UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERIZATION OF SrM0.5Fe11.5O19 DERIVED FROM MILL SCALE WITH SUBSTITUTION M= Co, Cu, Ni, Zn, Ti, Nd VIA MECHANICAL ALLOYING

NORUZAMAN BIN DAUD

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By

NORUZAMAN BIN DAUD

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

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DEDICATION

To my beloved late mother Bidah binti Ismail, father Daud bin Awang Noh and all family members

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

PREPARATION AND CHARACTERIZATION OF $SrM_{0.5}Fe_{11.5}O_{19}$ DERIVED FROM MILL SCALE WITH SUBSTITUTION M= Co, Cu, Ni, Zn, Ti, Nd VIA MECHANICAL ALLOYING

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Chairman : Raba'ah Syahidah binti Azis, PhD
Faculty : Science

It is interesting to see the changes on structural and magnetic properties of strontium hexaferrites on the addition of metal element such as Co, Cu, Ni, Zn, Ti, and Nd for future device applications. Here the aims of the projects are to produce the undoped and doped strontium ferrite (Co, Cu, Ni, Zn, Ti, and Nd) from mill scales as raw iron compound by using a high-energy ball milling (HEBM) technique. Secondly to study the effect of Co, Cu, Ni, Zn, Ti, and Nd substitution in strontium hexaferrite and compare with undoped strontium hexaferrite on its structural, microstructure, magnetic, thermal and density properties. In order to achieve the first objective, the undoped and doped strontium hexaferrites, mill scales as the main sources of iron oxide Fe_2O_3 undergo two stages of purification process that are magnetic separation technique and curie temperature separation technique. The powders of 0.5 molar ratio of various metal oxides (Co, Cu, Ni, Zn, Ti, and Nd), strontium carbonate ($SrCO_3$), and iron oxides (Fe_2O_3) were milling by employing HEBM following the formula $SrM_{0.5}Fe_{11.5}O_{19}$**.** The resulting powder were then moulded into rod and pellets with diameters and height 10 mm × 10 mm and 10 mm × 2 mm respectively and sintered at 1300 ^{0}C. For the second objective, the doped and undoped was characterized by XRD, FESEM, EDX, FTIR, VSM, BH-tracer, Photoflash Technique to measure thermal diffusivity (k) Precision Impedence Analyser to measure Curie temperature (T_c), and densimeter. The XRD patterns confirmed the formation of the single phase hexagonal ferrite structure for all samples, with space group $P6_3/mmc$. The XRD analysis exhibits an excess compound of Fe_2O_3 for Ti, Nd and Ni cations substitution. The analysis also shows increase in calculated lattice parameters a, c and cell volumes (V_{cell}) indicating the solubility of substituted cation in hexagonal structure of strontium ferrite. The average crystallite size from XRD for different substitution is in the range of 40 to 70 nm. From FESEM images, the samples with homogenous surface and hexagonal geometry have an average particle size in the range of 1 to 4 μm. The corresponding peaks of Co, Cu, Ni, Zn, Ti, and Nd were observed from EDX confirms the metal substitution. The FTIR spectra showed characteristic peaks for strontium

hexaferrite was detected between 650 cm^{-1} to 450 cm−1 for all samples. The T_c values for undoped, Co, Cu, Ni, Zn, Ti, and Nd were 390, 330, 292, 290, 287, 270 and 266 °C respectively. From B-H tracer the value of M_s for undoped is 2546 G_s was in the range of common magnetic properties for ferrite 2000 to 3000 G_s (Cullity and Graham, 2009) while M_s for Zn = 3284 G_s and Ni = 3154 G_s doped was higher than that of common ferrite. The H_c of strontium hexaferrite decreases largely from a value of 1160 Oe for the pure samples to 332, 02, 281, 260, 127 and 64 Oe for Cu, Co, Zn, Ti, Nd and Ni metal cations, respectively. The substitutions have decreased the value of H_c and M_r compared with undoped strontium hexaferrite. The value of M_r for undoped strontium hexaferrite is 1576 G_s while the remanence for Zn, Cu, Co, Ni, Ti and Nd was 955, 873, 839, 727, 714 and 165 G_s, respectively.

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

PENYEDIAAN DAN PENCIRIAN PENGGANTIAN M = Co, Cu, Ni, Zn, Ti, Nd DALAM STRONTIUM HEXAFERIT DARIPADA SISIK BESI MENGGUNAKAN PENGALOIAN MEKANIKAL

Oleh

NORUZAMAN BIN DAUD

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Adalah menarik untuk melihat perubahan sifat-sifat struktur dan magnet strontium hexaferrites pada penambahan elemen logam seperti Co, Cu, Ni, Zn, Ti, dan Nd untuk aplikasi peranti masa hadapan. Di sini, matlamat projek adalah untuk menghasilkan strontium ferrite (Co, Cu, Ni, Zn, Ti, dan Nd) yang tidak didop dan yang didop dari sisik besi kilang sebagai sebatian besi mentah utama menggunakan teknik HEBM. Kedua, untuk mengkaji kesan penggantian Co, Cu, Ni, Zn, Ti, dan Nd dalam strontium hexaferrite dan membandingkan dengan strontium hexaferrite yang tidak didop pada sifat struktur, mikrostruktur, magnetik, haba dan ketumpatannya. Untuk mencapai matlamat pertama, strontium hexaferrites yang tidak didop dan didop, sisik besi sebagai sumber utama besi oksida Fe_2O_3 menjalani dua peringkat proses pembersihan iaitu teknik perpisahan magnetik dan teknik pemisahan suhu curie. Nisbah 0.5 molar logam oksida (Co, Cu, Ni, Zn, Ti, dan Nd), strontium karbonat ($SrCO_3$), dan besi oksida (Fe_2O_3) telah melalui teknik HEBM mengikut formula $SrM_{0.5}Fe_{11.5}O_{19}$. Serbuk yang dihasilkan kemudiannya dibentuk menjadi rod dan pelet dengan diameter dan ketinggian 10 mm × 10 mm dan 10 mm × 2 mm dan disinter pada 1300 ^{0}C. Untuk objektif kedua, didop dan tidak didop SM dicirikan oleh XRD, FESEM, EDX, FTIR, VSM, BH-tracer, Teknik Photoflash untuk mengukur kekurangan haba (k) Precision Impedence Analyzer untuk mengukur suhu Curie (T_c), dan densimeter. Corak XRD mengesahkan pembentukan struktur ferit hexagonal fasa tunggal untuk semua sampel, dengan kumpulan ruang *P63* / mmc. Analisis XRD memperlihatkan lebihan sebatian Fe_2O_3 untuk penggantian Ti, Nd dan Ni kation. Analisis ini juga menunjukkan peningkatan dalam parameter kekisi yang dikira a, c dan volum sel (V_{cell}) yang menunjukkan kelarutan kation yang digantikan dalam struktur heksagon strontium ferit. Saiz kristal purata dari XRD untuk penggantian yang berbeza adalah dalam lingkungan 40 hingga 70 nm. Dari imej FESEM, sampel dengan permukaan homogen dan geometri heksagon mempunyai saiz zarah purata dalam julat 1 hingga 4 μm. Puncak yang sama Co, Cu, Ni, Zn, Ti, dan Nd diperhatikan dari EDX mengesahkan penggantian logam. Spektrum FTIR menunjukkan puncak ciri untuk strontium

