UNIVERSITI PUTRA MALAYSIA

MICROSTRUCTURAL, OPTICAL AND MAGNETIC PROPERTIES OF BARIUM HEXAFERRITE AND NICKEL ZINC FERRITE SYNTHESIZED VIA MECHANOCHEMICAL PROCEDURE

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By

LOW ZHI HUANG

Thesis submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

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Chairman: Assoc. Prof. Chen Soo Kien, PhD
Institute: Institute of Advanced Technology

Mechanochemical process is a powder processing technique that utilises mechanical energy to grind down bulk materials. Mechanochemical process has received a lot of interest for producing technologically important ferrites because it is a solvent-free technique and hence green process. Throughout the centuries, the applications of mechanochemical process are limited to diminution of particles because the lack of systematic studies on the process mechanisms of mechanochemical process. The immediate objective of this research is devoted to this subject by developing a systematic study on top-down approach mechanochemical process (referring to the production of nanoparticles by mechanochemical process) and mechanochemical activation-based synthesis (referring to mechanochemical process, used to activate the starting powders, before a sintering step to induce the formation of final product). For top-down approach mechanochemical process, starting bulk materials were mechanically treated for different milling time ranging from 1 to 20 hours at room temperature, for the preparation of nanoparticles. Evidence of the presence of single phase ferrites was identified by XRD. Rietveld refinement analysis suggested the deformation of a mechanically triggered polyhedral in the magnetoplumbite structure of $BaFe_{12}O_{19}$ and spinel structure $Ni_{0.5}Zn_{0.5}Fe_2O_4$. Three distinct stages of the mechanochemical mechanism were observed when the milling time was extended. The average crystallite size decreased at different rate during the first stage and the intermediate stage, and increased during the final stage of the mechanochemical process. FESEM micrographs showed the particle size decreased from 432.96 nm to 81.43 nm for $BaFe_{12}O_{19}$ and 371.68 nm to 158.49 nm for $Ni_{0.5}Zn_{0.5}Fe_2O_4$ during the first stage and the intermediate stage. In the final stage, particle size increased to 134.15 nm for $BaFe_{12}O_{19}$ and 193.60 nm for $Ni_{0.5}Zn_{0.5}Fe_2O_4$. HRTEM micrographs suggested the formation of a non-uniform nanostructure shell surrounding the ordered core materials. The thickness of the shell extended up to 12 nm during the first and intermediate stages, and diminished to approximately 3 nm during final stage. VSM results showed a mixture of ferromagnetic, superparamagnetic, and paramagnetic

behaviours attributed to the defects, distorted polyhedra, and non-equilibrium amorphous layers induced by the mechanical energy. The observed spectral shift from UV-Vis spectra was ascribed tothe competition between quantum confinement effects and structural disorder bandgap narrowing effect. For mechanochemical activation-based synthesis, mechanochemical process on the starting powders and subsequent sintering was carried out to synthesize $BaFe_{12}O_{19}$ and $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles. The XRD results indicated an improvement of crystallinity with increasing sintering temperature. Single phase ferrites were observed at 1100 °C for $BaFe_{12}O_{19}$ and 700 °C for $Ni_{0.5}Zn_{0.5}Fe_2O_4$. FESEM micrographs showed the particle size increased from 42.24 nm to 913.96 nm for $BaFe_{12}O_{19}$ and 66.39 nm to 1084.27 nm for $Ni_{0.5}Zn_{0.5}Fe_2O_4$ when sintering temperature were elevated from 600 ℃ to 1200 ℃. Morphological studies showed three stages of sintering with distinct microstructure features. By sintering from 600 °C to 1200 °C, a dependence of magnetic properties on sintering temperature was found. Maximum magnetization at 10 kOe improved with elevating sintering temperature. The optical bandgap values decreased with increasing crystallite size, showing the dominancy of quantum confinement effects. It can be concluded top-down approach mechanochemical process is capable of producing single phase nanoparticles; and mechanochemical activation-based synthesis has significantly reduced the sintering temperature required for the formation of final product. The systematic studies on the process mechanisms of top-down approach mechanochemical process and mechanochemical activation-based synthesis developed a fundamental knowledge to tailor nanoparticles with specific properties according to its possible industrial applications.

