UNIVERSITI PUTRA MALAYSIA

STRUCTURAL, MAGNETIC, OPTICAL AND ELECTRICAL CHARACTERIZATION OF METAL MANGANESE OXIDES WITH Ni, Zn AND Li NANOPARTICLES PREPARED VIA THERMAL TREATMENT METHOD

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NOORHANIM BINTI AHAD

Chairman: Professor Abdul Halim Shaari, PhD

Faculty: Science

Spinel and spinel-like materials are subjects of continuing study in materials science because of their optical, electrical, magnetic, and catalytic properties. 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. Various fabrication techniques have been reported including chemical, sol-gel, co-precipitation, hydrothermal and microwave. But, most of the present preparation technique of metal manganese oxide nanomaterials are difficult to employ on a larger scale because of their complicated procedures, high reaction temperatures, long reaction times, toxic reagents and contaminated with by products and their potential harm to the environment. In this study the spinel metal manganese oxide nanocrystals were first time synthesized by means of thermal treatment method. This method is cost-effective, environmentally-friendly, has low reaction temperatures, and produced no by-product effluents. An aqueous solution of poly (vinyl pyrrolidone) (PVP) was prepared by dissolving the polymer in deionized water at 90 ^{0}C before adding manganese nitrate and the respective metal nitrates for a constant stirring of 2 h. The homogeneous solution was dried at 100 ^{0}C for 24 h before grinding and calcined at temperatures ranging from 450 to 850 ^{0}C to decompose the organic matters and crystallized the metal manganese oxide nanoparticles.

The optimum calcination temperature was confirmed by Fourier transform infrared spectroscopy (FTIR) measurement by the presence of metal oxide bands at all temperatures and the absence of organic bands at 850 ^{0}C for $NiMn_2O_4$, $ZnMn_2O_4$, $LiMn_2O_4$ and $NiLiMn_2O_4$ nanoparticles. The transmission electron microscopy (TEM) images showed cubical metal manganese oxide nanoparticles that were slightly uniform in both morphology and particle size distribution. The x-ray diffraction (XRD) patterns showed crystalline phases that confirmed the formation of

nanocrystalline single-phase spinel metal manganese oxide nanoparticles with a face-centered cubic structure. The average particle sizes were determined from TEM images and it was found that the particle size increased with the calcination temperature from 10.3 to 33.8 nm for $NiMn_2O_4$, from 19.8 to 64.4 nm for $ZnMn_2O_4$, from 10.2 to 41 nm for $LiMn_2O_4$, and from 9.8 to 37.1 nm for $NiLiMn_2O_4$. The particle size obtained from TEM images larger than the particle size determined from the XRD data.
The magnetic properties were confirmed by the use of electron spin resonance (ESR) spectroscopy, which revealed the existence of unpaired electrons and also measured peak-to-peak line width (ΔH_{pp}), resonant magnetic field (H_r), and the g-factor for $NiMn_2O_4$ and $LiMn_2O_4$ and $NiLiMn_2O_4$ nanoparticles while $ZnMn_2O_4$ nanoparticles did not exhibit resonance signal. This could be possibly due to the super exchange interaction that occurs in these nanoparticles. The band gap energy for $NiMn_2O_4$, $ZnMn_2O_4$, $LiMn_2O_4$ and $NiLiMn_2O_4$ nanoparticles were determined from UV-vis reflectance spectra using the Kubelka-Munk function and the band gaps were found to decrease with increase in calcination temperature due to particle size increased. The energy band gap values decrease from 1.75 eV to 1.56 eV for $NiMn_2O_4$, from 2.43 eV to 1.84 eV for $ZnMn_2O_4$, from 2.4 eV to 1.18 eV for $LiMn_2O_4$ and decrease from 1.81 eV to 1.75 eV for $NiLiMn_2O_4$ when the calcination temperature increases from 450 ^{0}C to 850 ^{0}C. Electrical conductivities and dielectrics of the sample pellets of $NiMn_2O_4$, $LiMn_2O_4$ and $NiLiMn_2O_4$ nanoparticles were studied through impedance spectroscopy measurements and the calculated value of DC conductivity for the samples calcined at higher temperature, 850 ^{0}C are found to be 2.79 x 10^{-8}, 6.17 x 10^{-8} dan 1.15 x 10^{-8} Scm^{-1} for $NiMn_2O_4$, $LiMn_2O_4$ and $NiLiMn_2O_4$ nanoparticles, respectively. The higher particles size was obtained for zinc manganese oxide samples, which are between 19.8-64.4 nm compared to other samples. The energy band gap value for zinc manganese oxide and lithium manganese oxide samples higher than other samples, which are in the range between 1.80-2.43 eV. The lithium manganese oxide samples have higher DC conductivity value, 6.17 x 10^{-8} S/cm. Thus, this sample would give better performance for electrode. Our results show that zero dimensional spinel $NiMn_2O_4$, $ZnMn_2O_4$, $LiMn_2O_4$ and $NiLiMn_2O_4$ nanoparticles have been synthesized using the simple thermal treatment method.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Doktor Falsafah