hexaferrite dikesan antara 650 cm^{-1} hingga 450 cm^{-1} untuk semua sampel. Nilai T_c untuk tidak didop, Co, Cu, Ni, Zn, Ti, dan Nd masing-masing adalah 390, 330, 292, 290, 287, 270 dan 266 ° C. Dari B-H nilai M_s untuk tidak didop adalah 2546 G_s adalah dalam bacaan sifat magnet biasa untuk ferit iaitu 2000 hingga 3000 G_s (Cullity dan Graham, 2009) manakala M_s untuk dop Zn = 3284 Gs dan Ni = 3154 G_s adalah lebih tinggi daripada itu Daripada ferit yang biasa. H_c strontium hexaferrite berkurangan secara besar-besaran daripada nilai 1160 Oe untuk sampel tulen kepada 332, 02, 281, 260, 127 dan 64 Oe untuk kation logam Cu, Co, Zn, Ti, Nd dan Ni. Penggantiannya telah menurunkan nilai H_c dan M_r berbanding dengan strontium hexaferrite yang tidak didop. Nilai M_r untuk strontium hexaferrite yang tidak didop adalah 1576 G_s manakala remanens untuk Zn, Cu, Co, Ni, Ti dan Nd masing-masing adalah 955, 873, 839, 727, 714 dan 165 Gs.

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I certify that a Thesis Examination Committee has met on 16 January 2017 to conduct the final examination of Noruzaman bin Daud on his thesis entitled "Preparation and Characterization of $SrM_{0.5}Fe_{11.5}O_{19}$ Derived from Mill Scale with Substitution M = Co, Cu, Ni, Zn, Ti, Nd via Mechanical Alloying" 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.

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Name of Member of Supervisory Committee: Associate Professor Dr. Khamirul Amin bin Matori

Signature: ____________________

Name of Member of Supervisory Committee: Associate Professor Dr. Mansor bin Hashim

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f	frequency
μm	microns
M_s	saturation magnetization
H_c	coercivity
HEBM	High Energy Ball Milling
FESEM	Field Emission Scanning Electron Microscope
XRD	X-ray diffraction
A	cross-sectional area
ρ	density
T_c	Curie temperature
N	number of turn
L_s	inductance
l	length
D	grain size
PVA	polyvinyl alcohol
μ_B	magnetic moment
K_1	first anisotropy constant
Fe_2O_3	iron oxide
K_1	Anisotropy constant
Oe	Oersted
Mn	Manganese
nm	nanometer

CHAPTER 1

INTRODUCTION

1.1 General introduction

This Chapter reviews the basic concepts of mill scale, ferrite materials and importance on M-type ferrite particularly strontium ferrite permanent magnets. M-type ferrites are compared with other important permanent magnets and their historical developments were described. The crystal structure, magnetic structure and phase relationship of strontium ferrite were outlined. The intrinsic magnetic properties of M-type ferrite were presented in detail.

1.2 Mill Scales

The wastes management are important issue in the modern day as the waste materials was increase with the development of human civilization. In order to control the harmful of wastes materials to the environment a lot of study with sustainable development in material production were to reserve natural resources. Mill scales are steel wastes produced by hot metal and steel has become an important the burden for metals industry in environment crisis. Furthermore, the reduction of iron ores necessitates extensive research work to reuse the secondary raw materials produced as a by-product in steel companies and considered as waste materials. During hot rolling of steel, iron oxides form on the surface of the metal as scales.

The scale is accumulated as waste materials in all steel companies. In an integrated steel plant, a portion of the mill scale, the large size ones, was recycled in sintering plants. In some steel manufacturing companies, the bulk of mill scale waste was dumped in landfills and resulted in leaching of some percentages of heavy metals into soil and groundwater, thus threatening the environment. The continuous demand for more landfills and bad effect on the environment highlight the need for more effective methods of productive utilization of mill scale. The size of mill scale is usually less than 1 mm thick, blackish grey in colour and flakes-like form in variety of size .The function of mill scale is to protect steel form atmospheric corrosion provided no cracks happen. It is because mill scale is electrochemically cathodic to steel, thus any crack in mill scale will result in accelerated corrosion at exposed steel surface. Mill scales consist of iron ions which oxidized in the phase of wustite (FeO), magnetite (Fe_3O_4) and mostly major composition is hematite (Fe_2O_3). Mill scales also contain a small amount of impurity such as Mn, SiO, Al, Cu, Mg, and dust. Wustite have less density and lower Curie temperature than magnetite and wustite (FeO) can be converted to form hematite (Fe_2O_3) by oxidation process (Azis et al, 2015).