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

SIFAT-SIFAT MIKROSTRUKTURAL, OPTIKAL DAN MAGNETIK FERIT HEKSA BARIUM DAN FERIT NIKEL ZINK YANG DISINTESIS MENGGUNAKAN PROSEDUR MEKANOKIMIA

Oleh

LOW ZHI HUANG

Mei 2018

Pengerusi: Prof. Madya Dr. Chen Soo Kien, PhD
Institut: Institut Teknologi Maju

Proses mekanokimia adalah teknik pemprosesan serbuk yang menggunakan tenaga mekanikal untuk menghaluskan bahan-bahan pukal. Proses mekanokimia telah menerima banyak sambutan bagi menghasilkan ferit-ferit penting berteknologi tinggi kerana proses ini bebas pelarut dan dengan itu proses ini adalah proses hijau. Sepanjang abad yang lalu, penggunaan proses mekanokimia terbatas kepada pengecilan saiz zarah kerana kurangnya kajian sistematik ke atas mekanisme proses mekanokimia. Objektif utama kajian ini adalah untuk menumpukan kepada perkara ini dengan membangunkan sebuah kajian sistematik ke atas pendekatan proses mekanokimia atas ke bawah (merujuk kepada penghasilan zarah nano melalui proses mekanokimia) dan proses sintesis berdasarkan pengaktifan mekanokimia (berdasarkan proses mekanokimia, digunakan untuk mengaktifkan serbuk-serbuk permulaan sebelum langkah pensinteran untuk mendorong pembentukan produk akhir). Bagi pendekatan proses mekanokimia atas ke bawah, bahan-bahan pukal permulaan telah dirawat secara mekanikal pada masa pengisaran berbeza dari 1 hingga 20 jam pada suhu bilik untuk penyediaan zarah nano. Bukti kehadiran fasa tunggal ferit-ferit telah dikenalpasti menggunakan XRD. Analisis perbaikan Rietveld mencadangkan bahawa ubah bentuk polihedral yang dicetuskan secara mekanikal dalam struktur magnetoplumbit $BaFe_{12}O_{19}$ dan struktur spinel $Ni_{0.5}Zn_{0.5}Fe_2O_4$. Tiga peringkat berbeza bagi mekanisme mekanokimia telah diperhatikan apabila masa pengisaran dipanjangkan. Purata saiz kristal berkurangan pada kadar yang berbeza semasa peringkat pertama dan peringkat pertengahan, dan meningkat pada peringkat akhir proses mekanokimia. Mikrograf-mikrograf FESEM menunjukkan saiz zarah berkurang dari 432.96 nm kepada 81.43 nm untuk $BaFe_{12}O_{19}$ dan dari 371.68 nm kepada 158.49 nm untuk $Ni_{0.5}Zn_{0.5}Fe_2O_4$ semasa peringkat pertama dan peringkat pertengahan. Dalam peringkat akhir, saiz zarah meningkat kepada 134.15 nm bagi $BaFe_{12}O_{19}$ dan 193.60 nm bagi $Ni_{0.5}Zn_{0.5}Fe_2O_4$. Mikrograf-mikrograf HRTEM mencadangkan pembentukan kerangka nanostruktur tidak seragam yang mengelilingi bahan-bahan teras yang tersusun. Ketebalan lapisan kerangka adalah sehingga 12 nm semasa peringkat pertama dan pertengahan, dan berkurang kepada sekurang-kurangnya

