UNIVERSITI PUTRA MALAYSIA

SYNTHESIS AND CHARACTERIZATION OF STRUCTURE AND MAGNETIC PROPERTIES OF CHROMITE SPINEL NANOPARTICLES PREPARED BY THERMAL TREATMENT METHOD

SYUHADA BINTI ABU BAKAR

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MASTER OF SCIENCE

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By

SYUHADA BINTI ABU BAKAR

Thesis submitted to the School of Graduate Studies, Universiti Putra Malaysia,

in fulfilment of the requirement for the Degree of Master of Science

July 2013

DEDICATION

I dedicate this thesis from bottom of my heart

to my beloved husband,

family, supervisor and all my dearest friends.

Thanks for your guidance, support,

understanding, caring, love, encouragements

and fulfil my dream.

May ALLAH bless us always.

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

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July 2013

Chairman   **: Prof. Elias Bin Saion, PhD**

Faculty   **: Science**

The simple preparation of fine-particle nickel chromite, cobalt chromite and nickel cobalt chromite nanoparticles have been prepared from an aqueous solution containing respective metal nitrate, chromium (III) nitrate, polyvinyl pyrrolidone (PVP) as a capping agent and deionized water as a solvent. After proper mixing with appropriate amount of precursor concentrations, the mixtures were dried in the oven for 24 hours at temperature of 110°C. The samples were crushed into powder before putting into furnace for thermally treated at various temperatures from 550°C to 950°C. In thermal treatment, the samples undergo crystallization and become metal chromite nanoparticles due to calcination process.

The polymer (PVP) which controls the growth of the nanoparticles by creating a uniform distribution of the particles size and also preventing their agglomeration; were gradually removed from the samples and found completely calcined at temperature of 850°C for $NiCr_2O_4$ and $Ni_{0.5}Co_{0.5}Cr_2O_4$, while for $CoCr_2O_4$ at temperature of 950°C. The synthesized powders were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM) and electron spin resonance (ESR).

X-ray diffraction results for the calcined samples of the $NiCr_2O_4$, $CoCr_2O_4$ and $Ni_{0.5}Co_{0.5}Cr_2O_4$ nanoparticles at different temperatures show the reflection planes of (111), (220), (311), (400), (511) and (440). The main peak were centered at $2\theta = 35.74°$, $35.70°$ and $35.80°$ respectively, corresponds to a crystal plane with Miller indices of (311), which confirm the presence of single-phase $NiCr_2O_4$, $CoCr_2O_4$ and $Ni_{0.5}Co_{0.5}Cr_2O_4$ with face-centered cubic (FCC) spinels. The crystallographic studies of $NiCr_2O_4$, $CoCr_2O_4$ and $Ni_{0.5}Co_{0.5}Cr_2O_4$ show the intensification in crystallinity of the nanoparticles due to the particle size enlargement of the nuclei as the calcination temperature increased. The crystallization of $NiCr_2O_4$, and $Ni_{0.5}Co_{0.5}Cr_2O_4$ were completed at 850°C, whereas for $CoCr_2O_4$ at 950°C, as publicized by the absence of organic absorption band in FT-IR spectra measure in a range of 280-4000 cm^{-1}.

From FT-IR results, the absorption bands of pure $NiCr_2O_4$ spinel nanoparticles were observed at 594 cm^{-1} for Ni-O and 463 cm^{-1} for Cr-O at optimum temperature, 850°C. Whereas, the absorption bands of Co-O were observed at 608 cm^{-1}, 480 cm^{-1} and Cr-O at 376 cm^{-1} for pure $CoCr_2O_4$ nanoparticles at optimum temperature, 950°C.

