ZnCoMn ferrite nanoparticles resulted in different changes in their room temperature ferromagnetism. However, the particle size and cation distribution of Zn, Co, Mn and Fe have various effects on the magnetization of the as prepared solid.

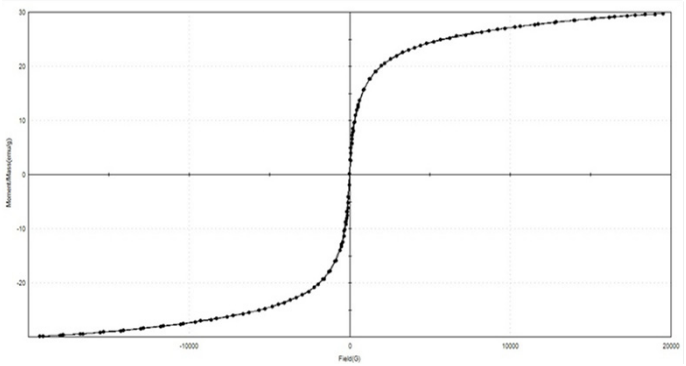

Figure 3: M-H curve at room temperature for the as synthesized ferrite.

Conclusions

Some significant data obtained in this allow for the following conclusion:

1. Glycine assisted auto-combustion route is a simple, cheap, and quick method to prepare $Zn_{0.2}Co_{0.4}Mn_{0.4}Fe_2O_4$ nanoparticles. Furthermore, this method has several advantages, including economic feasibility, ease of scale-up, shorter processing time, and environmental friendliness.

2. The characteristics IR bands of the ferrite crystallite were observed around 400 and 600 cm^{-1} with different intensities in the FTIR spectra of the investigated sample. This indicates that the as prepared sample consisted of $Zn_{0.2}Co_{0.4}Mn_{0.4}Fe_2O_4$ nanoparticles.

3. The as synthesized $Zn_{0.2}Co_{0.4}Mn_{0.4}Fe_2O_4$ nanoparticles have medium magnetization and lower coercivity depending upon presence of the oxygen vacancies at the surface/or interface of the particles and change of the cation distribution.

4. The prepared ferrite is very important due to their various applications, such as catalytic materials, gas sensors, and magnetic storage media and super capacetors.

5. This environmentally friendly approach of producing $Zn_{0.2}Co_{0.4}Mn_{0.4}Fe_2O_4$ nanoparticles could be applied to the production of other industrially important mixed ferrite nanoparticles in the future.

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