



UNIVERSITI PUTRA MALAYSIA

***STRUCTURAL, OPTICAL AND MAGNETIC CHARACTERIZATION OF
SPINEL ZINC CHROMITE ($ZnCr_2O_4$) NANOCRYSTALS SYNTHESIZED BY
THERMAL TREATMENT METHOD.***

ADAMU SALAHUDEEN GENE

FS 2014 31



**STRUCTURAL, OPTICAL AND MAGNETIC CHARACTERIZATION OF
SPINEL ZINC CHROMITE ($ZnCr_2O_4$) NANOCRYSTALS SYNTHESIZED BY
THERMAL TREATMENT METHOD.**

By

ADAMU SALAHUDEEN GENE

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in
Fulfillment of the Requirements for the Degree of Master of Science**

March 2014

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

STRUCTURAL, OPTICAL AND MAGNETIC CHARACTERIZATION OF SPINEL ZINC CHROMITE (ZnCr_2O_4) NANOCRYSTALS SYNTHESIZED BY THERMAL TREATMENT METHOD.

By

ADAMU SALAHUDEEN GENE

March 2014

Chair: Professor Elias Saion, PhD

Faculty: Science

Spinel and spinel-like materials are subjects of continuing study in materials sciences because their physical and chemical properties have a wide range of applications. In particular, zinc chromite (ZnCr_2O_4) nanocrystals are commonly used in catalysis and humidity sensors, on top of their main usage as magnetic material for devices. Various methods have been applied for the synthesis of spinels ZnCr_2O_4 including the mechanical activation, chemical, microwave, sol-gel, ball milling, combustion methods, among others, but most of these methods are difficult to employ on a large scale production because of their complicated procedures, longer reaction times, high reaction temperatures, toxic reagents and by-products which are potentially harmful to the environment.

In this study the spinel ZnCr_2O_4 nanocrystals were first time synthesized by means of thermal treatment method from an aqueous solution containing only zinc and chromic nitrates, poly(vinyl pyrrolidone), and deionized water. The solution was dried at 353 K for 24 h before grinding and calcination at temperatures ranging from 773 to 973 K to remove unwanted polymer and crystallize the material. The characterization studies of ZnCr_2O_4 nanocrystallines were carried out by X-ray Diffraction spectroscopy (XRD), Electron Dispersive X-ray spectroscopy (EDX), Transmission Electron Microscopy (TEM), Fourier Transform Infrared Spectroscopy (FT-IR), UV-Vis Spectrometer, and Electron Spin Resonance Spectroscopy (ESR). The corresponding peaks of Zn, Cr and O were observed in the EDX analysis of the sample which confirms the formation of ZnCr_2O_4 . The XRD patterns confirmed the formation of the single faced nanocrystallines of spinel ZnCr_2O_4 with a face-centered cubic structure. The average particle size of the synthesized nanocrystals was also determined by XRD using the Scherer's formula and was in good agreement with the TEM images which shows cubical zinc chromite (ZnCr_2O_4) nanoparticles with uniform morphology and particle

size distributions. The results of XRD and TEM showed that the particle size increased with the calcination temperature increases from 19 nm at 773 K to 24 nm at 973 K. The FT-IR spectra showed only two principle absorption bands of Cr-O and Zn-O located at 490 and 615 cm^{-1} respectively, indicating the calcined samples are very pure. The band gap energy was determined from UV-vis reflectance spectra using the Kubelka-Munk function and the band gaps were found to decrease with increase in calcination temperature from 4.03 eV at 773 K to 3.89 eV at 973 K due to particle size increased. The magnetic properties measured by ESR confirmed the existence of unpaired electrons and the resonant magnetic field and the g -factor of the calcined samples were measured. The g -factor was found to increase from 1.9598 to 1.9616 and the resonant magnetic field (H_r) decreased from 3.3468×10^{-7} to 3.3437×10^{-7} A/m as the calcination temperature increases from 773 to 973 K respectively.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Sarjana Sains

**PENCIRIAN STRUKTUR, OPTIK DAN MAGNET BAGI NANAKRISTAL ZINK
KROMIT DISINTESIS DENGAN KAEDAH RAWATAN TERMA.**

Oleh

ADAMU SALAHUDEEN GENE

Mac 2014

Pengerusi: Professor Elias Saion, PhD

Fakulti: Sains

Spinel dan bahan seperti spinel adalah subjek kajian berterusan dalam bidang sains bahan kerana sifat fizik dan kimia mereka mempunyai pelbagai aplikasi. Khususnya, zink kromit (ZnCr_2O_4) nanokristal yang lazimnya digunakan dalam pemangkinan dan sensor kelembapan, selain daripada penggunaan utama mereka iaitu sebagai bahan magnet untuk peranti. Pelbagai kaedah telah digunakan untuk sintesis spinel ZnCr_2O_4 termasuk kaedah-kaedah pengaktifan mekanikal, kimia, gelombang mikro, sol gel, pengkisar bebola, kaedah pembakaran, tetapi kebanyakan kaedah ini yang sukar untuk digunakan kepada pengeluaran besar-besaran kerana prosedur yang rumit, masa tindak balas yang lebih panjang, suhu reaksi yang tinggi, reagen toksik dan produk hiliran yang berbahaya kepada alam sekitar.

Dalam kajian ini, spinel ZnCr_2O_4 nanokristal adalah kali pertama disintesis melalui kaedah rawatan haba daripada larutan akueus yang mengandungi hanya nitrat zink dan kromik, poli (vinil pyrrolidone), dan air nyah ion. Larutan telah dikeringkan pada 353 K selama 24 jam sebelum mencanai dan pengkalsinan pada suhu antara 773-973 K untuk mengeluarkan polimer yang tidak diinginkan dan menghablurkan bahan tersebut. Kajian pencirian nanokristal ZnCr_2O_4 telah dijalankan oleh Spektroskopi Sinar X (XRD), Spektroskopi Sebaran Elektron (EDX), Mikrospektroskopi Penghantaran Elektron (TEM), Spektroskopi Infrared Transform Fourier (FT-IR), Spektrometer UV-vis dan Spektroskopi Resonant Elektron Spin (ESR). Puncak sempadan dengan Zn, Cr dan O telah diperhatikan dalam analisis EDX yang mengesahkan pembentukan ZnCr_2O_4 . Corak belauan XRD mengesahkan pembentukan nanokristal tunggal didapati daripada spinel ZnCr_2O_4 dengan struktur padu berpusat muka. Saiz zarah purata nanokristal yang disintesis juga ditentukan oleh puncak corak XRD dengan menggunakan formula Scherer dan setuju dengan imej TEM yang menunjukkan zink kromit (ZnCr_2O_4) nanopartikel adalah kubus dengan morfologi taburan saiz zarah seragam. Keputusan