For pure $Ni_{0.5}Co_{0.5}Cr_2O_4$ nanoparticles, the absorption bands appear at 604 cm^{-1} for Co-O, 478 cm^{-1} for Ni-O and 373 cm^{-1} for Cr-O at optimum temperature, 850°C. The average crystallite size observed from XRD data for $NiCr_2O_4$ (9-63 nm), $CoCr_2O_4$ (10-57 nm) and $Ni_{0.5}Co_{0.5}Cr_2O_4$ (10-51 nm) were found to increase with the calcination temperature as in a good agreement with the results obtained from TEM images. Three parameters namely g-factor, peak-to-peak linewidth (ΔH_{pp}) and magnetic resonance field (H_r) that characterize the magnetic properties of unpaired electron were measured by ESR. All the samples exhibit paramagnetism.

The results show that the values of g-factor and peak-to-peak linewidth (ΔH_{pp}) of the nanoparticles increase with the increase of calcination temperature whereas the magnetic resonance field (H_r) decreases as the calcination temperature increases according to the equation g = $h\nu/\beta H$. TEM results show the cubical spinel chromite nanoparticles prepared by thermal treatment method, were uniform in both morphology and particle size distribution. The average size of the nanoparticles increases from 7 nm to 63 nm for $NiCr_2O_4$, 12 nm to 50 nm for $CoCr_2O_4$ and 10 nm to 51 nm for $Ni_{0.5}Co_{0.5}Cr_2O_4$ when the calcination temperature increases. This advocates that several neighbouring particles fuse together to increase particle sizes by melting their surfaces.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai
memenuhi keperluan untuk Ijazah Master Sains

**SINTESIS DAN PENCIRIAN STRUKTUR SERTA SIFAT-SIFAT MAGNET
PADA PARTIKEL NANO KROMIT SPINEL DISEDIAKAN OLEH
KAEDAH RAWATAN TERMA**

Oleh

SYUHADA BINTI ABU BAKAR

Julai 2013

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Penyediaan mudah bagi sampel nikel kromit, kobalt kromit dan nikel kobalt kromit
bersaiz nano telah disediakan menggunakan larutan akueus yang mengandungi
logam nitrat masing-masing, kromium (III) nitrat, polyvinyl pyrrolidone (PVP)
sebagai agen penutup dan air ternyahion sebagai pelarut. Setelah bahan-bahan kimia
pada kepekatan tertentu ditambah dan disebatikan, larutan dikeringkan di dalam
oven pada suhu 110°C. Sampel kemudiannya dihancurkan menjadi serbuk sebelum
diletakkan di dalam relau untuk rawatan terma pada pelbagai suhu dari 550°C hingga
950°C. Dalam rawatan terma, sampel mengalami pengkristalan sebelum menjadi
zarah nano kromit logam melalui proses pengkalsinan.

Polimer (PVP) yang mengawal pertumbuhan saiz zarah, mewujudkan pengagihan saiz zarah yang seragam dan mencegah pengumpulan zarah telah dinyahkan secara beransur-ansur daripada sampel sehingga dinyahkan sepenuhnya pada suhu 850℃ bagi $NiCr_2O_4$ dan $Ni_{0.5}Co_{0.5}Cr_2O_4$ manakala bagi $CoCr_2O_4$ pada suhu 950℃. Sampel yang telah siap disintesis, telah dicirikan menggunakan pembelauan sinar-x (XRD), jelmaan Fourier inframerah (FT-IR), mikroskop elektron transmisi (TEM) dan putaran resonans elektron (ESR).

Keputusan pembelauan sinar-x untuk sampel $NiCr_2O_4$, $CoCr_2O_4$ dan $Ni_{0.5}Co_{0.5}Cr_2O_4$ pada suhu yang berbeza menunjukkan refleksi (111), (220), (311), (400), (511) dan (440). Puncak utama tertumpu pada $2\theta = 35.74°$, $35.70°$ dan $35.80°$ masing-masing, sepadan dengan satah Kristal dengan indeks Miller (311), yang mengesahkan kehadiran fasa tunggal $NiCr_2O_4$, $CoCr_2O_4$ dan $Ni_{0.5}Co_{0.5}Cr_2O_4$ dengan padu yang berpusat muka (FCC) spinel. Kajian kristalografi daripada sampel $NiCr_2O_4$, $CoCr_2O_4$ dan $Ni_{0.5}Co_{0.5}Cr_2O_4$ menunjukkan pengukuhan dalam kristaliniti zarah nano akibat pembesaran saiz zarah nukleus apabila suhu pengkalsinan meningkat. Kekristalan telah sempurna terjadi pada sampel $NiCr_2O_4$, dan $Ni_{0.5}Co_{0.5}Cr_2O_4$ pada suhu 850°C manakala bagi $CoCr_2O_4$ pada suhu 950°C, seperti yang digambarkan oleh ketiadaan jalur penyerapan bahan organik asing dalam pengukur spektrum FT-IR pada gelombang antara 280-4000cm^{-1}.