A study on the recycling mill scale for the production of magnetic material, soft and hard magnet were mostly reported by students and researchers of University Putra Malaysia and other study was carries out from other places with different approach and technique. The study exposed that mill scale can be converted into valuable products not only soft and hard magnet but also other valuable product such as an alternative to be used in ductile iron production, low carbon steel, and free cutting steel and many more since mill scale contain high purity iron that can be obtained. In this research work, impurities were separated from mill scale by magnetic separation technique (MST). MST technique is able to separate the magnetic particles by applying the external magnetic field on the mill scales (Azis et al., 2002). The impurities can be separated into light and heavy impurities. The impurities with lower density will float on the surface of the tube where the impurities with high density will fall to the bottom of the glass tube.

1.3 Ferrites

Ferrites are defined as oxide materials composed of Fe^{3+} ions as the main cationic component. These are members of mixed iron oxides $MO.Fe_2O_3$, where M is metal such as Ba, Sr, Pd, Co, etc. The iron oxides have been known for millennia used originally as pigments in paints and in the magnetic compass also known as *lodestones* to locate the magnetic 'north' (Smit and Wijin, 1959).Ferrite materials occupy a key position in many essential areas of interest such as electrical power, storage and processing of information and industrial machines including motors for various applications. Ferrites are the best-suited materials for communication including telephony, radio and television (Kools, 1991).

1.3.1 Soft and hard ferrites

Ferrites can be classified on the basis of their crystal structure, as cubic versus hexagonal and also based on their magnetic behaviour, i.e. soft versus hard ferrites. Soft ferrites can easily be magnetized and demagnetized as they have an obvious magnetism only in the presence of magnetic field. They high permeability, low coercivity (H_c <1000 A/m) and narrow hysteresis loop, e.g., Mn $ZnFe_2O_4$, $NiZnFe_2O_4$, etc. Soft ferrite materials are used extensively in applications such as in voltage and current transformers, electronic circuits, transformer cores, motors for generators, saturable reactors, magnetic amplifiers, inductors, and chokes, etc (Campbell, 1996).

The main composition of hard ferrites is $MFe_{12}O_{19}$ (M = Ba, Sr, Pd, Ca), which retain their obvious magnetization more or less permanently. These are characterized by high value of coercivity, typically 10,000 Am^{-1}, which makes them difficult to magnetize and demagnetize. The magnetism of a hard ferrite is strongly bound to its hexagonal axis, which is the reason for its hard magnetic behavior, i.e. high value of permeability in plane, remanent magnetization, and coercivity with a wide hysteresis loop. Such materials are referred to as permanent magnets because once magnetized they tend to remain magnetized for a long. Permanent magnets are used as magnetic field source-components in a wide range of products including consumer electronic equipment, computers, data storage devices and electrochemical devices, etc. It has been estimated that an average home contains more than fifty permanent magnets and every car uses an average about eight of them. The applications of permanent magnets range from electric motors, loudspeakers, generators, door latches, electric watches and microwave tubes (Campbell, 1996). The wide range of crystal geometries, the excessive improvements in material properties and their relative cost-effectiveness make these ferrite materials the potential candidate for innovative applications

1.4 Classification of ferrites

Ferrites can be divided into four families. Spinels $1Fe_2O_{3-1}MeO$ (MeO = transition metal oxide), garnets $5Fe_2O_{3-3}Me_2O_3$ (Me_2O_3 = Rare-earth metal oxide) and hexagonal ferrites $6Fe_2O_{3-1}MeO$ (MeO = group IIA oxide, e.g., CaO, BaO, SrO).

1.4.1 Hexagonal ferrites

Present day hexagonal ferrites plays important materials in hard ferrite production industry due to their novel electromagnetic properties. Hexaferrites are extensively useful in the field of telecommunication and electronic industries since their outstanding properties such as high frequency microwave devices and also as permanent magnets because of their high uniaxial anisotropy and high coercive force (Slama, 2004). The crystal structure of hexagonal ferrites can be considered as a system of close packed stacking of two types of oxygen layers parallel to the hexagonal basal plane (110 plane) (Smit, 1959). The first oxygen layer contains 4-oxygen ions and the second layer contains 3-oxygen ions and one barium or strontium ion etc. Between these layers several interstitial sites, namely tetrahedral surrounded by four equidistant nearest neighbors, octahedral have six octahedrally surrounded oxygen ions and trigonal bipyramidal site have five oxygen ions.

The crystal structure of hexagonal ferrites is built up from three basic sub-units namely S, R and T. The S^*, R^* and T^* are the rotational symmetry of S, R, and T at 180° around the hexagonal c-axis. The repeating unit 'S' has composition $[M^{2+}2Fe^{3+}{}_4O_8]$ (S^0) or $[Fe^{3+}{}_6\ O_8]^{2+}$ (S^{2+}) with neutral or uncompensated charge of (+2) per sub unit, respectively. It consists of two layers of oxygen ions having four ions per layer which are cubically closed packed. The 'R' sub-unit has the composition $[M^{2+}Fe^{3+}{}_6O_{11}]^{2-}$ and it is composed of three layers of oxygen ions, where one of the oxygen ions is substituted by one Me^{2+} ion in the middle layer. The layers of the R-block are hexagonally packed. The T block has composition $[M^{2+}2Fe^{3+}{}_8O_{14}]^0$ and composed of four layers of oxygen ions, where one of the oxygen ions is replaced by one Ba^{+2} ions in each of the two middle layers. The T block contains no mirror plane, consequently, there are no tetrahedral sites sharing faces (Kojima, 1982).The S, R and T blocks are considered as the basic blocks from which a range of hexagonal structures has been synthesized and can be classified into M, Y, W, Z, X and U type.