XRD dan TEM menunjukkan bahawa saiz zarah meningkat dengan peningkatan suhu pengkalsinan daripada 19 nm pada 773 K kepada 24 nm pada 973 K. Spektrum FT-IR menunjukkan terdapat hanya dua puncak penyerapan utama Cr-O dan Zn-O terletak masing-masing pada 490 dan 615 cm^{-1} yang menunjukkan sampel adalah sangat tulen. Jurang jalur tenaga telah ditentukan dengan spektrum pantulan UV-vis dengan menggunakan fungsi Kubelka - Munk dan jurang tenaga didapati berkurangan dengan peningkatan suhu pengkalsinan dari 4.03 eV pada 773 K kepada 3.89 eV pada 973 K disebabkan saiz zarah meningkat. Sifat-sifat magnet diukur dengan ESR mengesahkan kewujudan elektron berpasangan dan medan magnet salunan dan faktor-g sampel telah diukur. Didapati masing-masing faktor-g telah meningkatkan dari 1,9598 kepada 1,9616 dan medan magnet resonan (Hr) menurun dari $3,3468 \times 10^{-7}$ kepada $3,3437 \times 10^{-7}$ A/m apabila suhu pengkalsinan dinaikkan dari 773 kepada 973 K.



ACKNOWLEDGEMENTS

All praises be to Almighty Allah for his guidance, protection, and for the knowledge bestowed on us, for having successfully completed this research work.

To whom honour is due, they say, it is given. I would like to express my sincere gratitude to my supervisor, Prof. Dr. Elias Bin Saion, for his priceless supervision to research and constant supports to my study at all time. I highly appreciate him for introducing me to scientific research, giving me a chance to accelerate my research skills, and encouraging me to work in the field of nanoscience. His expertise and vision in nanoscience has been the source of inspiration to me for further research in the field. The present research work would, therefore, have never been completed without his proper guidance, regular supervision, and constant encouragement.

I would also like to extend my sincere appreciation to my supervision committee members Prof. Dr. Abdul Halim Shaari and Dr. Mazliana Ahmad Kamaruddin who were ever enthusiastic to give their supports throughout this study. I am grateful to them for their careful and critical reading of my thesis and invaluable suggestions. Their comments and suggestions would not only help to improve my research skill but also would be of great help to me to have deeper insight in future research.

Appreciation is also given to all the staffs of physics department of Faculty Science and Institute of Biological Sciences (IBS) Universiti Putra Malaysia for the assistance and help. I would also like to express my deepest gratitude to all my friends and colleagues, Naif Mohammed Al-Hada, Shyuada Abubakar, Alireza Kharazmi, and Gholamreza Vahedi, amongst others for their cooperation in the laboratory activities. I express my indebtedness to these friends for their encouragement to complete this work.

There can be no adequate acknowledgement for the loving encouragement I have received from my parents, brothers and sisters and all family members. Without their constant support and inspirations all this would never have been possible.

March 2014

I certify that an Examination Committee has met on _____ to conduct the final examination of Adamu Salahudeen Gene on his Master thesis entitled " Structural, Optical and Magnetic Characterization of Spinel Zinc Chromite ($ZnCr_2O_4$) Nanocrystals Synthesized by 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 Master of Science.

Members of the Examination Committee were as follows:

Prof. Madya Dr. Zulkifly B. Abbas

Physics Department
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Prof. Madya Dr. Halimah Bt. Mohamed Kamari

Physics Department
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Dr. Khamirul Amin B. Matori

Physics Department
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Y. Bhg. Prof. Dr. Yussof Wahab

Utm Razak Sekolah Kejuruteraan dan Teknologi
Termaju
Universiti Teknologi Malaysia
(External Examiner)

Zulkarnain Zainal, PhD

Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia
Date: March 2014

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

Elias Bin Saion, PhD

Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Abdul Halim Shaari, PhD

Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Mazliana Ahmad Kamaruddin, PhD

Senior lecturer
Faculty of Science
Universiti Putra Malaysia
(Member)

BUJANG BIN KIM HUAT, PhD

Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

DECLARATION

Declaration by graduate student

I hereby confirm that:

- this thesis is my original work;
- quotations, illustrations and citations have been duly referenced;
- this thesis has not been submitted previously or concurrently for any other degree at any other institutions;
- intellectual property from the thesis and copyright of thesis are fully-owned by Universiti Putra Malaysia, as according to the Universiti Putra Malaysia (Research) Rules 2012;
- written permission must be obtained from supervisor and the office of Deputy Vice-Chancellor (Research and Innovation) before thesis is published (in the form of written, printed or in electronic form) including books, journals, modules, proceedings, popular writings, seminar papers, manuscripts, posters, reports, lecture notes, learning modules or any other materials as stated in the Universiti Putra Malaysia (Research) Rules 2012;
- there is no plagiarism or data falsification/fabrication in the thesis, and scholarly integrity is upheld as according to the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) and the Universiti Putra Malaysia (Research) Rules 2012. The thesis has undergone plagiarism detection software.

Signature: _____ Date: _____

Name and Matric No.: _____

Declaration by Members of Supervisory Committee

This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
- supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) are adhered to.

Signature: _____

Name of Chairman of Supervisory
Committee: _____

Signature: _____

Name of Member of Supervisory
Committee: _____

Signature: _____

Name of Member of Supervisory
Committee: _____

Signature: _____

Name of Member of Supervisory
Committee: _____

TABLE OF CONTENTS

	Page
ABSTRACT	ii
ABSTRAK	iv
ACKNOWLEDGEMENTS	vi
APPROVAL	vii
DECLARATION	ix
LIST OF TABLES	xv
LIST OF FIGURES	xviii
LIST OF SYMBOLS	xix
ABBREVIATIONS	xix
CHAPTER	
1 INTRODUCTION	1
1.1 Introduction of Nanoscience and nanotechnology	1
1.2 Size Effect in nanomaterials	2
1.3 Magnetic metal nanoparticles	3
1.4 Problem statement	5
1.5 Significance of the study	5
1.6 Objectives of the study	6
1.7 Thesis outline	6
2 LITERATURE REVIEW	7
2.1 Chromites	7
2.2. Spinel structure	7
2.2.1 Normal Spinel	9
2.2.2 Inverse Spinel	9
2.2.3 Mixed Spinel	10
2.3 Applications of chromite spinels	11
2.4 Established Methods for Synthesis of nanocrystallines spinels	12
2.4.1 Combustion Method	12
2.4.2 Sol-gel Method	13
2.4.3 Microwave Method	13
2.4.4 Co-Precipitation Method	14
2.4.5 Hydrothermal Method	14
2.4.6 Ball Milling Method (Mechanical method)	14
2.4.7 Microemulssion Method.	15
2.4.8 Chemical Method	15
2.4.9 Spray Pyrolysis Method.	16