3 nm semasa peringkat akhir. Keputusan-keputusan VSM menunjukkan campuran sifat-sifat ferromagnetik, superparamagnetik dan paramagnetik yang disebabkan oleh kecacatan, polyhedra terherot, dan ketidakseimbangan lapisan-lapisan amorfus yang didorongkan oleh tenaga mekanikal. Anjakan spektrum dari spektra UV-Vis yang diperhatikan adalah disebabkan oleh persaingan diantara kesan-kesan kurungan kuantum dan kesan penyempitan jurang jalur struktur terganggu. Bagi sintesis berdasarkan pengaktifan mekanokimia, proses mekanokimia ke atas serbuk-serbuk permulaan dan seterusnya pensinteran telah dilakukan untuk mensintesis zarah nano $BaFe_{12}O_{19}$ dan $Ni_{0.5}Zn_{0.5}Fe_2O_4$. Keputusan XRD menunjukkan penambahbaikan penghabluran dengan peningkatan suhu pensinteran. Fasa tunggal ferit telah diperhatikan pada suhu pensinteran 1100 °C dan 700 °C masing-masing bagi $BaFe_{12}O_{19}$ dan $Ni_{0.5}Zn_{0.5}Fe_2O_4$. Mikrograf-mikrograf FESEM menunjukkan saiz zarah menambah dari 42.24 nm kepada 913.96 nm untuk $BaFe_{12}O_{19}$ dan dari 66.39 nm kepada 1084.27 nm untuk $Ni_{0.5}Zn_{0.5}Fe_2O_4$ apabila suhu persinteran meningkat dari 600 °C ke 1200 °C. Kajian-kajian morfologi menunjukkan tiga tahap pensinteran dengan ciri-ciri mikrostruktur yang berbeza. Dengan melakukan pensinteran dari 600 °C ke 1200 °C, suatu kebergantungan sifat-sifat magnetik ke atas suhu pensinteran telah dijumpai. Kemagnetan maksimum pada 10 kOe ditingkatkan dengan peningkatan suhu pensinteran. Nilai-nilai jalur tenaga optikal berkurang dengan peningkatan saiz kristal, menunjukkan dominasi kesan-kesan kurungan kuantum. Dapat disimpulkan bahawa pendekatan proses mekanokimia atas ke bawah mampu menghasilkan fasa tunggal zarah nano; dan sintesis berdasarkan pengaktifan mekanokimia telah merendahkan suhu pensinteran dengan ketara bagi menghasilkan produk akhir. Kajian-kajian sistematik ke atas mekanisme proses pendekatan mekanokimia atas ke bawah dan sintesis berdasarkan pengaktifan mekanokimia telah membangunkan pengetahuan asas untuk mengubahsuai zarah nano dengan sifat-sifat tertentu bergantung kepada aplikasi-aplikasi industri yang berkemungkinan.

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I certify that a Thesis Examination Committee has met on 31 May 2018 to conduct the final examination of Low Zhi Huang on his thesis entitled "Microstructural, Optical and Magnetic Properties of Barium Hexaferrite and Nickel Zinc Ferrite Synthesized via Mechanochemical Procedure" 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 Doctor of Philosophy.

Members of the Thesis Examination Committee were as follows:

Halimah binti Mohamed Kamari, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Abdul Halim bin Shaari, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Khamirul Amin bin Matori, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Xiaoding Qi, PhD
Professor
National Cheng Kung University
Taiwan
(External Examiner)

RUSLI HAJI ABDULLAH, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 30 July 2018

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:

Chen Soo Kien, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Ismayadi Ismail, PhD
Research Officer
Institute of Advanced Technology
Universiti Putra Malaysia
(Member)

Josephine Liew Ying Chyi, PhD
Senior Lecturer
Faculty of Science
Universiti Putra Malaysia
(Member)

Yap Wing Fen, PhD
Senior Lecturer
Faculty of Science
Universiti Putra Malaysia
(Member)

Tan Kim Song, PhD
Head of Programme
Rubber Research Institute Malaysia
Malaysia
(Member)

____

ROBIAH BINTI YUNUS, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

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I hereby confirm that:

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- the research conducted and the writing of this thesis was under our supervision;
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Signature: ______________________________
Name of Chairman of Supervisory Committee: Assoc. Prof. Dr. Chen Soo Kien

Signature: ______________________________
Name of Member of Supervisory Committee: Dr. Ismayadi Ismail

Signature: ______________________________
Name of Member of Supervisory Committee: Dr. Josephine Liew Ying Chyi

Signature: ______________________________
Name of Member of Supervisory Committee: Dr. Yap Wing Fen

Signature: ______________________________
Name of Member of Supervisory Committee: Dr. Tan Kim Song

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LIST OF ABBREVIATIONS AND SYMBOLS

$BaFe_{12}O_{19}$	Barium hexaferrite
$Ni_{0.5}Zn_{0.5}Fe_2O_4$	Nickel zinc ferrite
BU	Bottom-up approach
TD	Top-down approach
$ZnFe_2O_4$	Zinc ferrite
$CoFe_2O_4$	Cobalt ferrite
$BaCO_3$	Barium carbonate
$NiFe_2O_4$	Nickel ferrite
$Ni_{0.6}Zn_{0.4}Fe_2O_4$	Nickel zinc ferrite
$SrFe_2O_4$	Strontium ferrite
Fig.	Figure
ZnO	Zinc oxide
Fe_2O_3	Iron oxide
NiO	Nickel oxide
BPR	Ball-to-powder weight ratio
etc.	Other similar things
E_A	Magnetocrystalline anisotropy energy
M_s	Saturation magnetization
p	Porosity
μ_B	Bohr magneton
ρ	Density
χ_m	Magnetic susceptibility
λ	Magnetostriction
E_k	Anisotropy energy

