Sol gel method for synthesis of semiconducting ferrite and the study of FTIR, DTA, SEM and CV

Sagir Alva¹, Tang Ing Hua², Umar Kalmar Nizar³, Haris Wahyudi¹, and Rita Sundari¹

¹ Faculty of Engineering, Universitas Mercu Buana, 11650 Jakarta, Indonesia
² Department of Chemistry, Faculty of Science, Universiti of Technologi Malaysia, 81310 Skudai, Johor, Malaysia
³ Department of Chemistry, Universitas Negeri Padang, 25131 Padang, Indonesia

ritsun2003@yahoo.com

Abstract. In this study, a sol gel method using citric acid as an anionic surfactant is used for synthesis of magnesium ferrite. Calcinations of magnesium ferrite at temperature (300 °C, 600 °C and 800 °C) have been conducted after sol gel process. Characterization study of the prepared magnesium ferrite related to calcinations using Fourier transform infrared spectrometry (FTIR), Differential thermogravimetric analysis (DTA), and Scanning electron microscope (SEM) has been discussed. The study of Cyclic voltammetry (CV) of the prepared magnesium ferrite has been examined to assay the semiconducting behavior of magnesium ferrite in relation to its electrochemical behavior.

1. Introduction

Previous publications reported that ferrites were used for many applications such as composites, heterogeneous catalysts, magnetic materials, sensors and semi conductors [1 – 5]. The electrical and magnetic properties of ferrites depend on their size, shape, crystalline structure and cationic distributions, which can be controlled during fabrication process [3]. Furthermore, ferrites with their general formula, MFe₂O₄ (M= Co, Zn, Mg, etc.), possess important electrical and magnetic properties, where they form close packed face-centered cubic (fcc) crystals while the M²⁺ and Fe³⁺ ions can form either tetrahedral or octahedral structures placed inside the fcc unit cell [3,6].

The fabrication of ferrites has drawn much greater interest because ferrites show remarkable properties in many applications. A number of methods have been developed to fabricate ferrites including electrospinning [2,7], co-precipitation [8,9], high energy ball milling [10], solid state reaction [11], and oxidative thermal decomposition [12]. To the best of our knowledge, the sol–gel method yields more promising results in the synthesis of ferrites because this method gives many advantages with respect to good stoichiometric control and particle size distribution at fairly low temperature [6,9]. The study of characterizations of ferrites would provide a meaningful correlation of their structures and effective changes in the environment of ions related to different calcinations temperatures [3]. Therefore, we wish to expose the application of sol gel method using citric acid as an anionic surfactant for the synthesis of ferrite materials with respect to magnesium ferrite as an object of this study. The study of characterizations using FTIR spectroscopy to examine functional groups, DTA analysis to investigate thermal behavior of magnesium ferrite, and SEM mapping to study surface morphology are
included in this study. To assay the electrical properties of the prepared magnesium ferrites, a cyclic voltammetry (CV) examination will be used to highlight the electrochemical behavior of the fabricated magnesium ferrites.

2. Experimental

2.1. Materials

All chemicals were purchased and used without further purification. Deionized distilled water was used throughout the experiments. Magnesium nitrate hydrate (HmbG, 99.5%), iron nitrate hydrate (OReC, AR grade), citric acid monohydrate (OReC, AR grade), and sodium hydrogen phosphate dihydrate (GCE, AR grade) were used in this study.

2.2. Methods

2.2.1. Synthesis of Mg-ferrite. The magnesium ferrite was prepared through the method of Hua and Sundari [3]. Iron nitrate hydrate, magnesium nitrate hydrate and citric acid monohydrate were mixed and dissolved in deionized distilled water and made up to 100 mL in order to obtain concentration ratio of 0.5 M : 0.25 M : 0.5 M. The solution mixture was stirred and heated at 60°C for 3h and followed by heating up to 80°C until the mixture changed to gel form. Then the gel was dried in an oven at 100°C for 24h and followed by calcinations in a muffle furnace at 300, 600 and 800°C for 2h, respectively.

2.2.2. Characterizations.

The prepared magnesium ferrite was characterized using the following instruments. The functional group of the magnesium ferrite was determined by Fourier transform infrared spectrometer (FTIR, Perkin Elmer) using KBr pelletizer as reference for running samples of 20 scans per run. The exothermic and endothermic decomposition of the magnesium ferrite was examined by Differential thermogravmic analyzer (DTA, Mettler Toledo TGA/SDTA 851) with nitrogen flow rate at 10 scale units per minute. The surface morphology of the magnesium ferrite was

![Figure 1. The sol gel process for synthesis of magnesium ferrite using citric acid followed by calcinations.](image-url)
examined by Scanning electron microscope mapping (SEM, Philips XL) using an accelerating voltage of 25.0 kV integrated with Energy dispersive X-ray (EDX) to determine atomic distribution on material surface.

### 2.2.3 Semi conducting test

The semiconducting test was used to assay the electrical properties of the prepared magnesium ferrite. The test was based on the cyclic voltammetry (CV) performance executed by a system of three electrode configuration transduction, i.e. (i) the Ag/AgCl/KCl reference electrode, (ii) the glassy carbon counter electrode, and (iii) the screen printed carbon (SPC) working electrode attached by the prepared magnesium ferrite. All the electrodes immersed in a 5 mL beaker glass filled by a phosphate buffer solution. An Autolab PGSTAT 30 using a GPES software was applied to perform cyclic voltammograms (CVs) recorded between -0.5V and +0.5V with a scan rate of 0.02 V/s.