3	THEORY	17
3.1	Introduction	17
3.2	Optical properties of material.	17
3.2.1	Optical absorption	17
3.2.2	Quantum size effect	18
3.2.3	Optical band gap	19
3.3	Physical origin of magnetism	20
3.3.1	The Bohr Theory of Magnetism and Spin Moment	21
3.3.2	Magnetic Field and Magnetic Moment	22
3.3.3	Magnetic Behaviors	23
3.3.4	Domains	27
3.4	Electron spin resonance spectroscopy (ESR)	29
3.4.1	The essence of EPR	29
3.4.2	The Hyperfine Interaction	31
3.4.3	The Dipole-Dipole Interaction	32
4	METHODOLOGY AND EXPERIMENTAL	33
4.1	Introduction	33
4.2	Materials	33
4.3	Experimental procedure	33
4.3.1	Calcination process	35
4.4	Characterization	35
4.4.1	Thermogravimetry analysis (TGA)	36
4.4.2	X-ray diffraction spectroscopy (XRD)	36
4.4.3	Fourier transform infrared spectroscopy (FT-IR)	37
4.4.4	Transmission electron microscopy (TEM)	39
4.4.5	Energy dispersive X-ray spectroscopy (EDX)	40
4.4.6	Ultra violet visible spectrometer (UV-vis.)	40
4.4.7	Electron spin resonance spectroscopy (ESR).	42
5	RESULTS AND DISCUSSION	43
5.1	Introduction	43
5.2	Calcination of PVP at high temperature range	43
5.3	EDX analysis of zinc chromite ($ZnCr_2O_4$) nanoparticles	44
5.4	FT-IR spectra of zinc chromite ($ZnCr_2O_4$) nanoparticles	46
5.5	XRD patterns of zinc chromite ($ZnCr_2O_4$) nanoparticles	53
5.6	TEM Images of zinc chromite ($ZnCr_2O_4$) nanoparticles	55
5.7	UV-vis reflectance spectra of zinc chromite ($ZnCr_2O_4$) nanoparticles	57
5.8	Band gap energy of zinc chromite ($ZnCr_2O_4$) nanoparticles	56
5.9	EPR measurements of zinc chromite ($ZnCr_2O_4$) nanoparticles	60

5.10	Mechanism of interaction of PVP and metal ions in the formation of zinc chromite nanocrystals by thermal treatment method	63
6	CONCLUSSIONS AND FUTURE WORK	64
6.1	Conclusions	64
6.2	Future work	66
	REFERENCES	67
	APPENDICES	72
	BIODATA OF STUDENT	74
	LIST OF SUBMITTED ARTICLES	75
	LIST OF PROCEEDINGS	75
	LIST OF CONFERENCES ATTENDED	75

LIST OF TABLES

Table		Page
5.1	The atomic composition of ZnCr_2O_4 for sample calcined at 973 K	45
5.2	FT-IR absorption features and their assignments	53
5.3	The average particle size of zinc chromite measured by XRD and TEM compared with the band gap energy for samples calcined at 773, 823, 873, 923 and 973 K	57
5.4	Magnetic parameters of ZnCr_2O_4 observed for ESR analysis	62



LIST OF FIGURE

Figure		Page
1.1	The percentage of atoms in bulk and on surface as a function of particle size.	3
2.1	Schematic of two sub cells of a unit cell of the spinel structure, showing octahedral and tetrahedral sites.	8
2.2	Interionic distances in the spinel structure for the different types of lattice site interactions.	8
2.3	Cation distributions in normal spinels.	9
2.4	Cation distribution in inversed spinels.	10
2.5	Cation distributions in mixed spinels.	10
3.1	Schematic illustration of dependence of band gap to the size of quantum dot.	18
3.2	Schematic illustration of the sequence of direct and indirect electronic transitions from the initial state i to the final state f , which are photo-excited in the substrate.	20
3.3	Orbit of a spinning electron about the nucleus of an atom	21
3.4	Classical and quantum origins of magnetism.	22
3.5	Atomic dipole configurations for a diamagnetic material.	23
3.6	Atomic dipole configuration for a paramagnetic material.	25
3.7	Atomic dipole configurations for (a) ferromagnetic and (b) ferromagnetic material.	25
3.8	Atomic dipole configuration for an antiferromagnetic material.	25
3.9	Atomic dipole configuration for a super paramagnetic material.	26
3.10	Qualitative illustration of the behavior of the coercivity in ultrafine systems as the particle size changes, where H is the magnetic field amplitude (Oe) and D is the particle diameter (nm).	28
3.11	Splitting of the energy levels of an electron spin subjected to a magnetic field with corresponding resonance frequencies.	30
3.12	Splitting of the ESR line in Cr^{3+} owing to hyperfine interaction.	32
4.1	Schematic diagram of the process of synthesis of spinel nanoparticles by thermal treatment method.	34
4.2	Schematic diagram of X-ray Diffractometer.	37
4.3	Schematic diagram of FT-IR instrument	39
4.4	Schematic diagram of TEM	39
4.5	Schematic diagram for the principle of UV-visible spectroscopy and steps of taking the spectra.	41
5.1	The thermogravimetry (TG) and thermogravimetry derivative (DTG) curves for PVP.	44
5.2	EDX pattern of $ZnCr_2O_4$ for sample calcined at 973 K.	45
5.3 (a)	FT-IR spectra of precursor before calcination.	47
5.3 (b)	FT-IR spectrum of samples after calcination at temperature 773 K.	48