E_m	Magnetostatic energy
H_c	Coercivity
k_B	Boltzmann constant
γ	Specific surface energy
XRD	X-ray Diffraction
HRTEM	High Resolution Transmission Electron Microscope
VSM	Vibrating sample magnetometer
VNA	Vector network analyser
ESR	Electron spin resonance
FESEM	Field Emission Scanning Electron Microscope
NIR-UV-vis	Near infrared-ultraviolet- visible
h k l	Miller indices
λ	Wavelength
~	Approximately
mins	Minutes
B	Magnetic flux density
DUT	Device under test
μ_r	Complex permeability
ρx-ray	X-ray density
D	Crystallite size
2θ	2 theta degree
a.u.	Arbitrary unit
	Goodness of fit
$M_{10\ kOe}$	Magnetization at 10 k*Oe*
t_m	Milling time

w	Volume fraction
V_{shell}	Volume of shell
V_{core}	Volume of core
ΔH_{pp}	Peak-to-peak line width
R	Asymmetry parameter
H_r	Resonance field
h	Plank constant
k_B	Boltzmann constant
μ'	Real part of the permeability
μ''	Loss factor
α	Absorbance
E_g	Energy bandgap
v	Frequency
E_a	Activation energy
D_c	Critical size

CHAPTER 1

INTRODUCTION

1.1 Background of the study

Concerns with regard to the hazardous effects of current technologies on the environment and climate change are forcing industrialized and developing countries to seek for solutions and green technologies for a sustainable future. A more efficient utilisation of resources and energy implies a reduction in both waste and the environmental impact of human activities (Holdren, 2008). Therefore, rethinking the known current methodologies while maintaining or even improving productivity has become the major role of advancing fundamental and applied sciences. Mechanochemical procedure or mechanochemistry technology has attracted considerable interest because: (1) it is easy and simple to apply, (2) it allows fast chemical reactions under controlled conditions, and (3) it is a highly productive and relatively efficient methodology for the production of nanoscale materials. Therefore, mechanochemical procedure can be used as either a top-down approach synthesis technique to convert used bulk materials into raw nanopowder, or as a mechanochemical activation-based synthesis, which referring to the utilisation of mechanochemical process to increase the reactivity of the starting powders before heat treatment.

Ceramic composite powders can be synthesized by two techniques, which are known as the bottom-up and top-down approaches. The bottom-up approach synthesis method involves the construction of nanostructures in the material from small to large sizes. Examples of bottom-up approach synthesis methods include the sol–gel, melt spinning–melt quenching (MQ), chemical vapour deposition (CVD), and physical vapour deposition (PVD) methods. Typically, researchers would investigate variations in the properties of materials with a specific bottom-up synthesis technique with controlled parameters to obtain a controlled microstructure and fully dense polycrystalline material. On the other hand, the top-down approach synthesis method utilizes mechanical, chemical, or other forms of energy to break down macro-structured materials into smaller components (Sopicka-Lizer, 2010). The emergence of "Green Technology" recently has highlighted the importance of top-down approach synthesis method studies, which have been neglected by researchers in the past as the issues of conservation and preservation were not as urgent as at present. Nanomagnetic materials have attracted considerable interest from many researchers due to their novel properties when particles size decreases to nanoscale regime. These properties are different from those in bulk form. The correlation between particle size (1-100 nm) and critical magnetic parameters has led to a new study field called nanomagnetism. Nanostructured materials possess a high surface area to volume ratio, which allows the dominance of quantum confinement effects and a larger influence of surface atoms compared to those in the interior (Kumar, 2013).

