

PHASE FORMATION PROCESS OF CITRATE-GEL DERIVED HEXAGONAL FERRITE

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

Bachelor of Technology
in
Ceramic Engineering

By
VIJAY KUMAR



Department of Ceramic Engineering
National Institute of Technology
Rourkela
2007

PHASE FORMATION PROCESS OF CITRATE-GEL DERIVED HEXAGONAL FERRITE

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

Bachelor of Technology
in
Ceramic Engineering

By
VIJAY KUMAR

Under the Guidance of
Dr. JAPES BERA



Department of Ceramic Engineering
National Institute of Technology
Rourkela
2007



**National Institute of Technology
Rourkela**

CERTIFICATE

This is to certify that the thesis entitled, "PHASE FORMATION PROCESS OF CITRATE-GEL DERIVED HEXAGONAL FERRITE" submitted by Sri VIJAY KUMAR in partial fulfillments for the requirements for the award of Bachelor of Technology Degree in Ceramic Engineering at National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

Date:

Dr. JAPES BERA

Dept. of Ceramic Engineering
National Institute of Technology
Rourkela - 769008

Acknowledgement

I wish to express my deep sense of gratitude and indebtedness to Prof. J. Bera ,Department of Ceramic Engineering, N.I.T Rourkela for introducing the present topic and for their inspiring guidance, constructive criticism and valuable suggestion throughout this project work.

I would like to express my gratitude to Prof. S. Bhattacharyya (Head of the Department), Prof. S. Adak, Prof. S. K. Pratihari, Prof. D. Sarkar ,Prof. Bibhuti. B. Nayak and Prof. A. Mallik for their valuable suggestions and encouragements at various stages of the work. I am also thankful to Mr. G. Bera and all staff members of Department of Ceramic Engineering NIT Rourkela.

I am also thankful to Mr. Pradip Roy, Mr.R.P.Rana, Mr. J. Nayak and Ms. A.Chakravarti and other research scholars in Department of Ceramic Engineering for providing all joyful environment in the lab and helping me out in different ways.

CONTENTS

Chapter 1 INTRODUCTION

- 1.1 Introduction & classification of ferrite
- 1.2 Hexagonal ferrite
- 1.3 Types of Hexagonal ferrite
 - 1.3.1 M-Type Hexagonal ferrite
 - 1.3.2 W-Type Hexagonal ferrite
 - 1.3.3 Y-Type Hexagonal ferrite
 - 1.3.4 Z-Type Hexagonal ferrite
- 1.4 Application of hexagonal ferrite.
- 1.5 Plan of project work.

Chapter 2 LITERATURE REVIEW

- 2.1
 - 2.1.1. Variation in the hysteresis of different magnetic materials.
 - 2.1.2. High and ultra high resonant frequency.
 - 2.1.3. Influence of stoichiometry and heat treatment conditions on the magnetic properties and phase constitution of Ba-ferrite powders prepared by sol-gel method.
 - 2.1.4. Magnetic studies of Sn^{2+} - Sn^{4+} substituted barium hexa-ferrites synthesized by mechanical alloying.
 - 2.1.5 Effects of pH and calcination temperatures on the formation of citrate-derived hexagonal barium ferrite particles
- 2.2 Summary

Chapter 3 EXPERIMENTAL WORK

- 3.1 Introduction
- 3.2 Synthesis Techniques & experimental procedure
 - Calculation for batch compositions
- 3.3 General Characterization
 - 3.3.1 Phase formation
 - 3.3.2 Particle size

Chapter 4 RESULT

Chapter 5 CONCLUSIONS & REFERENCES

Chapter 1

INTRODUCTION

1.1 Introduction:

It is now some 70 yrs since ferrites debuted as an important new category of magnetic materials. They were prized for a range of properties that has no equivalents in existing metal magnetic materials, and it was not long before full-fledge research and development efforts were underway. Today ferrites are employed in a truly wide range of applications, and have contributed materially to advance in electronics. Research too, continue apace, and the efforts of many man and women working in this field are yielding many highly intriguing results. New high-performance products are appearing one after another, and it would seem we have only scratched the surface of the hidden possibilities of these fascinating materials.

Ferrite is a class of ceramic material with useful electromagnetic properties and an interesting history. Ferrite is rigid and brittle. These are electrically non-conductive ferrimagnetic ceramic compound materials, consisting of various mixtures of iron oxide such as hematite (Fe_2O_3) or magnetite (Fe_3O_4) and the oxide of other metals. There are basically two varieties of ferrite: soft and hard. This is not a tactile quality but rather a magnetic characteristic. 'Soft ferrite' does not retain significant magnetization whereas 'hard ferrite' magnetization is considered permanent. [1]

Classification of ferrite

Depending on crystal structure the ferrite can be classified into three groups. They are Spinel ferrite, Hexagonal ferrite and Garnet ferrite. The crystal structure of these materials holds the key to their diverse magnetic properties because in each case it defines the interactions between the various ions on an atomic level.