5.3 (c)	The FT-IR spectrum of samples after calcination at temperature 823 K.	49
5.3 (d)	FT-IR spectrum of samples after calcination at temperature 873 K.	50
5.3 (e)	FT-IR spectrum of samples after calcination at temperature 923 K.	51
5.3 (f)	FT-IR spectrum of sample after calcination at temperature of 973 K.	52
5.4	XRD patterns for ZnCr ₂ O ₄ powders calcined at temperatures of 773, 823, 873, 923 and 973 K.	55
5.5	TEM image and particle size distribution of samples calcined at (a) 773, (b) 823, (c) 873, (d) 923 and (e) 973 K.	56
5.6	Reflectance spectra of the nanocrystals calcined at temperature 773, 823, 873, 923 and 973 K	58
5.7	Plot of the square of Kubelka–Munk function $F(R)^2$ vs. Energy (a) 773, (b) 823, (c) 873, (d) 923 and (e) 973 K.	59
5.8	The electron spin resonance spectrum of ZnCr ₂ O ₄ calcined at (a) 773, (b) 823, (c) 873, (d) 923 and (e) 973 K.	61
5.9	The mechanism of interactions between PVP and metal ions in the formation of chromite nanocrystals.	64

LIST OF SYMBOLS

H	Applied field
H_r	Resonant magnetic field
Pa	Pascal
K	Kelvin degree
Φ	Magnetic flux
A/m	Ampere per meter
μ_B	Bohr magnetron
f	Frequency
Fd3m	Space group in cubic structure
X	Susceptibility
ΔH_{pp}	Peak-to-peak line width
H_{hrf}	Hyperfine spine interaction Hamiltonian
g-factor	Gromagnetic ratio
h	plank constant
Zn	Zinc
Cr	Chromium
eV	Electron volt
$^{\circ}\text{C}$	Degree Celsius
a	Lattice parameter

LIST OF ABBREVIATIONS

EDTA	Ethylenediaminetetraacetic acid
ESR	Electron spin resonance
FTIR	Fourier transform infrared
KM	Kubelka–Munk
PVP	Poly(vinyl pyrrolidone)
TEM	Transmission electron microscopy
TGA	Thermo gravimetric analysis
UV-vis	Ultraviolet visible
XRD	X-ray diffraction



CHAPTER 1

INTRODUCTION

1.1 Introduction of Nanoscience and nanotechnology

An historic talk was given by Richard P. Feynman on December 1959 at the annual meeting held by the American Physical Society at the California Institute of Technology, which was titled "There is plenty of room at the bottom...". He introduced the idea of "NANO" for first time, when he stated that "I would like to describe a field, in which little has been done, but in which an enormous amount can be done in principle." Professor Feynman in his speech also emphasize on the enormous number of technical applications of this new field.

Professor Norio Taniguchi from Tokyo Science University firstly defined Nanotechnology in 1974 as "consists of the processing of, separation, consolidation, and deformation of materials by one atom or by one molecule." which leads to the surge in broad study on nanotechnology. Further active development in this field emerged from the first international conferences held in 1990s and as a result, the field has been explored so quickly that some concepts and definitions about nanotechnology have not yet been clarified or settled. Over the past decades, most scientists have agreed on the concept that nanotechnology involves a broad field of applied science and technologies for the fabrication, characterization, manipulation of nanoscaled materials (typically 1 to 100 nm), and as well as the assembly of nonoscale devices. Generally, a nanostructured material can be referred to as materials that have at least one dimension that is less than 100 nm, some examples being atomic clusters, layered films, filamentary structures, and bulk nanostructured materials.

The studies of nanomaterials fall into two fundamental pedagogical themes. They are nanoscience and nanotechnology (Bandaru et al., 2005) . Nanoscience is relevant to the definition of fundamental aspects of nanomaterials including the experimental and theoretical aspect, synthesis and properties of nanomaterials (Krusin-Elbaum et al., 2004) . While nanotechnology is the collective term used for the engineering aspect involved in the manipulation of matter which includes the development, applications and commercial implication materials in nanoscales.

Nanotechnology is inherently a multi-disciplinary field of study which surpasses the conventional boundaries between physics, chemistry, biology, mathematics and engineering (Salata, 2004) . Using these principles, the nanotechnologist deliberately engineer materials at nonoscale to invent products that make use of these remarkable properties. Starting from nanoscaled structures, scientists restructure them and then assemble functional systems that can be integrated in to the products with unique properties classified by the size of the materials being developed and used, not by the process being used or product being produced (Drexler, 1986) .

Ever since the concept of nanotechnology was introduced, the nanostructured material, or nanomaterial, has been an area of intense research. The influence of these research efforts to both science and industrial applications has been significant and is still growing. Nanotechnology in itself is a cutting-edge and highly interdisciplinary research field involving disciplines such as applied physics, chemistry, materials science, interface and colloid science, device physics, molecular biology, chemical engineering, mechanical engineering and electrical engineering, to name a few (Yang, 2009). Nanotechnology, therefore, can be regarded as an extension of the existing sciences into nonoscale, or as a recasting of existing sciences using a newer, more modern term.

Synthesis and characterization of nanomaterial both play extremely important roles in nanomaterial development and research. In terms of producing nanomaterials, there are two major approaches for assembling nanomaterials, the top-down and the bottom-up. The top-down approach technique is where nanomaterials are constructed from large size objects without molecule level control (Yang, 2009). The bottom-up approach is the technique where materials and devices are built from a few molecule components by chemical self-assembling in solution into functional superstructures (Yang, 2009). The top-down approach is mostly used in industry because of its simplicity and short processing time, however, when it comes to less than 100 nm nanomaterials, production costs and time rise greatly. Other drawbacks include limited control of morphology and huge defects on the surfaces of nanomaterials. Consequently, the "bottom-up" approach has become the alternative approach being actively investigated.

1.2 Size Effect in nanomaterials

Nanomaterials have drawn a lot of attention from researchers around the world over the years, because of the "quantum size effect" phenomenon: When the size of the bulk material is reduced to nano-scale, the chemical, physical, optical, and electronic properties differ a lot from those in the bulk size. Conventionally, the chemical composition and crystal structure of a bulk size solid material determines most of the chemical and physical properties. As the surface atoms on the bulk-sized material account for only a fraction of total atoms, they play a negligible role in most bulk properties of the material. When the particle size decreases into nano-scale, the surface atoms account for a greater proportion of the total and are no longer negligible. It is important to note that the interactions between the external media and surface atoms, under certain situations, can dramatically affect reactions such as catalysis and crystal growth on either bulk or nonoscale materials. Figure 1 illustrates that surface atom proportion increases significantly when the particle size is less than 20 nm.

The dramatic increase of surface atom percentage in total atoms leads to the appearance of new chemical and physical properties of nanoparticles such as the emergence of catalytic ability, featured optical spectra, and a change of magnetization.