Daripada keputusan FT-IR, jalur penyerapan bagi spinel $NiCr_2O_4$ tulen diperhatikan pada jalur 594 cm^{-1} bagi Ni-O dan 463 cm^{-1} bagi Cr-O pada suhu optimum 850℃. Manakala jalur penyerapan $CoCr_2O_4$ tulen bagi Co-O pada jalur 608 cm^{-1} dan 480 cm^{-1} serta Cr-O pada jalur 376 cm^{-1} pada suhu optimum 950℃.

Bagi $Ni_{0.5}Co_{0.5}Cr_2O_4$ pula, jalur penyerapan muncul pada 604 cm^{-1}, 478 cm^{-1} dan 373 cm^{-1} bagi Co-O, Ni-O dan Cr-O masing-masing pada suhu optimum, 850°C. Purata saiz kristal yang diperoleh daripada data XRD menunjukkan peningkatan saiz selari dengan suhu pengkalsinan bagi $NiCr_2O_4$ (9-63 nm), $CoCr_2O_4$ (10-57 nm) dan $Ni_{0.5}Co_{0.5}Cr_2O_4$ (10-51 nm) yang mana sama seperti keputusan yang ditunjukkan oleh imej TEM. Tiga parameter yang mencirikan sifat-sifat magnet bagi elektron berpasangan ialah g-faktor, puncak-ke-puncak lebar (ΔH_{pp}) dan bidang resonans magnet (H_r) telah diukur oleh ESR spektroskopi yang membuktikan semua sampel terbabit bersifat paramagnetik.

Keputusan menunjukkan nilai g-faktor dan nilai puncak-ke-puncak lebar (ΔH_{pp}) bagi sampel $NiCr_2O_4$, $CoCr_2O_4$ dan $Ni_{0.5}Co_{0.5}Cr_2O_4$ meningkat dengan peningkatan suhu pengkalsinan manakala nilai bidang resonans magnet (H_r) menurun mengikut persamaan g = $h\nu/\beta$H. Keputusan TEM menunjukkan saiz zarah nano bagi spinel kromit berkubus dengan seragam dalam morfologi dan taburan zarah. Saiz purata zarah nano meningkat dengan kenaikan suhu pengkalsinan bagi $NiCr_2O_4$, dari 7 nm ke 63 nm, bagi $CoCr_2O_4$ dari 12 nm ke 50 nm dan yang terakhir dan tidak dilupakan, saiz zarah $Ni_{0.5}Co_{0.5}Cr_2O_4$ dari 10 nm ke 51 nm. Ini menyokong pendapat bahawa zarah-zarah yang berjiran bergabung bersama untuk meningkatkan saiz dengan meleburkan permukaan mereka.