PENCIRIAN STRUKTUR, OPTIK, MAGNET DAN ELEKTRIK BAGI ZARAH NANO LOGAM MANGAN OKSIDA DENGAN Ni, Zn DAN Li DISEDIAKAN MELALUI KAEDAH RAWATAN TERMA

Oleh

NOORHANIM BINTI AHAD

Pengerusi: Profesor Abdul Halim Shaari, PhD

Faculti: Sains

Spinel dan bahan seperti spinel adalah subjek kajian berterusan dalam bidang sain bahan kerana sifat optik, elektrik, magnet dan sebagai pemangkin. Sifat-sifat ini bergantung kepada komposisi kimia dan ciri-ciri mikrostruktur di mana saiz zarah dan bentuknya mungkin boleh dikawal dalam proses fabrikasi. Pelbagai kaedah fabrikasi telah digunakan untuk menghasilkan zarah nano logam mangan oksida termasuk keedah kimia, sol-gel, pemendakan, hidroterma dan gelombang mikro. Tetapi kebanyakan kaedah ini sukar untuk dilaksanakan dalam penggunaan besar-besaran kerana prosedur yang rumit, suhu reaksi yang tinggi, masa tindak balas yang panjang, reagen dan biproduk yang toksik, dan berpotensi membawa kemudaratan kepada alam sekitar. Dalam kajian ini, spinel logam mangan oksida adalah pertama kali disintesis melalui kaedah rawatan terma. Kaedah ini adalah kos efektif, mesra alam, mempunyai suhu tindak balas yang rendah, dan tidak menghasilkan produk efluen. Laruan akueus poli (vinil pyrrolidone) (PVP) telah disediakan dengan melarutkan polimer di dalam air tak berion pada suhu 90 ^{0}C sebelum menambah nitrat mangan dan nitrat logam lain yang berkenaan dan sentiasa dikacau selama 2 jam. Larutan homogen dikeringkan pada suhu 100 ^{0}C selama 24 jam sebelum dikisar dan mengalami pengkalsinan pada suhu daripada 450 hingga 850 ^{0}C untuk menguraikan bahan organik dan proses penghabluran zarah nano logam mangan oksida.

Suhu optimum proses pengkalsinan telah disahkan oleh pengukuran spektroskopi Fourier inframerah (FTIR) dengan kehadiran spektrum hablur oksida logam pada semua suhu dan ketidakhadiran spektra jalur organik pada suhu 850 ^{0}C untuk zarah nano $NiMn_2O_4$, $ZnMn_2O_4$, $LiMn_2O_4$ dan $NiLiMn_2O_4$. Imej mikroskopi electron transmisi (TEM) menunujukan struktur zarah nano logam mangan oksida berkubus yang agak seragam dalam kedua-dua morfologi dan taburan saiz zarah. Corak pembelauan sinar x (XRD) menunjukkan fasa hablur yang mengesahkan pembentukan hablur nano fasa tunggal dengan struktur kubus muka berpusatkan

(FCC). Purata saiz zarah ditentukan dari imej TEM dan mendapati saiz zarah meningkat dengan suhu dari 10.3 hingga 33.8 nm untuk $NiMn_2O_4$, dari 19.8 nm hingga 64.4 nm untuk $ZnMn_2O_4$, dari 10.2 hingga 41 nm untuk $LiMn_2O_4$ dan dari 9.8 nm hingga 37.1 nm untuk $NiLiMn_2O_4$. Saiz zarah terhasil daripada imej TEM adalah lebih besar daripada saiz zarah yang dikira dari XRD.