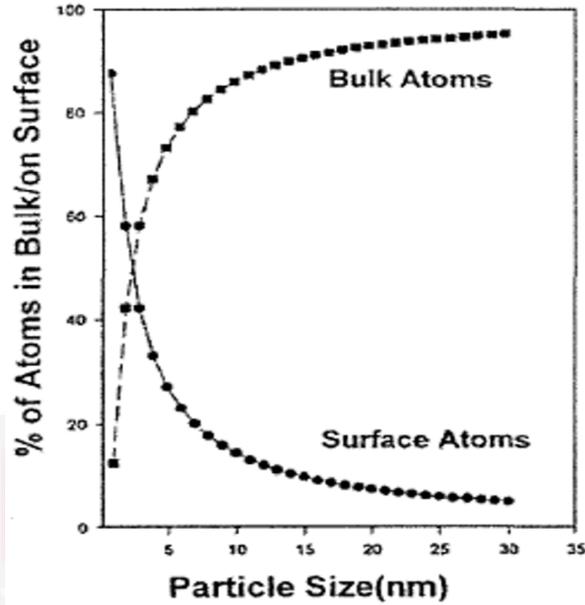


Figure 1.1: The percentage of atoms in bulk and on surface as a function of particle size (Fuller, 2002).

Greater surface area exposes more atoms to the external environment, which changes not only physical properties but also chemical properties of nanoparticles. Surface chemistry is of great importance in the areas of corrosion, catalysis, and absorption. Since most chemical reactions take place in the interface between two phases, larger area of interface raises more chances of contact between reactants, resulting in more active interactions. Thus many reactions, which cannot happen in bulk-sized materials, can now occur in nano-sized materials.

In summary, the increase of surface area, or more surface atoms, makes NPs more reactive and sensitive to outer environment, leading to unique potential applications and market needs that can't be met from materials in bulk size. These promising applications can be in a wide range of areas including pharmaceutical research and disease detection, genetic study, magnetic storage, solar cells, lithium ion batteries, catalysts, and sensors. Moreover, in the past decade, different disciplines have begun to interact with each other to develop more advanced technologies and cutting edge instruments for advancing nanotechnology. The unusual physical and chemical properties and the huge potential applications are the main driving force behind the explosion in nanomaterials research interest.

1.3 Magnetic metal nanoparticles

Nanoparticles that can be manipulated using magnetic field are referred to as magnetic nanoparticles. The constituent elements of such types of nanoparticles usually consist of magnetic elements or chemical compounds of iron, nickel and cobalt. While nanoparticles are usually 5 – 100 nm (smaller than 1 mm in diameter), the larger microbeads are about 100 – 500 nm in diameter. The magnetic nanoparticles have

been the emphasis of much research recently because they retain attractive properties which has potential applications in catalysis including nanomaterial-based catalysts (Lu et al., 2004) , biomedicine (Gupta and Gupta, 2005) , magnetic resonance imaging (Mornet et al., 2006) , magnetic particle imaging (Gleich and Weizenecker, 2005) , data storage (Virden et al., 2007) , and environmental remediation (Elliott and Zhang, 2001) .

The physical and chemical properties of magnetic nanoparticles largely depend on the synthesis method and chemical structure. At present there are three types of magnetic nanoparticles that are being produced and used; these magnetic nanoparticles are oxides, metallic and metallic with shell (Goodarz 2012). Magnetic nanoparticles are applicable in many branches of science. Some of the utmost applications of magnetic nanoparticles in different branches of science were discussed in this section of the chapter and there applications in physics will be further discussed in chapter two.

Medical diagnostic and treatments: Based on the fact that magnetic nanoparticles are heated when subjected to another magnetic field, magnetic nanoparticles can be used in an experimental treatment of cancer known as the magnetic hyperthermia. Additional possible cancer treatment consists of attaching magnetic nanoparticle to free uncontrolled cancer cell, permitting the cancerous cells to be netted and removed out of the organ. This method of treating cancer has been experimented in the laboratory on mice and it is now been observed in survival studies (Scarberry et al., 2008) .

Magnetic immunoassay (MIA): these is a new form of diagnosing immunoassay using magnetic nanoparticles as tags instead of the usual conventional, enzymes, radioisotopes or fluorescent moieties (Nikitin et al., 2007) . This experiment consists of the binding of precise antibody to its antigen, in which a magnetic tag is attached to one of the element pair. The presences of the magnetic nanoparticles are then identified by a magnetometer and then the magnetic field is measured by the change made in the magnetic field. Then the signal measured by the magnetometer is proportional to the analyzed quantity (for instance the quantity of toxin, virus, bacterial and cardiac markers) in the original sample.

Treating contaminated water: magnetic nanoparticles have a worthy possibility for solving the issues of effective way of treating contaminated water due to the easy separation of magnetic impurities by simply using magnetic nanoparticles with a large surface to area volume ratio, (Koehler et al., 2009) . This technique involves attaching EDTA-like chelates to metal nano-magnets coated carbon which results in a magnetic reagent used for the quick removal of heavy metals in contaminated solutions or water by their magnitude of magnetism or concentration for as low as micrograms per liter.

Chemistry: Magnetic nanoparticles have the potential application as a catalyst or catalyst supports (Schätz et al., 2010) . In chemistry, a catalyst supports are materials, generally solids having a high surface area, in which a catalyst can be attached to it. Reactivity of heterogeneous catalysts takes place at the surface of the atoms. Thus, for maximizing the surface area of a catalyst, great effort is made by dispensing it all over the support. The support itself might be inert or partakes in the catalyst reaction. Examples of supports include different types of silica, carbon and alumina.

Imaging for biomedical purpose: CoPt magnetic nanoparticles are used as MRI contrast agent in transplanting neural stem cells detection (Meng et al., 2011) .

Genetic engineering: magnetic nanoparticles are used for various genetic engineering applications. One of the important uses is in the separation of mRNA. This can be achieved within a short period of time, normally within 15 minutes. Particularly in this application, the magnetic tag is tagged to a poly T tail. The poly A tail of the mRNA will attach to the tag's poly T tail when combined with mRNA and the separation takes place simply by putting a magnet on the side of the tube and pouring out the liquid. This types of magnetic dynabeads are supplied by Invitrogen (Lu et al., 2004) .

1.4 Problem statement

The spinels are class of minerals with general formulation $A^{2+}B_2^{3+}O_4^{2-}$ that crystallizes in the cubic (isometric) crystal system, with the oxide anions arranged in a cubic close-packed lattice. The cations A and B occupy some or all of the tetrahedral and octahedral sites in the lattice. A and B can be divalent, trivalent, or quadrivalent cations, which includes magnesium, zinc, iron, manganese, aluminium, chromium, titanium, and silicon. Although the anion is normally oxygen, the analogous thiospinel structure includes the rest of the chalcogenides.