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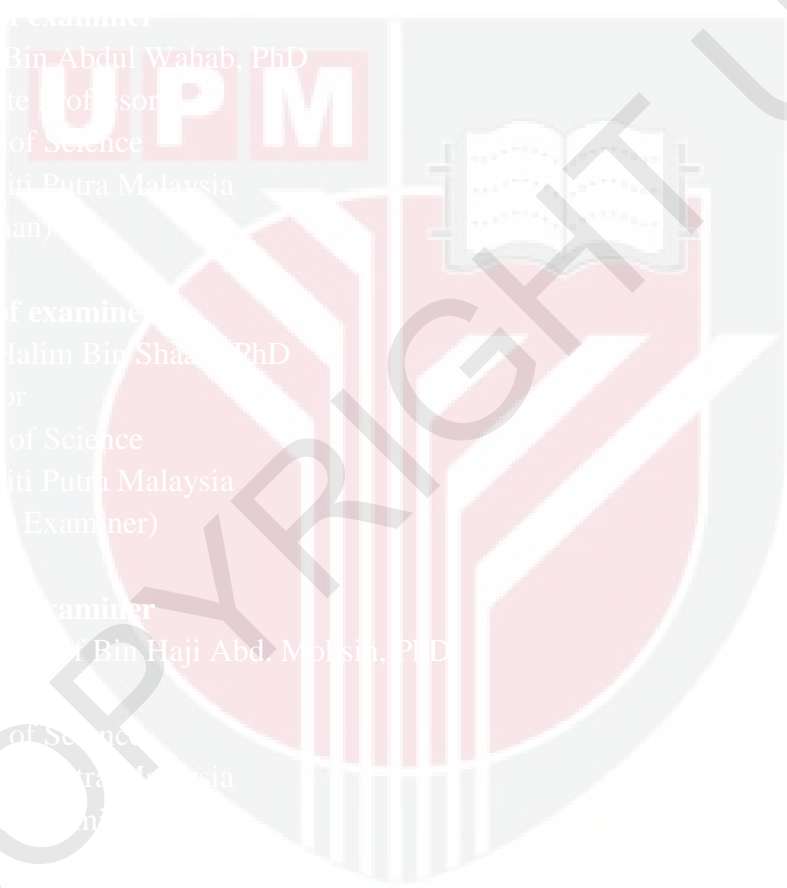
This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisor Committee were as follows:

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DECLARATION

I declare that this thesis is on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or other institutions.

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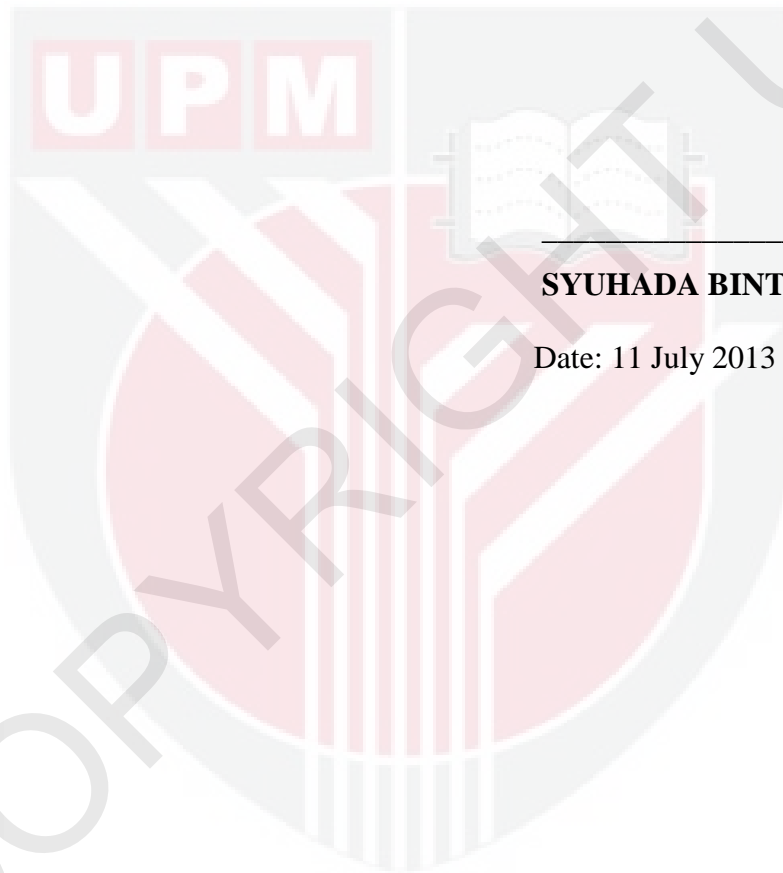
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LIST OF SYMBOLS AND ABBREVIATIONS