Sifat- sifat magnet telah disahkan oleh penggunaan spektroskopi resonan electron spin (ESR) yang mendedahkan kewujudan elekron berpasangan dan juga diukur talian puncak ke puncak lebar (□Hpp), salunan medan magnet (H_r), dan fakor-g untuk zarah nano $NiMn_2O_4$, , $LiMn_2O_4$ dan $NiLiMn_2O_4$ manakala zarah nano $ZnMn_2O_4$ tidak menunjukkan isyarat resonan. Ini mungkin disebabkan oleh interaksi pertukaran super berlaku dalam zarah nano. Jurang jalur tenaga bagi zarah nano $NiMn_2O_4$, $ZnMn_2O_4$, $LiMn_2O_4$ dan $NiLiMn_2O_4$ telah ditentukan daripada spectrum pantulan UV-vis dengan menggunakan fungsi Kubleka-Munk dan jurang tenaga didapati berkurangan dengan peningkatan suhu pengkalsinan disebabkan oleh saiz zarah yang meningkat. Jurang jalur tenaga berkurangan daripada 1.75 eV kepada 1.56 eV untuk $NiMn_2O_4$, from 2.43 eV to 1.84 eV for $ZnMn_2O_4$, daripada 2.4 eV to 1.18 eV untuk $LiMn_2O_4$ dan berkurang daripada 1.81 eV kepada 1.75 eV untuk $NiLiMn_2O_4$ apabila suhu pengkalsinan meningkat daripada 450 ^{0}C kepada 850 ^{0}C. Kekonduksian elektrik dan dielektrik bagi zarah nano berbentuk pelet $NiMn_2O_4$, $LiMn_2O_4$ dan $NiLiMn_2O_4$ dikaji melalui pengukuran spekroskopi impedans. Nilai kekondusian DC yang dikira unuk zarah nano yang mengalami pengkalsinan pada suhu tertinggi, 850 ^{0}C adalah 2.79 x 10^{-8}, 6.17 x 10^{-8} dan 1.15 x 10^{-8} Scm^{-1} untuk zarah nano $NiMn_2O_4$, $LiMn_2O_4$ dan $NiLiMn_2O_4$, masing-masing. Keputusan kami menunjukkan bahawa spinel zarah nano berdimensi sifar $NiMn_2O_4$, $ZnMn_2O_4$, $LiMn_2O_4$ dan $NiLiMn_2O_4$ telah disintesis menggunakan kaedah rawatan terma yang mudah.

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I certify that a Thesis Examination Committee has met on 17th May 2018 to conduct the final examination of Noorhanim Binti Ahad on her thesis entitled "Structural, Magnetic, Optical and Electrical Characterization of Metal Manganese Oxides with Ni, Zn and Li Nanoparticles Prepared via Thermal Treatment Method" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The committee recommends that the student be awarded the Degree of Doctor of Philosophy.

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Associate Professor
Faculty of Science
Universiti Putra Malaysia
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Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Chen Soo Kien
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Professor
(External Examiner)

NOR AINI AB. SHUKOR, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

Abdul Halim Shaari, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
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Faculty of Science
Universiti Putra Malaysia
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LIST OF ABBREVIATIONS AND SYMBOLS

$NiMn_2O_4$	Nickel Manganese Oxide
$ZnMn_2O_4$	Zinc Manganese Oxide
$LiMn_2O_4$	Lithium Manganese Oxide
$NiLiMn_2O_4$	Nickel Lithium Manganese Oxide
PVP	Polyvinyl pyrrolidone
H_2O	Deionized water
MW	Molecular weight
FTIR	Fourier Transform Infrared Spectroscopy Thermal conductivity
σ	Electrical conductivity
TEM	Transmission Electron Microscopy
XRD	X-ray Diffraction
ESR	Electron Spin Resonance

CHAPTER 1

INTRODUCTION

1.1 Introduction to Nanotechnology and Nanomaterials

From the consumers' perspective, nanotechnology touches every part of our everyday lives without us even realizing it such as stay-clean and anti-UV windows, scratchproof glasses, DVDs, security lighting, etc. From an industrial's perspective, nanotechnology promises products that use lesser energy, environmental friendly, cost effective, and intelligent. Even though nanotechnology has been under development for many years, it is just only recently that the issues behind the science are rising in the scientific and engineering communities, as well as the political and broadcasting arena. The future development and application of nanotechnologies shapes the human civilization. Nanotechnology deals with the construction and use of functional structures designed from an atomic or molecular scale with at least one characteristic dimension measured in nanometers. In the past decade, the movement towards nanoscience in many areas of nanotechnology had stimulated huge interest in new materials. Due to this reason, modern technologies such as microelectronics, sensors, biosensors, and chemical and biochemical engineering etc. are all calling for these new materials. New materials with size ranged from 1-100 nm are classified as nanomaterials because of their dimensions. They exhibit physical and chemical properties differ from those displayed by either their molecular or bulk properties. Metal nanoparticles relatively considered as new materials and at the present is broadly investigated. Recently, nanostructurization of metal nanoparticles and their composites emerged as new fields of research and development in nanotechnology.