Various methods has been previously applied for the synthesis of spinels $ZnCr_2O_4$, which includes mechanical activation, chemical method, microwave method, sol-gel method, ball milling method, combustion method, among others. But most of these synthesis methods are difficult to apply on a larger scale of production due to their complicated procedures, longer reaction times, high reaction temperatures, toxic reagents and by-products which are potentially harmful to the environment.

In order to overcome the drawbacks of the previous method of synthesis, we have introduced the thermal treatment method for synthesizing spinel zinc chromite. In this study, we investigated the influence of calcination temperature on the formation of spinel $ZnCr_2O_4$ by thermal treatment method followed by characterization of the physical properties.

1.5 Significance of the study

Spinels and spinel-like materials are attractive subjects of continuous scientific interest and have been deeply investigated in materials sciences, because of their physical-chemical properties and their wide range of applications as a humidity sensor, semiconductors, magnetic materials, catalysts, super hard materials, high temperature ceramics, among others. In particular, zinc chromite ($ZnCr_2O_4$) ceramic spinels are commonly used as catalytic materials, humidity sensors and as magnetic material.

In our opinion, it is time for a broad search for the preparation techniques of spinel nanoparticles. In this study, the synthesis of spinel $ZnCr_2O_4$ nanocrystals by means of thermal treatment method from an aqueous solution containing metal nitrates, poly(vinyl pyrrolidone), and deionized water was described. The solution was dried at 80 °C for 24

h before grinding and calcination at temperatures ranging from 773 to 973 K. This method has the advantages of simplicity, less expensive, no unwanted by-products, and it is environmentally friendly. Possibly this method is employable on a large scale production.

1.6 Objectives of the study

This research work is aimed at synthesizing spinel zinc chromite nanocrystals using the thermal treatment method followed by the characterization of the physical properties of the synthesized nanocrystals. The objectives of this study are listed below:

- i. To synthesize spinel zinc chromite nanocrystals using the thermal treatment method.
- ii. To investigate the influence of calcination temperature on the physical properties (structural, optical and magnetic properties) of spinel zinc chromite nanocrystals synthesized by the thermal treatment method.
- iii. To study the influence of calcination temperature on the formation of spinel zinc chromite nanocrystals synthesized by the thermal treatment method.

1.7 Thesis outline

Synthesis and characterization of zinc chromite nanocrystals by thermal treatment method is the main feature of evaluation in this thesis. Summary of nanoscience and nanotechnology in addition to the statement of problem, significance of the study and study objectives were stated in Chapter one. A brief discussion on the general background of spinel nanoparticles and common preparation and synthesizing methods presented in Chapter 2. While in Chapter 3, the optical properties of materials and the theoretical background of magnetic materials such as the magnetic field, magnetic momentum and magnetic behavior were discussed. The detailed clarification of the procedures involved in the synthesis of spinel zinc chromite nanocrystals by the thermal treatment method are explained in Chapter 4. The results and discussion for every characterization measurement including the thermogravimetry analysis (TGA), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), ultra violet visible spectroscopy (UV-vis.) and electron spin resonance (ESR) techniques were explained in Chapter 5. The summary and conclusions of the research work with suggestions for future work are given in Chapter 6. In the last section of the thesis, list of references, list of publications and conferences by the author were presented.

REFERENCES

- Atwater, H. A. (1962). Introduction to microwave theory. McGraw-Hill.
- Bandaru, P. R., Chiara D., Sungho J., and Rao A. M. (2005). "Novel Electrical Switching Behaviour and Logic in Carbon Nanotube Y-Junctions." *Nature materials* 4, no. 9: 663-66.
- Bangale, S. V., and Sambhaji R. B. (2011). "Preparation, Wetability and Electrical Properties of Nanocrystalline ZnCr₂O₄ Oxide by Combustion Route." *Archives of Applied Science Research* 3, no. 4: 300-08.
- Bayhan, M., Hashemi T., and Brinkman A. W. (1997). "Sintering and Humidity-Sensitive Behaviour of the ZnCr₂O₄-K₂Cr₂O₇ Ceramic System." [In English]. *Journal of Materials Science* 32, no. 24 (1997/12/01 1997): 6619-23.
- Bhargava, R., Prashant K. S., Amit K. C., Sanjeev K., Ramesh C., Avinash C. P., and Naresh K. (2011). "Variation in Structural, Optical and Magnetic Properties of Zn_{1-x}Cr_xO (x = 0.0, 0.10, 0.15, and 0.20) Nanoparticles: Role of Dopant Concentration on Non-Saturation of Magnetization." *Materials Chemistry and Physics* 125, no. 3: 664-71.
- Bleaney, B. and Abragam, A. (1970). EPR of transition ions.
- Bozorth, R. M. (1993). Ferromagnetism. *Ferromagnetism*, by Richard M. Bozorth, pp. 992. ISBN 0-7803-1032-2. Wiley-VCH, August 1993., 1.
- Bradford, M. C. J., Mahesh V. K., and Digna X. F. (2003). "Preparation, Characterization and Application of Cr₂O₃/ZnO Catalysts for Methanol Synthesis." *Fuel processing technology* 83, no. 1: 11-25.
- Brus, L. E. (1984). Electron-electron and electron-hole interactions in small semiconductor crystallites: The size dependence of the lowest excited electronic state. *The Journal of chemical physics*, 80(9), 4403-4409.
- Callister, W. (2003). Materials science and engineering an introduction. Sixth ed. New York: John Wiley & Sons, Inc.
- Chen, Z., Shi, E., Zheng, Y., Li, W., Wu, N., & Zhong, W. (2002). Synthesis of mono-dispersed ZnAl₂O₄ powders under hydrothermal conditions. *Materials Letters*, 56(4), 601-605.
- Drexler, K. E. (1986). "Engines of Creation, Anchor." *Garden City*.
- Elliott, D. W., and Wei-Xian Z. (2001). "Field Assessment of Nanoscale Bimetallic Particles for Groundwater Treatment." *Environmental Science & Technology* 35, no. 24: 4922-26.
- Esparza, I., Myriam P., Roberto M., Adriana G., Guadalupe S. L., Luisa M. F., and Octavio D. (2011). "Solid State Reactions in Cr₂O₃-ZnO Nanoparticles Synthesized by Triethanolamine Chemical Precipitation." *Materials Sciences and Applications* 2, no. 11: 1584-92.
- Fuller, S. B., Wilhelm, E. J., & Jacobson, J. M. (2002). Ink-jet printed nanoparticle microelectromechanical systems. *Microelectromechanical Systems, Journal of*, 11(1), 54-60.
- George, M., Asha M. J., Swapna S. N., Joy P. A., and Anantharaman M. R. (2006). "Finite Size Effects on the Structural and Magnetic Properties of Sol-Gel Synthesized NiFe₂O₄ Powders." *Journal of Magnetism and Magnetic Materials* 302, no. 1: 190-95.