1.4.2 M-type hexagonal ferrites

M type hexaferrites is a class of ferrites is called a "magnetoplumbite" structure. The magnetoplumbite formula is $MFe_{12}O_{19}$ or $MO.6Fe_2O_3$, where M can be Ba^{2+}, Sr^{2+} or Pb^{2+}. The Fe^{3+} cations may also be replaced by other trivalent ions, e.g., Al^{3+}, Mn^{3+}, Ga^{3+}, or by a binary mixture of divalent and tetravalent ions, such as Co^{2+} and Ti^{4+}, without distorting the crystal structure. The addition of such metal oxides in various amounts may result in many different materials with tailored properties.

The unit cell of magnetoplumbite structure comprises of two formula units; as five oxygen layers constitute one formula unit and two such units constitute one unit cell. Each molecule shows 180° rotational symmetry around the hexagonal *c*-axis. The O^{2-} layer containing M^{2+} act as a mirror plane since it is perpendicular to the *c*-axis. It can be said, therefore, that each unit cell consists of 10 oxygen layers, sequentially built up from 4 blocks as, S (spinel), R (hexagonal), S* and R*. The S* and R* have similar arrangement of atoms as that of the S and R blocks but rotated 180° with respect to S and R about the c axis. The S (spinel) or S* block consists of two oxygen ions layers; while R or R* block contains three oxygen layers, with one oxygen site in the middle layer substituted by one M^{2+} ion (Hosseini and Naghibolashraphy, 2008). Each block has 6 interstitial Fe^{3+} ions in different crystallographic lattice sites, having spins in upward and downward directions. The space group of the M-type compound is denoted as *P63/mmc* ($D^4 6h$) with the values of lattice constants are c = 23.2 Å and a = 5.88 Å (You et al., 2008)

The cations (M^{2+}, Fe^{3+}) occupy the interstitial positions of the oxygen lattice. The M-type hexaferrite crystallizes in hexagonal geometry with 64 ions per unit cell distributed in 11 different symmetry sites (Liu et al., 2009). The unit cell contains 38 oxygen, 24 iron and 2 M ions (M= Ba^{+2}, Sr^{+2}, Pb^{+2} and La^{+3}). The 24 iron ions are distributed over five different lattice sites that is $2a$, $2b$, $12k$, $4f_1$ and $4f_2$. Out of these five sites, $2a$, $12k$ and $4f_2$ are octahedral, $4f_1$ is tetrahedral and $2b$ is a trigonal bipyramid site (Iqbal and Ashiq, 2008). The oxygen ions occupy $4e$, $4f$, $6h$, and $12k$ sites form a closed pack lattice and M ions (M^{2+} = Ba, Sr, Pb and La) occupy $2d$ sites (Kim, 2000). The number and spin of the $12Fe^{+3}$ is shown below at different sites located in R (hexagonal) and S (spinel) blocks (Figure 1.1). They are arranged as 6 Fe^{+3} are in $12k$ site having the spin up, 2 ions in $4f_2$ and $4f_1$ having spin down and 1 ion in $2a$ and $2b$ site having spin up. So the 8 Fe^{+3} are in the upward direction and 4 in the downward direction, hence, 4 upward and downward cancel each other and the net moments is obtained of $4Fe^{+3}$ per formula units. As each Fe^{+3} ion has 5 unpaired electrons in the 3d orbital contributing magnetic moment of $5\mu_B$, where μ_B is a Bohr magnetons so according to the spin orientation. The total magnetic moment per formula unit is 20 μ_B (Iqbal and Ashiq, 2007).

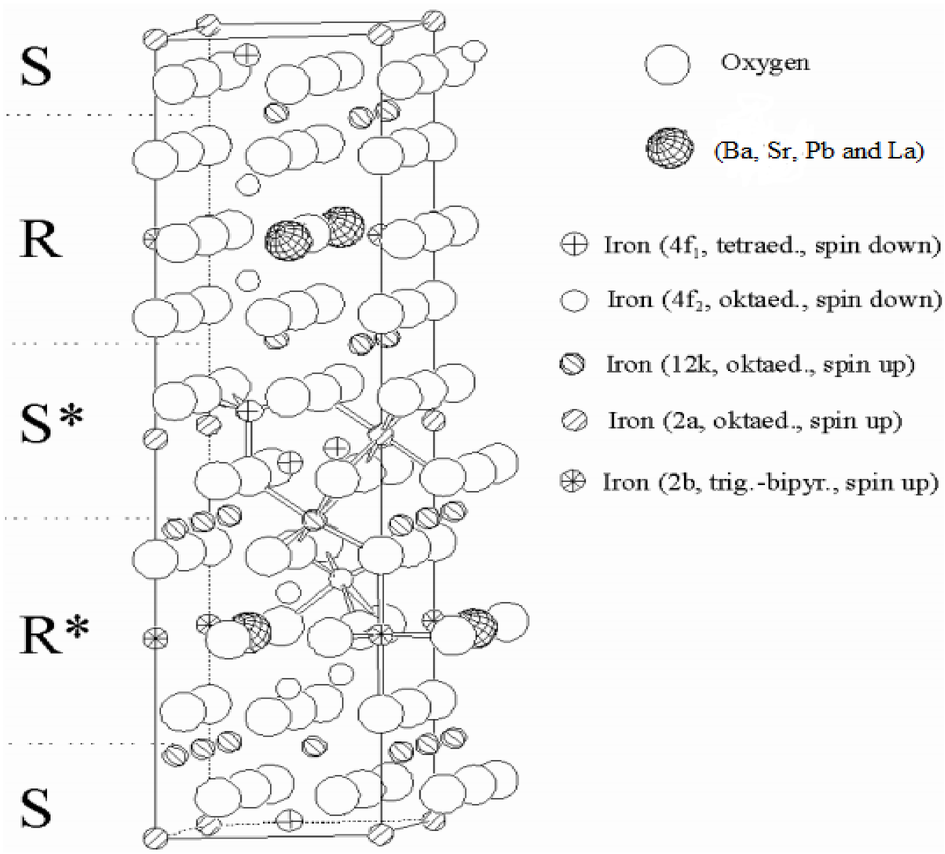

Figure 1.1 : Unit cell of M-type hexaferrite based on two formula units of $MFe_{12}O_{19}$ (Pullar, 2012)

1.4.3 Strontium Ferrite

Magnetoplumbite crystal structure of strontium hexaferrite was characterized by the space group *P6₃/mmc*. The magnetism of $SrFe_{12}O_{19}$ is due to the Fe^{3+} ions, each carrying a spin moment of 5 μB. Apart from the intrinsic properties, microstructural factors are important for understanding strontium hexaferrites behaviour that changes their magnetic properties. The ferrite crystallites are bonded to solid bodies either by sintering or by chemical bonding and may be randomly oriented or aligned with the *c*-axis in one direction (Kools, 1991).