XRD	X-Ray Diffraction
FT-IR	Fourier Transform Infrared
TEM	Transmission Electron Microscopy
ESR	Electron Spin Resonance
PVP	Polyvinyl Pyrrolidone
FCC	Face-centered-cubic
IR	Infrared
AEP	Atmospheric Poroellipsometry
AFM	Atomic Force Microscopy
g	Gyromagnetic ratio
μ_B	Electron Bohr Magneton
H_0	Applied magnetic field
M_s	Spin state
DE	Energy difference
h	Planck's constant
v	Frequency of the radiation
H_r	Magnetic field resonance
μ_s	Magnetic moment
r	Electron distant
$Cr(NO_3)_3$	Chromium(III) nitrate
$Ni(NO_3)_2$	Nickel (II) nitrate
$Co(NO_3)_2$	Cobalt (II) nitrate
H_2O	Deionized water
$NiCr_2O_4$	Nickel Chromite

$CoCr_2O_4$	Cobalt Chromite
$NiCoCr_2O_4$	Nickel Cobalt Chromite
Cr_2O_3	Chromium oxide
Ni	Nickel
Co	Cobalt
Cr	Chromium
MW	Molecular weight
Å	Angstrom
d	Inter-planar spacing
ATR	Attenuated total reflection
ΔH_{pp}	Peak-to-peak line width
Fd3m	Space group in cubic structure
χ	Susceptibility
g-factor	Geomagnetic ratio

CHAPTER 1

INTRODUCTION

1.1   Introduction of Nanosized Materials

In nanotechnology, a particle is defined as a small object that behaves as a whole unit in terms of its transport and properties. It was further classified according to size in terms of diameter. Ultrafine particles or nanoparticles have the size between 1 and 100 nanometers. Nanosized materials and their aptitude have revealed up a world of potential with even tiny nanosized particles, making them even more useful for a variety of applications.

The applications of it in a variety of industries and scientific deeds was the focus of much research in the last few years because of nanotechnology are fundamentally a set of techniques that allow the manipulation of properties at very small size. According to Hobbs (2012) from Savannah River National Laboratory (SRNL), by making each particle smaller, the amount of surface area will increase compared to the large volume of the particles. Since the surface of particle where the reaction takes place, it will increase the nanosized material's working area. The large surface-to-volume ratio and quantum size when the size shrinks to the nanoscale will affect the materials to give rise to unique electrical, optical, magnetic, mechanical and chemical properties of the materials.

Furthermore, they can be used in diverse applications such as optoelectronics, sensors, catalysts, medical cures and have been proposed as the building blocks of future electronics. Nanoparticles actually have a very long history although they were generally considered a discovery of modern science. In fact, nanoparticle materials were used since 19th century to spawn the effect on the pot's surface mainly in Mesopotamia (Jessica *et. al.,* 2006).

1.1.1   Synthesis and Processing of Nanopowders.

At present, researchers have found two advances way, which are 'top-down' and 'bottom-up' approaches, in synthesizing and fabricating the nanomaterials and nanostructures in order to developed the potential of nanopowders for technology (Vincent, 2004). The breakings down of bulks materials into nanosized structure of particles are called 'top-down' approach. The 'top-down' approach is one of the techniques that were extension of those who are being used in producing microsized particles such as high-energy ball milling.

The more economical and creating less waste of chemicals is 'bottom-up' approach. Building up materials from the bottom by means of atom, molecule or cluster is referring to 'bottom-up' manner where the techniques are still under development. But, some of them are being practise and used for commercial production of nanopowders; for example thermal treatment method.
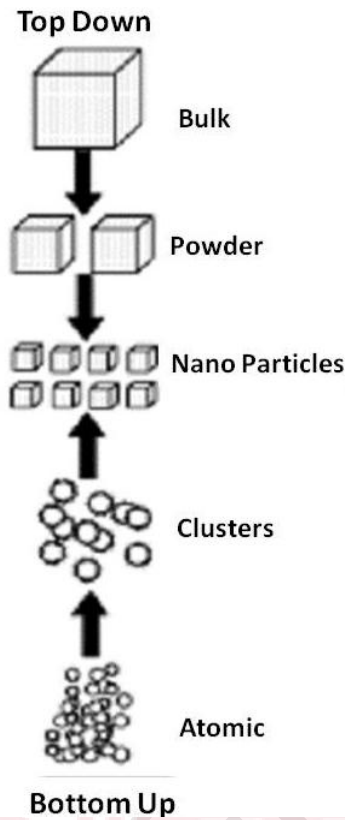
Figure 1.1: Schematic representation of the 'top-down' and 'bottom-up' synthesis processes of nanomaterials