- Ghosh, G., Milan K. N., Amitava P., and Minati C. (2006). "Synthesis and Characterization of Pvp-Encapsulated Zns Nanoparticles." *Optical Materials* 28, no. 8: 1047-53.
- Gleich, B., and Jürgen W. (2005). "Tomographic Imaging Using the Nonlinear Response of Magnetic Particles." *Nature* 435, no. 7046: 1214-17.
- Goldman, A. (1990). *Modern ferrite technology*. Van Nostrand Reinhold, New York.
- Goodarz N. M., Elias B. S., and Ahmad K.i. (2012). "An Overview on Nanocrystalline Znfe₂o₄, Mnfe₂o₄, and Cofe₂o₄ Synthesized by a Thermal Treatment Method." *ISRN Nanotechnology* 2012: 11.
- Gupta, A. K., and Mona G. (2005). "Synthesis and Surface Engineering of Iron Oxide Nanoparticles for Biomedical Applications." *Biomaterials* 26, no. 18: 3995-4021.
- Jenkins, A., & Stephens, P. W. (1991). *U.S. Patent No. 5,007,072*. Washington, DC: U.S. Patent and Trademark Office.
- Koebel, M. M., Louis C. J., and Gabor A. S. (2008). "Preparation of Size-Tunable, Highly Monodisperse Pvp-Protected Pt-Nanoparticles by Seed-Mediated Growth." *Journal of Nanoparticle Research* 10, no. 6: 1063-69.
- Koehler, F. M., Michael R., Markus W., Evangelos K. A., Ludwig K. L., Robert N. G., Detlef G., and Wendelin J. S. (2009). "Magnetic Edta: Coupling Heavy Metal Chelators to Metal Nanomagnets for Rapid Removal of Cadmium, Lead and Copper from Contaminated Water." *Chemical Communications*, no. 32: 4862-64.
- Krusin-E. L., Newns D. M, Zeng H., Derycke V., Sun J. Z., and Sandstrom R. (2004). "Room-Temperature Ferromagnetic Nanotubes Controlled by Electron or Hole Doping." *Nature* 431, no. 7009: 672-76.
- Kumar, S. V., Musturappa T. E., Prasannakumar S., Mahadevan K. M., and Sherigara B. S. (2007). "N-Vinylpyrrolidone and Ethoxyethyl Methacrylate Copolymer: Synthesis, Characterization and Reactivity Ratios." *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry* 44, no. 11: 1161-69.
- Lau, C., and Yongli M. (2002). "A Study of Blending and Complexation of Poly (Acrylic Acid)/Poly (Vinyl Pyrrolidone)." *Polymer* 43, no. 3: 823-29.
- Li, H., Wu, H., and Xi, G. (2010). Effects of synthetic conditions on particle size and magnetic properties of NiFe₂O₄. *Powder Technology*, 198(1): 157-166.
- Loría-Bastarrachea, M. I., Herrera, K. W., Cauch-Rodríguez J.V., Cervantes-Uc, J.M., Vázquez, T. H., and Ávila, O. A. (2011). "A Tg/Ftir Study on the Thermal Degradation of Poly (Vinyl Pyrrolidone)." *Journal of thermal analysis and calorimetry* 104, no. 2: 737-42.
- Lu, A. H., Wolfgang S., Nina M., Helmut B., Bernd S., Bernd T., Eckhard B., Wolfgang K., and Ferdi S. (2004). "Nanoengineering of a Magnetically Separable Hydrogenation Catalyst." *Angewandte Chemie* 116, no. 33: 4403-06.
- Maaz, K, Karim S., Mumtaz A., Hasanain S. K., Liu J., and Duan J. L. (2009). "Synthesis and Magnetic Characterization of Nickel Ferrite Nanoparticles Prepared by Co-Precipitation Route." *Journal of Magnetism and Magnetic Materials* 321, no. 12: 1838-42.
- Mančić, L. T., Zorica V. M., Vulić P., and Olivera B. M. (2004). "The Synthesis: Structure Relationship in the ZnO-Cr₂O₃ System." *Science of Sintering* 36, no. 3: 189-96.

- Marinković Z. V., Romčević N., and Stojanović B. (2007). "Spectroscopic Study of Spinel $ZnCr_2O_4$ Obtained from Mechanically Activated $ZnO-Cr_2O_3$ Mixtures." *Journal of the European Ceramic Society* 27, no. 2–3: 903-07.
- Marinković, Z. V., Mančić L., Marić R., and Milošević O. (2001). "Preparation of Nanostructured Zn–Cr–O Spinel Powders by Ultrasonic Spray Pyrolysis." *Journal of the European Ceramic Society* 21, no. 10–11: 2051-55.
- Mathew, G., John, A. M., Nair, S. S., Joy, P. A., and Anantharaman, M. R. (2006). Finite size effects on the structural and magnetic properties of sol-gel synthesized $NiFe_2O_4$ powders. *Journal of Magnetism and Magnetic Materials*, 302(1): 190-195.
- Marinković, Z. V., Mančić L., Vulić P., and Milošević O. (2005). "Microstructural Characterization of Mechanically Activated $ZnO-Cr_2O_3$ System." *Journal of the European Ceramic Society* 25, no. 12: 2081-84.
- Meng, X., Hugh C. S., Le T. L., Ian A. P., Nguyen T. K. T., and Bing S. (2011). "Magnetic Copt Nanoparticles as Mri Contrast Agent for Transplanted Neural Stem Cells Detection." *nanoscale* 3, no. 3: 977-84.
- Mornet, S., Sébastien V., Fabien G., Veverka P., Graziella G., Alain D., Josik P., Pollert E., and Etienne D. (2006). "Magnetic Nanoparticle Design for Medical Applications." *Progress in Solid State Chemistry* 34, no. 2: 237-47.
- Mott, N. F., and Davis E. A. (2012). *Electronic Processes in Non-Crystalline Materials* [in English]. Oxford: Oxford University Press.
- Nabiyouni G., Jafari F. M., Mozafari M. and Amighian J. (2010). Characterization and Magnetic Properties of Nickel Ferrite Nanoparticles Prepared by Ball Milling Technique. *Chinese Phys. Lett.* 27 126401.
- Naseri, M. G., Elias B. S., Hossein A. A., and Abdul Halim S. (2013). "Fabrication, Characterization, and Magnetic Properties of Copper Ferrite Nanoparticles Prepared by a Simple, Thermal-Treatment Method." *Materials Research Bulletin* 48, no. 4: 1439-46.
- Nikitin, P. I., Vetoshko P. M., and Ksenevich T. I. (2007). "Magnetic Immunoassays." *Sensor Letters* 5, no. 1: 296-99.
- Pankove, J. I. (1976). *Optical Processes in Semiconductors* [in English]. New York; London: Dover Publications [etc.] ; Constable.
- Parhi, P., and Manivannan V. (2008). "Microwave Metathetic Approach for the Synthesis and Characterization of $ZnCr_2O_4$." *Journal of the European Ceramic Society* 28, no. 8: 1665-70.
- Ponti, J., Sabbioni, E., Munaro, B., Broggi, F., Marmorato, P., Franchini, F., ... & Rossi, F. (2009). Genotoxicity and morphological transformation induced by cobalt nanoparticles and cobalt chloride: an in vitro study in Balb/3T3 mouse fibroblasts. *Mutagenesis*, 24(5), 439-445.
- Poole, C. P. (1967). *Electron spin resonance*, Interscience publishers.
- Pokhrel, S., & Nagaraja, K. S. (2003). Electrical and humidity sensing properties of Chromium (III) oxide–tungsten (VI) oxide composites. *Sensors and Actuators B: Chemical*, 92(1), 144-150.
- Qu, Y., Haibin Y., Nan Y., Yuzun F., Hongyang Z., and Guangtian Z. (2006). "The Effect of Reaction Temperature on the Particle Size, Structure and Magnetic Properties of Coprecipitated $CoFe_2O_4$ Nanoparticles." *Materials Letters* 60, no. 29–30: 3548-52.