Hexaferrites with the magnetoplumbite crystal structure have been receiving much attention, because it is widely used in application for technological area such as permanent magnets, microwave devices, magnet optic device, recording media, telecommunication, and magnet-recording media (Zi et al., 2008). There are some advantages of strontium ferrite where the raw material is abundant, the manufacture cost is low, low density, large electrical resistivity, high microwave magnetic loss, and also the properties are stable and the sample cannot be oxygenated for strontium ferrite (Yongfei, 2009). Ultrafine strontium ferrite powder (>0.1μm) with homogenous particle size distribution and controlled magnetic properties are important for ideal performance in many magnet materials application.

1.5 Problem statement

This research was about to knowing the changes of properties of the substituting different metal element into the strontium hexaferrite. Strontium hexaferrite, is the parent compound that is a material which has been investigated by previous study primarily because of their magnetic properties which make it suitable for use in magnetic recording media and microwave devices. The starting point for this thesis came from an attention in strontium hexaferrite materials as hard magnet with wide hysteresis loop and other characteristic. A review of the literature currently existing on metal substituted strontium hexaferrite produced a handful of papers which were limited in scope to either a single or double substitution case result rather than comparison between single metal substitutions with different metal on strontium hexaferrite.

1.6 Objectives

This research is to investigate the effect of Me substitution in strontium hexaferrite on its structural, magnetic parameters and microstructure. The Me is define as the transition metal ions (Ti, Co, Ni, Cu, Zn) and rare earth element (Nd). The results were comparing to pure strontium hexaferrite. The density and thermal properties of the substitution samples sintered at 1300°C were also analysed. Thus, the investigation with the following main objective has been carried out:

i) To produce the undoped and doped strontium hexaferrite (Co, Cu, Ni, Zn, Ti, Nd) from mill scales as raw iron compound by using (HEBM) technique in order to obtain high performances permanent magnet.
ii) To study the effect of Co, Cu, Ni, Zn, Ti, Nd substitution in strontium hexaferrite and compare with undoped strontium hexaferrite on its structural, microstructure, magnetic, thermal and density properties.

1.7 Hypothesis and Scope of Works

The hypothesis of this research is would we produce undoped strontium hexaferrite and substituted bulk samples from mill scales as raw iron compound by using (HEBM) technique in order to obtain high performances permanent magnet. Besides that, what would be the effect of Co, Cu, Ni, Zn, Ti, Nd substitution in strontium hexaferrite and compare with undoped strontium hexaferrite on its structural, microstructure, magnetic, thermal and density properties?

In summary, this thesis will contribute to scientific knowledge by investigating the structural and magnetic properties of substituted Co, Cu, Ni, Zn, Ti, and Nd strontium hexaferrite. This work secondly seeks to address this gap in the literature by providing a more comprehensive study with a wider range of metal dope in strontium hexaferrite is limited to presenting hysteresis loops and associated data for this study. Results presented here are for different of metals substitution allowing more detailed conclusions to be drawn.

REFERENCES

Ali, I., Islam, M. U., Awan, M. S., Ahmad, M. (2013). Effects of Ga–Cr substitution on structural and magnetic properties of hexaferrite (BaFe12O19) synthesized by sol–gel auto-combustion route. *Journal of Alloys and Compounds*. 547: 118-125.

Alsmadi, A. M., Bsoul, I., Mahmood, S. H., Alnawashi, G., Al-Dweri, F. M., Maswadeh, Y., & Welp, U. (2015). Magnetic study of M-type Ru–Ti doped strontium hexaferrite nanocrystalline particles. *Journal of Alloys and Compounds*, *648*, 419-427.

Aravind, G., Gaffoor, A., Ravinder, D., & Nathanial, V. (2015). Impact of transition metal ion doping on electrical properties of lithium ferrite nanomaterials prepared by auto combustion method. *Advanced Materials Letters*, 6(2), 179-185.

Ashiq, N., M., Fahad Ehsan, M., Javed Iqbal, M., Najam-ul-Haq, M. (2013). Role of Zr–Co substitution at iron site on structural, magnetic and electrical properties of Sr-hexaferrites nanomaterials synthesized by the sol–gel combustion method. *Journal of Magnetism and Magnetic Materials*. 332: 93-9

Ashiq, M. N., Iqbal, M. J., Gul, I. H. (2009). Structural, magnetic and dielectric properties of Zr–Cd substituted strontium hexaferrite ($SrFe_{12}O_{19}$) nanoparticles. *Journal of Alloys and Compounds*. 487 (1–2): 341-345

Ashiq, M. N., Javed Iqbal, M., Hussain Gul, I. (2011). Effect of Al–Cr doping on the structural, magnetic and dielectric properties of strontium hexaferrite nanomaterials. *Journal of Magnetism and Magnetic Materials***.** 323 (3–4): 259-263.

Asghar, G., and Anis-ur-Rehman, M. (2012). Structural, dielectric and magnetic properties of Cr–Zn doped strontium hexa-ferrites for high frequency applications. *Journal of Alloys and Compounds*. 526: 85-90.