Ferrites are a family of materials, in which the main constituent of the material is mixed metal oxides, typically iron oxide which contains Fe^{3+} ions. Ferrites are categorized into two groups based on how ease these materials are to be magnetized or demagnetized. Materials that can be permanently magnetized and require strong applied magnetic field to demagnetize are known as hard ferrites. Hard ferrites are widely used in speakers, recording devices, magneto-optical sensors. On the other hand, materials that are easily and temporarily magnetised under magnetic field are known as soft ferrites. In contrast with hard ferrites, soft ferrites are used in communication and electronic devices like transformers and inductors, and recently, in the field of biomedicine. Ferrites can also be categorized according to their structures into three groups: (1) spinel ferrites, (2) garnet ferrites, and lastly (3) hexagonal ferrites, which are known as magnetoplumbite ferrites. In terms of magnetic characteristics, spinel ferrites and garnet ferrites are soft ferrites and hexagonal ferrites are hard ferrites. Both hard and soft ferrites play important roles in various current technologies. Hard ferrites, particularly $BaFe_{12}O_{19}$, barium hexaferrite, exhibits some salient properties. It has strong magnetocrystalline anisotropy and an easy magnetization at the *c*-axis. Besides, barium hexaferrite has a high coercivity, high saturation magnetization, excellent chemical stability, and is resistant to corrosion. Due to its unique characteristics, barium hexaferrite is one of the most important magnetic materials with great scientific and technological roles (Shafie et al., 2014). On the other hand, nickel zinc ferrite, which is the most popular composition of soft ferrites, is one of the most abundant magnetic materials found in electrical devices and telecommunication devices. Characteristics like high resistivity, low eddy current loses, low coercivity, low cost, and easily altered magnetic behaviours due to its compositional sensitive nature, has made nickel zinc ferrite an important material in high frequency applications such as microwave devices, transformers, antennas, and inductors (Ibrahim et al., 2014; Ismail et al., 2011). In this study, $BaFe_{12}O_{19}$ and a well-known composition $Ni_{0.5}Zn_{0.5}Fe_2O_4$ are chosen as the specimens.

1.2 Relationship between Characteristics and Mechanically Induced Microstructural Response of Ferrites

The response of the structure and size of hexaferrites and spinel ferrites to mechanical energy through high energy ball milling and its impacts on their optical, physical, and magnetic properties are interesting because mechanical energy makes them differ from their bulk counterparts. Investigations in the field of mechanically induced materials, especially iron-based ceramics, have been considerably developed recently (Rodziah et al., 2012; Shafie et al., 2014). Šepelák et al. (2014), and Waje et al. (2010) recognised mechanochemical process was capable of producing nano-sized powder, and the changes in the microstructural properties were the main factor responsible for the changes in the investigated properties. Ferrites exhibit complicated disordering phenomena under mechanical impacts. Šepelák et al. (2014) found several disordering phenomena such as redistribution of cations over non-equivalent cation sublattices, the formation of canted spin arrangements, the changes of polyhedra geometry, and formation of cation with unsaturated oxygen coordination. Heat treatment like sintering provides a recovery path or recrystallization process: to enable the excited unstable metastable state transforms to the low energy crystalline state (Idza et al., 2012). The reformation of crystalline phase in ferrites changed the behaviours or characteristics of mechanical alloyed induced metastable materials in terms of microstructural properties, caused an increase in crystalline volume, thus had a direct relationship with the investigated physical, chemical, and magnetic properties (Low et al., 2015). On the other hand, for top-down approach, mechanically induced microstructural defects and disordering structures remained in ferrite specimens (Šepelák et al., 2014). Studies on the mechanically induced response of both hard and soft ferrites, are essential not only for fundamental understanding of science, but also due to the industrial and technological importance of these materials in telecommunication, microwave, memory storage, ferrofluids, and even biomedical applications. To strengthen the fundamental science knowledge on the evolutional relationship between characteristics and microstructural response of ferrites, this study undertakes the response of fine nanoparticles made up of mechanical alloyed Ba-hexaferrite and NiZn-spinel ferrite to vary in the sintering temperature (mechanochemical activation-based synthesis), and further investigate the correlations by comparing with the response of single phase Ba-hexaferrite and NiZn-spinel ferrite to mechanical action through mechanochemical process (top-down approach mechanochemical process). For both approaches, their physical, optical, and magnetic properties are investigated. Many researchers involving, but not restricted to the following (Rodziah et al., 2012; Šepelák et al., 2014; Shafie et al., 2014; Waje et al., 2010) have performed investigations on nano-sized ferrites. However, studies of systematic mechanochemical activation-based synthesis and the production of nanoparticles via mechanochemical process are very scarce in literature.