Getting simply a small size is not the only requirement for nanotechnology. They should have identical size of all particles also called mono sized or with distribution and identical shape or morphology. Furthermore, it should have identical chemical composition and crystal structure that are yearning among different particles, for instance core and composition must be the same also should have individually dispersed or mono dispersed or else no agglomeration.

1.1.2 Thermal Treatment Synthesis of Nanopowders

Thermal treatment method is one of the 'bottom-up' approaches to synthesis of nanopowders. Thermal treatment as well as heat-treating is a term used to represent all of the controlled heating and cooling operations performed on a material in the solid state for the intention of altering its nanostructure or properties. A simple thermal treatment method to synthesize transition metal oxide has been introduced for the first time in this laboratory last three years ago. Thermal treatment offer good advantage of producing nanopowders such as high flexibility, constant quality, environmentally friendly process and clean, uniform surfaces and easy to handle (Mahmoud *et. al.,* 2010).

It is important to first understand about fundamental principle of metal structure to fully understand the advantages of heat-treating process. The atoms orient themselves into a repetitive pattern as a molten metal solidifies that we call a crystal structure. Face centered cubic (FCC) is one of the most common crystal structure instead of body centered cubic (BCC) (Herring, 2012). Each of metal has a specific chemical composition hence the structural and physical properties of the different metals will change at crucial temperature when they are respond to treatment at different temperature. By reason of some movement of dislocations or even increasing and decreasing in solubility of atom, it will change the atomic structure or microstructure of the materials. In detail, the formation of new grains of different or same phases, rise in grain size or other mechanisms also change the structure of materials.

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All of the changes in mechanism of the structure are depending on the thermal treatment used. Even 'carbon' as a small percentage of elements in the metal compositions will affect the time, method, temperature and rate of cooling that in the heat treatment process it needs to be used (NDT Resource Center).

1.2   The Spinel Structure

The spinel structure of material have the general composition formula of AB_2O_4, where A is a cation with +2 charges be fond of Mg, Cr, Mn, Fe, Cd, Ni, Cu, Zn, Co, Sn and B is a cation with +3 charges akin to Al, Ga, In, Ni, V, Co, Mn, Fe, Cr, Ti which crystallise in the cubic crystal system. Oxygen atoms in spinel have cubic close-packed structure. It is essentially cubic with the oxygen ions forming a face-centered-cubic (FCC) lattice. Two types of spinel structures at ambient conditions are normal spinels (AB_2O_4) and inverse spinel (B_2AO_4). For normal spinels, the cations (usually metals) occupy only 1/8 of the tetrahedral sites and   one-half of the octahedral sites and there are totally 32-O ions in the unit cell while there are ex-changed places of cations in inverse spinels structure (Jeremy *et. al.,* 1982).