Auwal, I. A., Güngüneş, H., Baykal, A., Güner, S., Shirsath, S. E., & Sertkol, M. (2016). Structural, morphological, optical, cation distribution and Mössbauer analysis of Bi 3+ substituted strontium hexaferrite. *Ceramics International*, *42*(7), 8627-8635.

Azis, R.S., M. H., N.M.Saiden, N.Daud, N.M.M.Shahrani. (2015). Study the iron environments of the steel waste product and its possible potential applications in ferrites. *Advanced Materials Research. 1109*: 295-299.

Baniasadi, A., Ghasemi, A., Nemati, A., Azami Ghadikolaei, M., Paimozd, E. (2014). Effect of Ti–Zn substitution on structural, magnetic and microwave absorption characteristics of strontium hexaferrite. *Journal of Alloys and Compounds.* 583: 325-328.

Campbell, P. (1996).*Permanent magnet materials and their application*. Cambridge University Press.

Cernea, M., Sandu, S. G., Galassi, C., Radu, R., & Kuncser, V. (2013). Magnetic properties of $Ba_xSr_{1-x}Fe_{12}O_{19}$ (x= 0.05–0.35) ferrites prepared by different methods. *Journal of Alloys and Compounds*, *561*, 121-128.

Che, S., Wang, J., & Chen, Q. (2003). Soft magnetic nanoparticles of BaFe12O19 fabricated under mild conditions. *Journal of Physics: Condensed Matter*. 15 (22): L335.

Chen, D.-H. and Y.-Y. Chen (2002). Synthesis of strontium ferrite nanoparticles by coprecipitation in the presence of polyacrylic acid. *Materials Research Bulletin*. 37(4): 801-810.

Coey, J. M. (2010). *Magnetism and magnetic materials*. Cambridge University Press.

Cullity, B. D., Graham, C. D. (2009). *Introduction to magnetic materials* (2nd ed.). New Jersey: John Wiley & Sons Inc.

Davoodi, A., and Hashemi, B. (2012). Investigation of the effective parameters on the synthesis of strontium hexaferrite nanoparticles by chemical coprecipitation method. *Journal of Alloys and Compounds*. 512 (1): 179-184.

Doroftei, C., Rezlescu, E., Rezlescu, N., Tudorache, F., Popa, P. D. (2008). Strontium ferrite for magnetic recording prepared by self-combustion method. *Journal of Optoelectronics and Advanced Materials*. 10 (11): 2919-2923.

Ebrahimi, Y., Sabbagh Alvani, A. A., Sarabi, A. A., Sameie, H., Salimi, R., Sabbagh Alvani, M., Moosakhani, S. (2012). A comprehensive study on the magnetic properties of nanocrystalline SrCo0.2Fe11.8O19 ceramics synthesized via diverse routes. *Ceramics International*. 38 (5): 3885-3892.

Fang, Q., Cheng, H., Huang, K., Wang, J., Li, R., Jiao, Y. (2005). Doping effect on crystal structure and magnetic properties of chromium-substituted strontium hexaferrite nanoparticles. *Journal of Magnetism and Magnetic Materials*. 294 (3): 281-286.

Ghazanfar, U., Siddiqi, S. A., & Abbas, G. (2005). Structural analysis of the Mn–Zn ferrites using XRD technique. *Materials Science and Engineering: B*,*118*(1), 84-86.

Ghobeiti, H., M., Seyyed Ebrahimi, S. A., Badiei, A. (2007). An investigation on physical properties of strontium hexaferrite nanopowder synthesized by a sol–gel auto-combustion process with addition of cationic surfactant. *Journal of the European Ceramic Society*. 27 (13–15): 3637-3640.

Goldman, A. (2006).*Modern ferrite technology*. New York:Springer Science & Business Media.

Goldman, A. (1999). *Handbook of Modern Ferromagnetic Materials*. The Netherlands : Kluwer cademic Publishers. p. 62.

Gruskova, A., Lipka, J., Papanova, M., Kevicka, D., Gonzalez, A., Mendoza, G., Slama, J.(2004). Mössbauer Study of Microstructure and Magnetic Properties (Co, Ni)–Zr Substituted Ba Ferrite Particles. *Hyperfine Interactions*. 156 (1):187-194.

Gurbuz, A., Onar, N., Ozdemir, I., Karaoglanli, A. C., Celik, E. (2012). Structural, thermal and magnetic properties of barium-ferrite powders substituted with Mn, Cu or Co and X (X= Sr and Ni) prepared by the sol-gel method. *Materials and technology*. 46(3): 305-310.

Hosseini, H. M.,& Naghibolashraphy, N. (2008). The effects of Misch-Metal oxide addition on magnetic properties and crystal structure of $Sr_{1-x} MM_x Fe_{12}O_{19}$ ferrite. *Journal of Alloys and Compounds. 448*(1): 284-286.

Hessien, M. M., Rashad, M. M., El-Barawy, K. (2008). Controlling the composition and magnetic properties of strontium hexaferrite synthesized by co-precipitation method. *Journal of Magnetism and Magnetic Materials* 320 (3–4): 336-343.

Huang, X.-H. and Z.-H. Chen (2006). "$CoFe_2O_4$ nanoparticles hosted in silica xerogels." *Scripta Materialia.* 54(2): 169-173.

Hua, Z. H., Li, S. Z., Han, Z. D., Wang, D. H., Lu, M., Zhong, W., ... & Du, Y. W. (2007). The effect of La–Zn substitution on the microstructure and magnetic properties of barium ferrites. *Materials Science and Engineering: A*,*448*(1), 326-329.

Iqbal, M. J., Naeem Ashiq, M., Hussain Gul, I. (2010). Physical, electrical and dielectric properties of Ca-substituted strontium hexaferrite ($SrFe_{12}O_{19}$) nanoparticles synthesized by co-precipitation method. *Journal of Magnetism and Magnetic Materials.* 322 (13): 1720-1726.