### 3. Results and discussion

#### 3.1 Functional group of magnesium ferrite

The functional group of the prepared magnesium ferrites were determined by FTIR spectroscopy. As shown in Figure 2, the prepared magnesium ferrite (100°C) showed the presence of strong stretching vibration of O-H group at 3421 cm⁻¹, whereas the calcinations temperature increased the stretching vibration of O-H group gradually disappeared. A strong absorption peak at 1400 cm⁻¹ (spectrum of 100°C) attributed to trace CO₂ adsorption related to oxidation of citric acid during sol gel process. When magnesium ferrite was calcined at 300°C, some functional groups were eliminated attributed by the absence of several absorption peaks except for O-H and NO₃⁻ groups in the range of 1000 – 400 cm⁻¹, which were retained in the tetrahedral or octahedral structure due to stronger chemical bonding. This phenomenon is in agreement with previous investigations [3 – 4, 6, 13].

**Figure 2.** FTIR spectra of magnesium-ferrites. Sol gel method using citric acid at 100°C followed by calcinations at 300°C, 600°C and 800°C.

#### 3.2 Thermal properties of magnesium ferrite

The exothermic or endothermic decomposition of the prepared magnesium ferrite was investigated by DTA examination. As shown in Figure 3, the sol gel process at 80 – 100°C showed an endothermic dehydration attributed by H₂O and CO₂ removal. The DTA profile showed a flat line when the calcination of magnesium ferrite increased to 800°C due to exothermic decomposition of C-N bond and removal of NO and NO₂ groups. A similar phenomenon is also found in the study of Lick and Soria [12] in the synthesis of manganese ferrite, as well as in the study of ferrite using electro spinning method [2].

3
3.3 Surface morphology of magnesium ferrite
The surface analysis of the prepared magnesium ferrite was examined by SEM mapping. Figure 4 showed the SEM mapping of magnesium ferrite after sol gel process at 80-100°C (Fig. 3a). When magnesium ferrite was calcined until 600°C, the density of iron distribution on material surface increased from 26.2% to 50.6% as recorded by the EDX data (Fig. 3b). The white dots in Figure 3 indicate iron particles scattering over the material surface. High temperature calcination (600°C) yielded stronger thermal agitation causing higher iron distribution on the material surface [3].

![Figure 3](image_url)

Figure 3. The DTA profiles of magnesium-ferrite at 100°C and 800°C. Sol gel method using citric acid followed by calcinations.

(a) (b)

![Figure 4](image_url)

Figure 4. SEM mapping of magnesium-ferrite for iron distribution at 100°C (a) and 600°C (b). Sol gel method using citric acid followed by calcinations. White dots indicated iron particles scattering.

3.4 Semi conducting test of magnesium ferrite
The electrical properties of prepared magnesium ferrite were demonstrated by CV profiles related to electrochemical behavior of magnesium ferrite. Figure 5 showed CV profiles of magnesium ferrite calcined at 300°C and 600°C, respectively. Both reduction and oxidation peaks of the CV profile of 600°C – magnesium ferrite was shown stronger than that of 300°C – magnesium ferrite caused by higher calcination temperature induced higher electrical conductivity of the ferrite to some extent. This phenomenon is similar to that one of earlier investigation using magnesium ferrite doping by nickel and cobalt elements [5].
4. Conclusions
The CV profiles related to electrochemical behavior of the prepared magnesium ferrite show that the sol gel method has been successful in the synthesis of semi conducting magnesium ferrite. The sol gel method followed by calcinations process at higher temperatures may enhance the electrical properties of the prepared magnesium ferrite to some extent. The characterization study showed meaningful correlation between structures and effective changes related to different calcination temperatures.

Acknowledgement
The research was financially supported by GUP tier 2 through RMC-UTM project funding, which is gratefully acknowledged.

Reference
[1] Willey R J, Noirclerc P and Busca, G 1993 Chem. Eng. Commun. 123
[2] Maensiri S, Sangmanee M and Wiengmoon A 2009 Nanoscale Res. Lett. 4 221
[3] Hua T I and Sundari R 2012 Malaysian J. Fundamental Appl. Sci. 8 149
[4] Sundari R, Hua T I, Aziz M and Nizar U K 2014 Malaysian J. Anal. Sci. 18 485
[5] Erdawati, Yusmaniar and Sundari R 2015 Asian J Chem. 27 4693
[6] Pradeep A, Priyadharsini P and Chandrasekaran G 2008 J Magnetism & Magnetic Mater. 320 2774
[7] Liu C P, Li M W, Zhong C, Huang J R, Tian Y L, Tong L and Mi W B 2007 J Mater. Sci. 42 6133
[8] Siemons M, Weirich Th, Mayer J and Simon U 2004 J Inorg. General Chem. 630 2083
[9] Pradeep A and Chandrasekaran G 2005 Mater. Lett. 60 371
[10] Pradhan S K, BidB S, Gateshki M and Petkov V 2005 J Mater. Chem. Phys. 93 224
[11] Mishra S, Kundu T K, Barick K C, Bahadur D and Chakravorty D 2006 J Magnetism & Magnetic Mater. 307 222
[12] Lick I D and Soria D B 2009 J. Argentine Chem. Soc. 97 102
[13] Tolstoy V P, Chernyshova I V and Skryshecsky V A 2003 Handbook of Infrared Spectroscopy of Ultrathin Films, John Wiley & Sons, USA, Hoboken, New Jersey 670