1.3 Problem statement

Mechanochemical process is one of the promising candidates of 'green processes' which can be used to develop methods which minimise damage to the environment. However, extensive research had been merely carried out on sample synthesized by mechanochemical procedure by neglecting the parallel evolution of microstructure and material properties at various intermediate controlling process factors. Therefore, much of the essential information of process mechanisms has been neglected, thus reducing the capability of attaining good fundamental scientific knowledge which lies behind the parallel evolution of the microstructural-material properties. Characteristics or behaviours of hard and soft ferrites are directly related to the microstructural properties, which are strongly dependant on the preparation route, therefore, the evolutional relationship between microstructural properties with controlling process factors has to be investigated. This study will carefully track the fundamental evolution of hard and soft ferrites synthesized from mechanochemical procedure. The research questions are listed as:

1. What are the characteristics of materials synthesized by mechanochemical activation-based synthesis and top-down approach mechanochemical process?
2. What is the relationship of evolving microstructure properties with optical and magnetic properties of material?
3. What would be the structural properties of bulk materials after the top-down approach mechanochemical process?

4. What would be the unique characteristics possessed by materials synthesized by the top-down approach that would make the recycling of used materials possible?

1.4 Objectives and hypotheses of the study

The main objective of this study is to investigate and compare the parallel evolution of microstructural, optical bandgap, physical and magnetic properties of two different approaches of mechanochemical procedure: (1) top-down approach mechanochemical process (at different milling time) and (2) mechanochemical activation-based synthesis (at different sintering temperature). The achieved goals from this research work can be utilised to develop fundamental knowledge on mechanochemical procedure. Furthermore, the understanding on the parallel evolution of the microstructure and various properties of the materials will help to develop a general theoretical model for future studies. In this research, the work-step objectives are presented as below:

1. To prepare $BaFe_{12}O_{19}$ and $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles using top-down approach by breaking bulk materials via mechanochemical process.
2. To study the microstructure-optical and magnetic properties of $BaFe_{12}O_{19}$ and $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles as a consequence of milling time.
3. To prepare $BaFe_{12}O_{19}$ and $Ni_{0.5}Zn_{0.5}Fe_2O_4$ using mechanochemical activation-based synthesis by pre-treating the starting powders with mechanochemical process before sintering.
4. To study the microstructure-optical and magnetic properties of $BaFe_{12}O_{19}$ and $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles as a consequence of sintering temperature.

Thus, according the above main objectives, this study is hypothesized as follows:

1. Top-down approach mechanochemical process would induce defects or amorphous phases in the $BaFe_{12}O_{19}$ and $Ni_{0.5}Zn_{0.5}Fe_2O_4$, while effectively decrease the size of the ferrites.
2. The existence of amorphous and crystalline mixture state with nanocrystalline microstructure would deteriorate the optical and magnetic properties.
3. Mechanochemical activation based synthesis would increase the reactivity of the starting powders, thus reduce the sintering temperature for the formation of single phase ferrites.
4. The parallel evolving of microstructural properties with elevating sintering temperature of polycrystalline $BaFe_{12}O_{19}$ and $Ni_{0.5}Zn_{0.5}Fe_2O_4$ would affect the optical and magnetic properties of the materials.

1.5 Scope of the Study

This study will focus on synthesizing barium hexaferrite ($BeFe_{12}O_{19}$) and nickel zinc ferrite ($Ni_{0.5}Zn_{0.5}Fe_2O_4$) powders via two different mechanochemical procedures in their nominal composition (Costa et al., 2003; Pullar, 2012). These ferrites with their nominal compositions have increasing degree of interest due to their importance in commercial and technology. Key mechanisms associated with both preparation routes have been studied. In particular, a considerable investigation has been carried out to understand the microstructural, magnetic, and optical properties of $BaFe_{12}O_{19}$ and $Ni_{0.5}Zn_{0.5}Fe_2O_4$.

1.6 Thesis outline

Chapter One comprehensively describes the general introduction of hard and soft ferrites, mechanochemistry, the difference between top-down and bottom-up approaches, correlation between microstructural properties and various properties, and some research questions. In Chapter Two, related literature reviews about previous studies on synthesis techniques, mechanochemical process or high energy ball milling with its optimization of variable parameters, and the effects of particle size and microstructural properties are summarised. Chapter Three describes hard and soft ferrites, mechanical alloying mechanisms, magnetism, particle size related properties in terms of fundamental theories. Chapter Four focuses on employed methodologies for sample preparation and equipment and measurement involved in the characterisation of the study. Chapter Five presents obtained data and results of current research work, followed by precise discussion. Chapter Six concludes the research findings. A research summary was made, followed by future research recommendations. At last, Chapter Six was attached with references, appendix, and a list of publications.

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