The main interests of these smart materials are that their noble and unique properties to be exploited for a wide range of potential applications. Encompassing nanoscale science, engineering and technology, nanotechnology involves imaging, measuring, modeling, administering, and manipulating matter at nanometer size.

1.2 Metal Oxide Nanoparticles

In this technologically advanced world of materials, metal oxides play a very important role in many areas of science and technology. Metal oxides are abundant in the earth's crust. Almost all the metals can form their oxides through oxidation by oxygen from air at an appropriate temperature and pressure. Indeed, the existence of different metal oxides such as alkali and alkaline earth metal oxides, rare-earth oxides, etc., transition metal oxides are of special interest because of the interesting electrical and magnetic properties that they exhibit. The transition metals of interest can be easily accommodated in the interstices of the close packed layers of O_2^- ions. Depending on the electronic configuration of the metal ions and the structural geometries, oxides can be insulators, semiconductors or metals. Oxides are chemically stable and therefore, attract attention towards various applications. Potentially important properties exhibited by the metal oxides are the high-Tc superconductivity such as in layered cuprates, colossal magnetoresistance (CMR) observed in perovskite manganites, ferroelectricity, ferro- and ferrimagnetism, multiferroicity where magnetism and ferroelectricity coexists together, etc. Also, metal oxides are both technologically and industrially important because of their interesting properties and overall characteristics such as hardness, thermal stability, thermal conductivity, and chemical resistance. For example, SiO_2 is well known for its optical properties, ferrimagnetic iron oxides such as the spinel ferrite, γ-Fe_2O_3 and as hexagonal ferrite $BaFe_{12}O_{19}$, are must known for their application in data storage and hard magnets. Metal oxides with variable electron mobility are used as semiconductors (ZnO, V_2O_5) or superconductors ($YBa_2Cu_3O_7$). Ferroelectric or dielectric perovskite type oxides such as $BaTiO_3$, $PbZrTiO_3$, etc are extensively used in electronic devices. In addition, metal oxides are widely used in many fields such as in refractories to withstand very high temperatures, in catalysis as an active material, promoter and support, in the field of gas sensors, Li-ion batteries, fluuorescent lights, cellular phones, fuel cells, etc. It is worth noting here and highlight the application of oxides to reduce environmental pollution by their use as a catalyst or sorbent to remove CO, NOx and SOx during combustion of fossil derived fuels.

Spinel metal manganese oxide nanoparticles have attracted special attention because of their unique physical and chemical properties. The manganese nanoparticles have copious industrial applications in supercapacitors, catalysis, biosensors, ion sieves, molecular adsorption, high density magnetic storage media, batteries, and magnetic resonance imaging. Since, the properties of nanoparticles are sizes and shapes dependent, the synthesis process involves good control on monodispersity, where sizes and shapes become important areas of the research. Currently, different chemical and physical methods are employed for the synthesis of metal manganese oxide nanoparticles

Spinels and perovskites are two classes of oxide structures with attractive properties and extensive applications.

1.3 The Spinel Structure

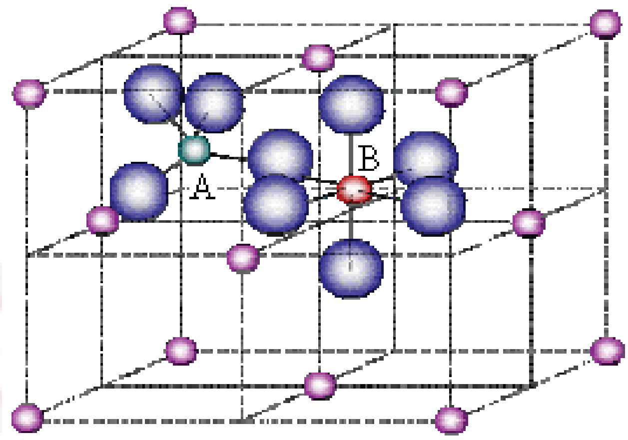

Figure 1.1: Schematic of two subcells of a unit cell of the spinel structure, showing octahedral and tetrahedral sites (Spaldin et al., 2003).