Iqbal, M. J., Ashiq, M. N., & Gomez, P. H. (2009). Effect of doping of Zr–Zn binary mixtures on structural, electrical and magnetic properties of Sr-hexaferrite nanoparticles. *Journal of Alloys and Compounds*, *478*(1), 736-740.

Iqbal, M. J., & Ashiq, M. N. (2007). Comparative studies of $SrZr_xMn_xFe_{12-2x}O_{19}$ nanoparticles synthesized by co-precipitation and sol–gel combustion methods. *Scripta materialia*, *56*(2), 145-148.

Jacobo, S. E., Arana, M., & Bercoff, P. G. (2016). Gadolinium substitution effect on the thermomagnetic properties of Ni ferrite ferrofluids. *Journal of Magnetism and Magnetic Materials, 415*, 30-34.

Jean, M., Nachbaur, V., Bran, J., & Le Breton, J. M. (2010). Synthesis and characterization of $SrFe_{12}O_{19}$ powder obtained by hydrothermal process.*Journal of Alloys and compounds*, *496*(1), 306-312.

Kanagesan, S., Jesurani, S., Velmurugan, R., Prabu, S., Kalaivani, T. (2012). Structural and magnetic properties of conventional and microwave treated Ni–Zr doped barium strontium hexaferrite. *Materials Research Bulletin*. 47 (2): 188-192.

Kim, C. S., Lee, S. W., An, S. Y. (2000). Mössbauer studies of $BaFe_{11.9}Mn_{0.1}O_{19}$ by a sol–gel method. *Journal of Applied Physics*, *87*(9), 6244-6246.

Kim, S. D., & Kim, J. S. (2006). Magnetic properties of Sr-ferrites synthesized in molten (NaCl+ KCl) flux. *Journal of magnetism and magnetic materials*, *307*(2), 295-300.

Kojima, H. (1982).Ferromagnetic materials: *A handbook on the properties of magnetically ordered substances*, (Ch.5, pp. 318).North-Holland, Amsterdam: Wiley-VCH.

Kools, F. (1991). Hard Magnetic Ferrites A2-BROOK, RJ: *Concise Encyclopedia of Advanced Ceramic Materials* (200-206).Pergamon: Oxford.

Langford, J. I., & Wilson, A. J. C. (1978). Scherrer after sixty years: a survey and some new results in the determination of crystallite size. *Journal of Applied Crystallography*, *11*(2), 102-113.

Lee, S. W., An, S. Y., Shim, I.-B., Kim, C. S. (2005). Mössbauer studies of La–Zn substitution effect in strontium ferrite nanoparticles. *Journal of Magnetism and Magnetic Materials*. 290–291, Part 1: 231-233.

Li, Z. W., Chen, L., Ong, C. K. (2002). Studies of static and high-frequency magnetic properties for M-type ferrite $BaFe_{12-2x}Co_xZr_xO_{19}$. *Journal of applied physics.* 92(7): 3902-3907.

Li, W., Qiao, X., Li, M., Liu, T., Peng, H. X. (2013). La and Co substituted M-type barium ferrites processed by sol–gel combustion synthesis. *Materials Research Bulletin.* 48 (11): 4449-4453.

Liyanage, L. S. I., Kim, S., Hong, Y.-K., Park, J.-H., Erwin, S. C., Kim, S.-G. (2013). Theory of magnetic enhancement in strontium hexaferrite through Zn–Sn pair substitution. *Journal of Magnetism and Magnetic Materials.* 348: 75-81.

Liu, X., Hernández-Gómez, P., Deng, Y., Huang, K., Xu, X., Qiu, S., & Zhou, D. (2009). Analysis of magnetic disaccommodation in La^{3+}–Co^{2+}-substituted strontium ferrites. *Journal of Magnetism and Magnetic Materials, 321*(16), 2421-2424.

Liu, Y., Drew, M. G. B., Liu, Y. (2011). Preparation and magnetic properties of barium ferrites substituted with manganese, cobalt, and tin. *Journal of Magnetism and Magnetic Materials*. 323 (7): 945-953.

Luo, J. (2012). Structural and magnetic properties of Nd-doped strontium ferrite nanoparticles. *Materials Letters*. 80: 162-164.

Mali, A. and A. Ataie (2005). Structural characterization of nano-crystalline BaFe12O19 powders synthesized by sol–gel combustion route. *Scripta Materialia.* 53 (9): 1065-1070.

Morel, A., Le Breton, J. M., Kreisel, J., Wiesinger, G., Kools, F., Tenaud, P. (2002). Sublattice occupation in $Sr_{1-x}La_xFe_{12-x}Co_xO_{19}$ hexagonal ferrite analyzed by Mössbauer spectrometry and Raman spectroscopy. *Journal of Magnetism and Magnetic Materials.* 242–245. Part 2: 1405-1407.

Mozaffari, M., Arab, A., Yousefi, M. H., Amighian, J. (2010). Preparation and investigation of magnetic properties of MnNiTi-substituted strontium hexaferrite nanoparticles. *Journal of Magnetism and Magnetic Materials*. 322 (18): 2670-2674.

Mukai, K., Sasaki, K., Hashimoto, T., Suzuki, A., Hoshino, T., & Terai, T. (2011). Effect of Li/Ti ratio on microstructure and thermal diffusivity of lithium titanate for solid breeding material. *Fusion Engineering and Design*, *86*(9), 2643-2646.

Nabiyouni, G., Fesharaki, M. J., Mozafari, M., & Amighian, J. (2010). Characterization and magnetic properties of nickel ferrite nanoparticles prepared by ball milling technique. *Chinese Physics Letters*, *27*(12), 126401.

Narang, S. B., Singh, C., Bai, Y., & Hudiara, I. S. (2008). Microstructure, hysteresis and microwave absorption analysis of $Ba_{(1-x)}Sr_xFe_{12}O_{19}$ ferrite. *Materials Chemistry and Physics*, *111*(2), 225-231.