- Rossetti, R., Nakahara, S., & Brus, L. E. (1983). Quantum size effects in the redox potentials, resonance Raman spectra, and electronic spectra of CdS crystallites in aqueous solution. *The Journal of Chemical Physics*, 79(2), 1086-1088.
- Saion, E., and Elham G. (2011). "On the Theory of Metal Nanoparticles Based on Quantum Mechanical Calculation." *Malaysian Journal of Fundamental and Applied Sciences* 7, no. 1.
- Salata, O. V. (2004). "Applications of Nanoparticles in Biology and Medicine." *Journal of nanobiotechnology* 2, no. 1: 3.
- Scarberry, K. E., Erin B. D., John F. M., and John Z. (2008). "Magnetic Nanoparticle–Peptide Conjugates for in Vitro and in Vivo Targeting and Extraction of Cancer Cells." *Journal of the American Chemical Society* 130, no. 31: 10258-62.
- Schätz, A., Oliver R., and Wendelin J. S. (2010). "Nanoparticles as Semi-Heterogeneous Catalyst Supports." *Chemistry-A European Journal* 16, no. 30: 8950-67.
- Silva, M. F, da Silva C. A, Fogo F. C, Pineda E. A. G, and Anita A.W., H. (2005). "Thermal and Ftir Study of Polyvinylpyrrolidone/Lignin Blends." *Journal of thermal analysis and calorimetry* 79, no. 2: 367-70.
- Slayter, E. M. (1992). *Light and electron microscopy*. Cambridge University Press
- Smith, R. A. (1978). *Semiconductors* second edit. Cambridge University Press.
- Spaldin, N. (2003). *Magnetic materials. Fundamental and device applications*. Cambridge: Cambridge University Press.
- Stefanescu, M., Mirela B., Titus V., Paul B., Lucian B. T., and Marcela S. (2011). "Novel Low Temperature Synthesis Method for Nanocrystalline Zinc and Magnesium Chromites." *Thermochimica Acta* 526, no. 1–2: 130-36.
- Stoner, E. C., and Wohlfarth, E. P. (1948). A mechanism of magnetic hysteresis in heterogeneous alloys. *IEEE Transactions on Magnetics*, 27 (4): 3475-3518.
- Sui, Y., Xinfan H., Zhongyuan M., Wei L., Feng Q., Kai C., and Kunji C. (2003). "The Effect of Thermal Annealing on Crystallization in a-Si: H/SiO₂ Multilayers by Using Layer by Layer Plasma Oxidation." *Journal of Physics: Condensed Matter* 15, no. 34: 5793.
- Syuada A. (2013). *Synthesis and caharacterization of MCr2O4 (M= Ni, Co) by thermal treatment method*. (Master thesis).
- Tartaj, P., Maria, P. M., Sabino V. V., Teresita G. C., and Carlos J. S. (2003). "The Preparation of Magnetic Nanoparticles for Applications in Biomedicine." *Journal of Physics D: Applied Physics* 36, no. 13: R182.
- Tauc, J. (1974). *Amorphous and Liquid Semiconductors* [in English]. London: Plenum Press.
- Uhlenbeck, G. E., & Goudsmit, S. (1926). Spinning electrons and the structure of spectra. *Nature*, 117, 264-265.
- Venugopal, A., Reema S., Chatla A., Vankudoth K., and Mandari K. K. (2012). "Synthesize 2-Methylpyrazine Using Aqueous Glycerol and Ethylenediamine over Zinc Oxide-Zinc Chromite Catalysts: Structure Activity Relationship." *Applied Catalysis A: General*.
- Virden, A., Wells S., andGrady K. O. (2007). "Physical and Magnetic Properties of Highly Anisotropic Cobalt Ferrite Particles." *Journal of Magnetism and Magnetic Materials* 316, no. 2: e768-e71.

- Wan, X., Ashvin V., and Sergey Y. S. (2012). "Computational Design of Axion Insulators Based on 5 D Spinel Compounds." *Physical review letters* 108, no. 14: 146601.
- White, A. D. (2006). *High pressure study of spinel chromite* (Doctoral dissertation)
- Yamasaki, Y., Miyasaka, S., Kaneko, Y., He, J.-P., Arima, T., Tokura, Y. (2013). Magnetic reversal of the ferroelectric polarization in a multiferroic spinel oxide. *Phys. Rev. Lett.* **96**, 207204
- Yazdanbakhsh, M., Iman K., Elaheh K. G., and Abbas Y. (2010). "Fabrication of Nanospinel $Zn_{1-x}Co_xO$ Using Sol-Gel Method and Its Application on Removal of Azo Dye from Aqueous Solution." *Journal of Hazardous Materials* 184, no. 1: 684-89.