Spinel type oxide is a class of material which crystalizes in a face centered cubic structure with the general formula AB_2O_4 where A and B are cations occupying tetrahedral and octahedral sites, respectively, while O designates the oxygen anion position. In the spinel structure, A and B can be divalent, trivalent, or quadrivalent cations including magnesium, zinc, manganese, aluminium, chromium, titanium, etc. It is essentially cubic with the oxygen ions forming a face-centered-cubic (FCC) lattice. The unit cell of a spinel consists of eight formula units and therefore, may be represented as $8[AB_2O_4]$ so it may be represented as $A_8B_{16}O_{32}$. Within the face-centered cubic lattice formed by 32 oxygen ions there exist two types of interstitial positions which can be occupied by the metallic cations. There are 64 tetrahedral interstitial sites surrounded by 4 oxygens (called as A site) and 32 octahedral sites surrounded by 6 oxygens (called as B site). The space group for the spinel has been identified as Fd3m. Depending on the distribution of the cations in the tetrahedral and octahedral sites, spinels can be classified as normal, inverse and mixed spinels which can be represented in general as $(A_xB_{1-x})[A_{1-x}B_{1+x}]O_4$ where (A_xB_{1-x}) representing the tetrahedral sites and $[A_{1-x}B_{1+x}]$ representing the octahedral sites. If each sublattice is occupied by only one type of cation i.e. when x = 1, the spinel is said to be normal where as if x = 0, it is called as inverse spinel. When $0 < x < 1$ the spinel is defined as the mixed one. In the normal spinels, the cations (generally metals) occupy 1/8 of the tetrahedral sites and 1/2 of the octahedral sites and there are totally 32-O ions in the unit cell while there are exchanged places of cations in inverse spinel structure (Jeremy et al., 1982). Table 1.1 depict the types of spinels with the general formula of representation. The spinel type oxide has various applications in the field of catalysis, sensors, batteries, pigments, fuel cells, solar cells, memory devices, transformers, and others. Table 1.2 show some of the applications of spinel type oxides.

Table 1.1 Different types of spinels

Type	General formula
Normal	$(A^{2+})\ [B_2^{3+}]O_4$
Inverse	$(B^{3+})\ [A^{2+}B^{3+}]O_4$
Mixed	$(A_{1-x}^{2+}\ B_x^{3+})\ [A_x^{2+} + B_{2-x}^{3+}]O_4$

Table 1.2 Applications of Spinel Metal Oxide (Vijayanand, 2010)

Spinel Metal Oxide	Applications
Co_3O_4, $ZnCo_2O_4$	Sensor, batteries, catalysts, etc.
$MgAl_2O_4$	Refractory
$CoAl_2O_4$	Pigments, catalyst, H_2 production
$Li_{1-x}Mn_2O_4$	Batteries
Fe_3O_4	MRI, Magnetic hyperthermia, Drug delivery
$Ni_{1-x}Zn_xFe_2O_4$	Pulsed current monitor, transformer cores antenna rods, microwave devices, telecommunication.

1.4 Problem statement

Zero dimensional nanomaterials such as nanoparticles, quantum dots and metal oxide nanparticles of less than 100 nm in dimension have attracted interest in recent years due to their excellent physical and chemical properties that are different from their respective bulk counterparts (Hornyak et al., 2008). In particular spinel metal manganese oxides (AMn_2O_4) (where A= Ni, Zn or/and Li) nanoparticles are important class of mixed-metal manganese oxides, owing to their diverse properties such as photocatalytic (Bessekhouad et al., 2002), magnetoresistance (Hosseini et al., 2012) properties, or being used as lithium ion batteries (Yang et al.,2008). Therefore, the A-Mn-O binary and ternary systems belong to a class of interesting and useful materials in terms of their electrical, optical and magnetic properties.

Novel routes were recently explored to attain innovative techniques for the synthesis of metal manganese oxide including chemical method, co-precipitation (Bassekhoud et al., 2002), hydrothermal (Zhang et al., 2007), sol-gel (Hosseini et al., 2012), microwaves (Yan et al., 1999), ultrasonic spray pyrolysis (Taniguchi et al., 2002), reverse micelles (Maria et al., 2010), aerosol (Fauteux et al., 1997) and laser ablation (Julien et al., 2000). Most of the present preparation techniques of metal manganese oxide nanomaterials are difficult to apply on a larger scale of production because of complicated and difficult procedures to control their size distribution and shape, long reaction times, high reaction temperatures, toxic reagents and by-products which are potentially harmful to the environment.