The ideal structure of normal spinels (Figure 1.2) show the divalent A^{2+} ions dwell in the tetrahedral voids, whereas the trivalent B^{3+} reside in the octahedral voids in the close packed arrangement of oxide ions. In the inverse spinels, the A^{2+} ions dwell in the octahedral voids, whereas half of B^{3+} ions reside in the tetrahedral voids. The number of octahedral sites occupied may be efficient or arbitrary therefore leads to defected spinels. The inversion degree (λ) for spinel where only divalent and trivalent cations are present is defined as a fraction of A-sites occupied by trivalent ions (Jeremy *et. al.*, 1982).
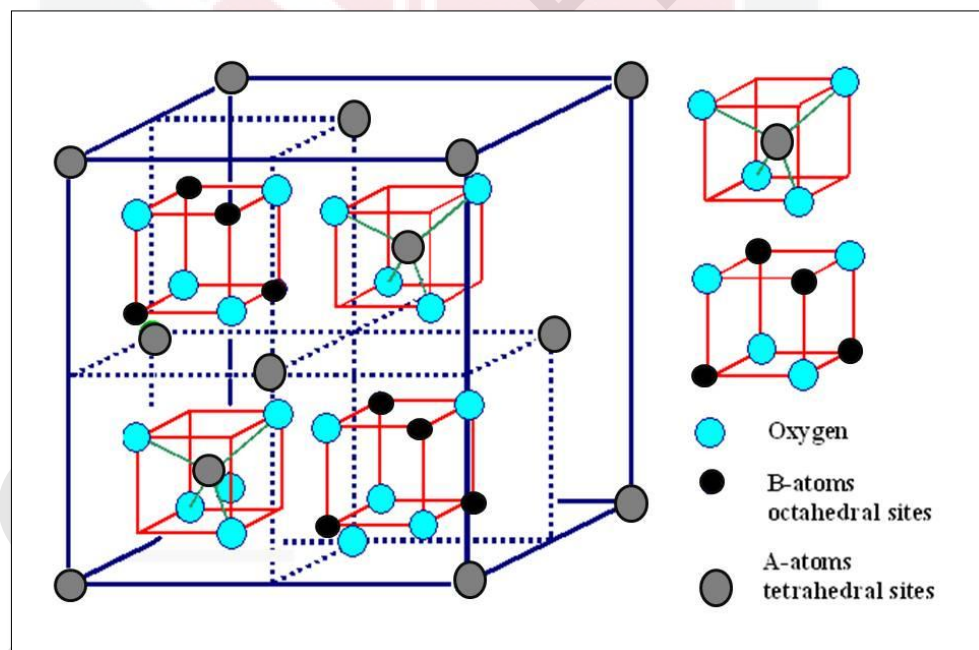
Figure 1.2: The spinel structure.

In the preparation of spinel materials, there are some factors affecting the structure of spinels. For example, the relative size of A and B in tetrahedral and octahedral site where the smaller cation prefers to occupy the site of lower coordination, tetrahedral site. Ligand-field stabilization energies or LFSE would affect the structure of spinels by their relative values of metal ions. In fact, the ion with more LFSE value in octahedral site when compared to LFSE in tetrahedral site leans to occupy octahedral sites (Jeremy *et. al.,* 1982).

Thermal treatment offers a good manner in preparing spinel type material because of their ability to control the movement of the metal ions during heating process. The arrangement of oxygen atom and A^{2+} and B^{3+} ions preserved to occupy either tetrahedral or octahedral site as attest with the work done by Kalendova (1998), Manova *et. al.,* (2006), Mahmoud *et. al.,* (2011) also Yue and Kaimin (2012).

1.2.1   Spinel Structure for Industry and Technology

The spinel structures of material which are binary oxide occur in an abundant industry processes and draw in the earlier substantial consideration and research effort. The catalytic and physical properties of the spinel oxides may be influence by the nature of their distribution in the spinel structure, and not only persuade by the oxidative state of transition metal ions which the intention of the cation distribution in the spinel expands a great significance on their chemical and physical properties.

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Sanghera *et. al.,* (2009) described that the availability of high-optical-quality spinel ceramic in different shapes and sizes makes it an excellent window material for many applications. Spinel ($MgAl_2O_4$) is a cubic crystalline material with a unique combination of ruggedness and excellent transmission from the ultra-violet ($0.2\mu m$) to the mid-infrared ($5\mu m$) region. DDG 1000 destroyer, photonic mast for virginia class submarine, high energy lasers and domes for missile protection system are some of the applications of spinel that being pursued.