Nikzad, A., Ghasemi, A., Tehrani, M. K., & Gordani, G. R. (2015). Y-Type Strontium Hexaferrite: the Role of Al Substitution, Structural, and Magnetic Consequence. [journal article]. *Journal of Superconductivity and Novel Magnetism, 28*(12), 3579-3586.

Pieper, M. W., Morel, A., Kools, F. (2002). NMR analysis of La+Co doped M-type ferrites. *Journal of Magnetism and Magnetic Materials*. 242–245. Part 2: 1408-1410.

Pullar, Robert C. "Hexagonal ferrites: a review of the synthesis, properties and applications of hexaferrite ceramics." *Progress in Materials Science* 57.7 (2012): 1191-1334.

Rai, B. K., Mishra, S. R., Nguyen, V. V., & Liu, J. P. (2013). Synthesis and characterization of high coercivity rare-earth ion doped Sr 0.9 RE 0.1 Fe 10 Al 2 O 19 (RE: Y, La, Ce, Pr, Nd, Sm, and Gd). *Journal of Alloys and Compounds*, *550*, 198-203.

Rane, M. V., Bahadur, D., Nigam, A. K., Srivastava, C. M. (1999). Mössbauer and FT-IR studies on non-stoichiometric barium hexaferrites. *Journal of Magnetism and Magnetic Materials*. 192 (2): 288-296.

Rezlescu, N., Doroftei, C., Rezlescu, E., Popa, P. D. (2006). Structure and humidity sensitive electrical properties of the Sn^{4+} and/or Mo^{6+} substituted Mg ferrite. *Sensors and Actuators B: Chemical*. 115 (2): 589-595.

Rodziah, N., Hashim, M., Idza, I. R., Ismayadi, I., Hapishah, A. N., & Khamirul, M. A. (2012). Dependence of developing magnetic hysteresis characteristics on stages of evolving microstructure in polycrystalline yttrium iron garnet. *Applied Surface Science*, *258*(7), 2679-2685.

Sanchez, D. J. F., Bolarín.M., A., Cortes, E.C. A., Valenzuela, R., Ammar, S. (2014). Mechanosynthesis, crystal structure and magnetic characterization of M-type $SrFe_{12}O_{19}$. *Ceramics International*. 40 (3): 4033-4038.

Shepherd, P., Mallick, K. K., Green, R. J. (2007). Magnetic and structural properties of M-type barium hexaferrite prepared by co-precipitation. *Journal of Magnetism and Magnetic Materials.* 311 (2): 683-692.

Slama, J., Gruskova, A., Papanova, M., Kevicka, D., Dosoudil, R., Jancarik, V., Mendoza, G. (2004). Magnetic properties of Me–Zr substituted Ba–hexaferrite. *Journal of Magnetism and Magnetic Materials.* 272–276, Part 1: 385-387.

Smit, J., Wijin, H. P.J. (1959). Ferrites: *Physical properties of ferromagnetic oxides in relation to their technical applications* (Ch. 5). Netherlands: Wiley.

Soman, V. V., Nanoti, V. M., Kulkarni, D. K (2013). Dielectric and magnetic properties of Mg–Ti substituted barium hexaferrite. *Ceramics International.* 39 (5): 5713-5723.

Sözeri, H., Deligöz, H., Kavas, H., Baykal, A. (2014). Magnetic, dielectric and microwave properties of M–Ti substituted barium hexaferrites ($M=Mn^{2+}$, Co^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}). *Ceramics International*. 40(6): 8645-8657.

Teh, G. B., Nagalingam, S., Jefferson, D. A. (2007). Preparation and studies of Co (II) and Co (III)-substituted barium ferrite prepared by sol–gel method. *Materials chemistry and physics* .101(1): 158-162.

Thakur, A., Singh, R. R., Barman, P. B. (2013). Synthesis and characterizations of Nd^{3+} doped $SrFe_{12}O_{19}$ nanoparticles. *Materials chemistry and physics*. 141 (1): 562-569.

Thomas, S., Kalarikkal, N., Jaroszewski, M., & Jose, J. P. (Eds.). (2016).*Advanced Polymeric Materials: From Macro-to Nano-Length Scales*. CRC Press.

Wagner, T. R. (1998). Preparation and Crystal Structure Analysis of Magnetoplumbite-Type $BaGa_{12}O_{19}$. *Journal of Solid State Chemistry*. 136 (1): 120-124.

Wang, H. Z., Yao, B., Xu, Y., He, Q., Wen, G. H., Long, S. W., Gao, L. L. (2012). Improvement of the coercivity of strontium hexaferrite induced by substitution of Al^{3+} ions for Fe^{3+} ions. *Journal of Alloys and Compound*. 537: 43-49.

Yang, Z., Wang, C. S., Li, X. H., Zeng, H. X. (2002). (Zn, Ni, Ti) substituted barium ferrite particles with improved temperature coefficient of coercivity. *Materials Science and Engineering: B*. 90 (1–2): 142-145.

Yang, G., Migone, A. D., & Johnson, K. W. (1994). Relationship between thermal diffusivity and mean free path. *American Journal of Physics*, *62*(4), 370-372.

You, L., Qiao, L., Zheng, J., Jiang, M., Jiang, L., & Sheng, J. (2008). Magnetic properties of La-Zn substituted Sr-hexaferrites by self-propagation high-temperature synthesis. *Journal of Rare Earths, 26*(1), 81-84.

Zhong, W., Ding, W., Zhang, N., Hong, J., Yan, Q., & Du, Y. (1997). Key step in synthesis of ultrafine $BaFe_{12}O_{19}$ by sol-gel technique. *Journal of Magnetism and Magnetic Materials.* 168 (1–2): 196-202.

Zi, Z. F., Sun, Y. P., Zhu, X. B., Yang, Z. R., dai, J. M., Song, W. H. (2008). Structural and magnetic properties of $SrFe_{12}O_{19}$ hexaferrite synthesized by a modified chemical co-precipitation method. *Journal of Magnetism and Magnetic Materials, 320*(21), 2746-2751.