In this research, attempts are made to synthesize the nanostructured of nickel manganese oxide, $NiMn_2O_4$, zinc manganese oxide, $ZnMn_2O_4$, lithium manganese oxide, $LiMn_2O_4$ and nickel lithium manganese oxide, $NiLiMn_2O_4$ using a simple and low temperature (below 1000 ^{0}C) thermal treatment method because these materials have never been synthesized using this method before.

1.4 Significance of the study

With the development of nanostructured materials, manganese-based transition-metal spinel oxide nanoparticles has attracted much more researchers' attention to deeply investigate several areas, such as optics and electronics due to their particular electrical, optical and magnetic properties, which emerge from the mixed valence states of manganese. This material is also of considerable technological importance owing to its use in catalysts, thermistors, supercapacitors, sensors, magnetic and electrode materials. For example, $NiMn_2O_4$ has a high activity with respect to the reactions of ozone decomposition and CO and CH oxidation in the presence of ozone at room temperature (Mehandijev et al., 2006). $ZnMn_2O_4$ is an efficient catalyst for the reduction of NO to N_2, and, all cases, its best selectivity to N_2 and CO_2 (Ferraris et al., 2002). $LiMn_2O_4$ is a low cost, abundant resources and no environmental pollution and can be considered as the ideal cathode material (Manjunatha et al., 2011). $NiLiMn_2O_4$ is also extensively studied as a promising positive electrode material for lithium ion batteries, because of its many advantages (Kumar et al., 2014).

In this research, a new route of synthesis for metal oxide nanoparticles was implemented, first introduced for spinel metal ferrites nanoparticles by Naseri and co-workers (2012), by a simple thermal treatment method. The thermal treatment method suggest several advantages of environmental friendly in that it neither uses nor produces toxic substances, simple, low cost production, no unwanted by-products and low reaction temperatures.

1.5 Objective(s) of the research:

The aim of this research is to synthesize the metal manganese oxide nanoparticles such as nickel manganese oxide, zinc manganese oxide, lithium manganese oxide and nickel lithium manganese oxide prepared by thermal treatment method. The objectives of the present work are:

1) To synthesize metal manganese oxide (AMn_2O_4) (A=Ni, Zn, Li) and mixed metal manganese oxide (AMn_2O_4) (A=Ni_xLi_{1-x}) nanocrystals by thermal treatment method.

2) To characterize the morphological structures, particles size and size distribution of the (AMn_2O_4) (A=Ni, Zn, Li) and (AMn_2O_4) (A=Ni_xLi_{1-x}) nanocrystals.

3) To investigate calcination temperature on the magnetic and optical properties of the $NiMn_2O_4$, $ZnMn_2O_4$, $LiMn_2O_4$ and $NiLiMn_2O_4$ nanocrystals.

4) To investigate calcination temperature on the electrical properties of the $NiMn_2O_4$, $LiMn_2O_4$ and $NiLiMn_2O_4$ nanocrystals.

1.6 Outline of the thesis

In chapter 1, summary of nanoscience and nanotechnology in addition to the statement of problem, significance of the study and study objectives were stated. In chapter 2, a discussion is given on the general background of the metal manganese oxide nanoparticles and common preparation and synthesizing methods. Chapter 3 presents some theoretical background of material characterizations such as X-Ray Diffraction, electron spin resonance (ESR), optical absorption and electrical behaviors. In chapter 4, the detailed clarification of the procedures involved in the synthesis of metal manganese oxide, $NiMn_2O_4$, $ZnMn_2O_4$, $LiMn_2O_4$ and $NiLiMn_2O_4$ nanocrystals by the thermal treatment method are explained. Details of the instruments used for characterizing the prepared samples and some equations involved were also stated in this chapter. The results and discussion for every measurement including thermogravimetry analyses (TGA), X-ray Diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), Electron spin resonance (ESR), UV- visible spectrophotometer (UV-vis) and impedance analyzer techniques are expressed in chapter 5. Finally, the summary and conclusions of the research work with suggestions for future work are given in Chapter 6. List of references, list of publications and vitae of the author are available in the at last section of the thesis.

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