Manova *et. al.,* (2006) discussed about the potential of spinel oxides as catalysts for methanol decomposition on supporting the activity of the bulk analogues and carbon materials. They were successfully synthesis the iron and iron-cobalt spinel oxides in nanosized as catalyst by thermal treatment method. They reported that the reaction medium extensively effects the phase transformation of the catalytic and reductive properties of the samples. The reaction medium containing the merging of spinel Fe_3O_4 with cobalt ions and binary metal ferrites formation is a well-defined propensity for increasing the catalytic activity; and the selectivity of CO was found for the cobalt containing spinels as compared with the monocomponent.

Kalendova (1998) reported that the stability of spinel-like compound of pigment in anticorrosive heat-resistant coating, will improve the stability of physicochemical structure and the constancies of colour and application properties of the pigment. The preparation of spinels coating Ca, Zn and Fe cations were allowed by the high-temperature synthesis procedure running in the solid state. The anticorrosive pigments based on the spinels compound are nontoxic and the pigments are suitable for both solvent-type and water-dilutable coating compare to the phosphate-based pigments.

Ahmed *et. al.,* (2011) in their studies were successfully fabricated the refractory ceramics of single phase crystalline cyan $Ni_xMg_{1-x}Al_2O_4$ spinels which was the one of the application of spinel-like structure as being heat resistant pigment. The work was done by using urea as a fuel followed by the low temperature combustion method. Undergoes severe condition of temperature's elevated and chemical attack, the design for colouring enamel and glaze were specially comes from the ceramic pigments as well as thermoresistant pigments. Spinel-type structure would make some modification in physical properties of the resistant pigment with the change of defect in the structure of compound and associated with the dopant cation of the solid solution.

1.3   Problem Statement

Novel routes were recently explored to attain innovative technique for producing nanoparticles. Many of the methods come with some disadvantages for examples difficulty in their preparation and difficult to control either size or size distribution, not being homogenous and sometimes takes a long time period in the furnace. The aim of this current study was to apply a low temperature (below 1000°C) thermal treatment route to synthesis nanosized nickel chromite, cobalt chromite and nickel cobalt chromite spinels and environmentally friendly (lack of by-product effluents). In addition, attempts are made to characterize the structure of nanosized nickel chromite, cobalt chromite and nickel cobalt chromite spinels at different calcination temperature because less attention has been paid to their structure and properties in spite of the importance in applications to the industry such as catalyst and industry of pigment.

1.4   Significance of the Study

The thermal treatment method suggest the advantages of low cost production, simple, comparatively low reaction temperature, an alternative of environmentally friendly and lack of by-product effluents to the mixture solution. It also has significance capability to amend the chemical structure of material resulting in desirable properties such as controlling size of metal nanoparticles.

1.5 Scope of the Present Study

A main goal of this work is to synthesize and characterize the nanosized nickel chromite, cobalt chromite and nickel cobalt chromite spinels by using thermal treatment method. In this research, a low temperature (below 1000°C) thermal treatment route was used to synthesis nanosized nickel chromite, cobalt chromite and nickel cobalt chromite spinels at different calcination temperatures.

1.6 Objectives of the Study

- To synthesize and characterize the nanosized nickel chromite, cobalt chromite and nickel cobalt chromite spinels using thermal treatment method.

- To determine the influences of different calcination temperatures on the structure and properties of prepared nickel chromite, cobalt chromite and nickel cobalt chromite spinels.

1.7 Layout of the Thesis

The synthesis and characterization of nanosized nickel chromite, cobalt chromite and nickel cobalt chromite spinels by thermal treatment method are the core aspect of the study in this thesis. In the beginning, an overview of nanosized material as well as spinel structure arrangement together with problem statement, significance of the study, scope of the present study and objectives of the study are given in chapter 1. Chapter 2 provides the information about chromites and the work done by the previous researchers. Chapter 3 deals with the theory that characterized all the samples in this study. Chapter 4 discussed about the methodology and all materials used. Chapter 5 focuses on the result of synthesized and characterized nanosized nickel chromite, cobalt chromite and nickel cobalt chromite spinels. Last but not least, chapter 6 gives conclusions and some suggestions.

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