- The spinel is by far the most widely used ferrite. It has spinel structure to that of mineral spinel MgAl_2O_4 and the magnetic spinel have general formula MFe_2O_4 , where M is divalent metal cation.
- Magnetic rare earth garnet ferrite have crystal structure related to the mineral garnet. The general formula is $3\text{M}_2\text{O}_3 \cdot 5\text{Fe}_2\text{O}_3$ or $\text{MFe}_5\text{O}_{12}$.
- Hexagonal ferrites are also called magnetoplumbite as it has same crystal structure to that of naturally occurring magnetoplumbite ($\text{PbFe}_{7.5} \text{M}_{3.5}\text{Al}_{0.5}\text{Ti}_{0.5}\text{O}_{19}$).

1.2 Hexagonal ferrite

Hexagonal ferrites are discovered at Philips in 1950. It has strong magnetic properties. So it is used for making magnets. It has some advantages over Spinel ferrite. Spinel ferrite has low resonant frequency, so it is not applicable in hyper frequency range (300-1000 MHz) but the hexagonal ferrites are most suitable to be used in hyper frequency range.

Properties:

- High magnetocrystalline anisotropy.
- High saturation magnetization.
- High resistivity
- Low dielectric loss.
- Good thermal stabilities.

1.3 Types of Hexagonal Ferrite

1.3.1. M-type Hexagonal ferrite – $\text{BaFe}_{12}\text{O}_{19}$

This is the most popular hard ferrite. It is used in permanent magnets and H.D. perpendicular recording media. The materials exhibit strong magnetic-field non-linearities and well expressed time dependence of the AC magnetic susceptibility, similarly to disordered magnetic materials with strong magnetic interactions. The hexagonal ferrites based on $\text{BaFe}_{12}\text{O}_{19}$ presented as $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ are regarded as efficient replacements for the metallic magnets in recording media and in microwave devices. Their high stability in air up to temperatures 1400°C , non-metallic electrical properties, high volume density of magnetic material achievable in powders and thin films, corrosion resistance as well as sharp switching-fields are their advantages over the metallic magnets.

e.g. $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$, $\text{SrO} \cdot 6\text{Fe}_2\text{O}_3$.

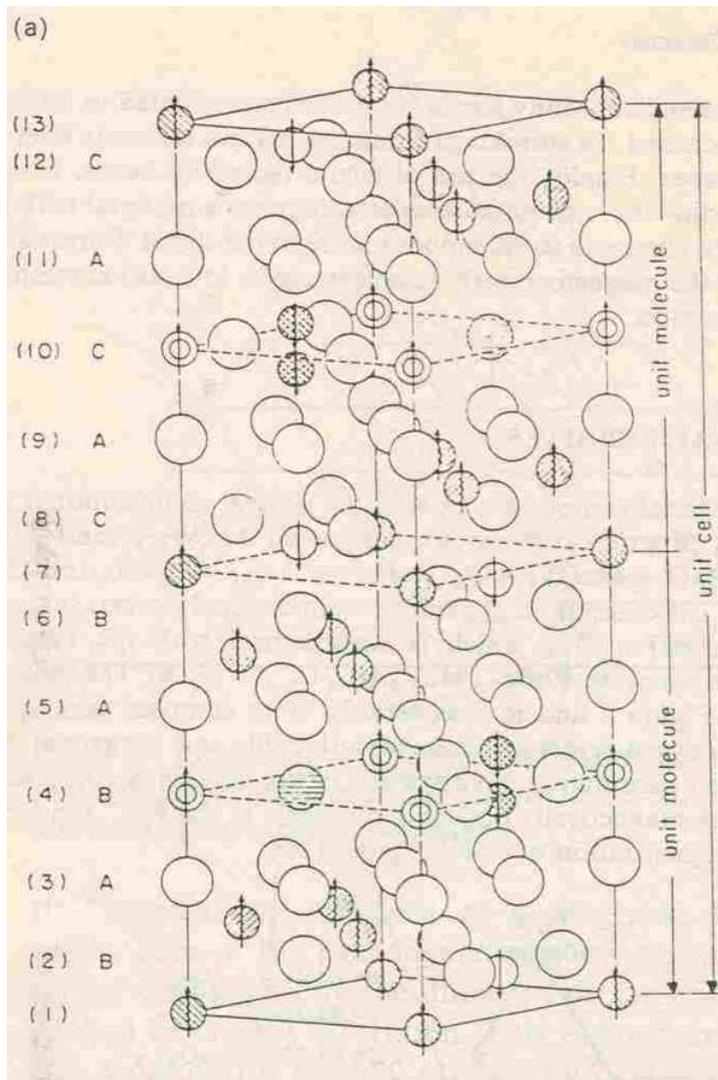


Fig.1 Unit cell structure of M-type hexagonal ferrite ($M^{2+}F_{12}O_{19}$) stacking of oxygen layers in C (magnetically active) direction shows both cubic and hexagonal close packing.

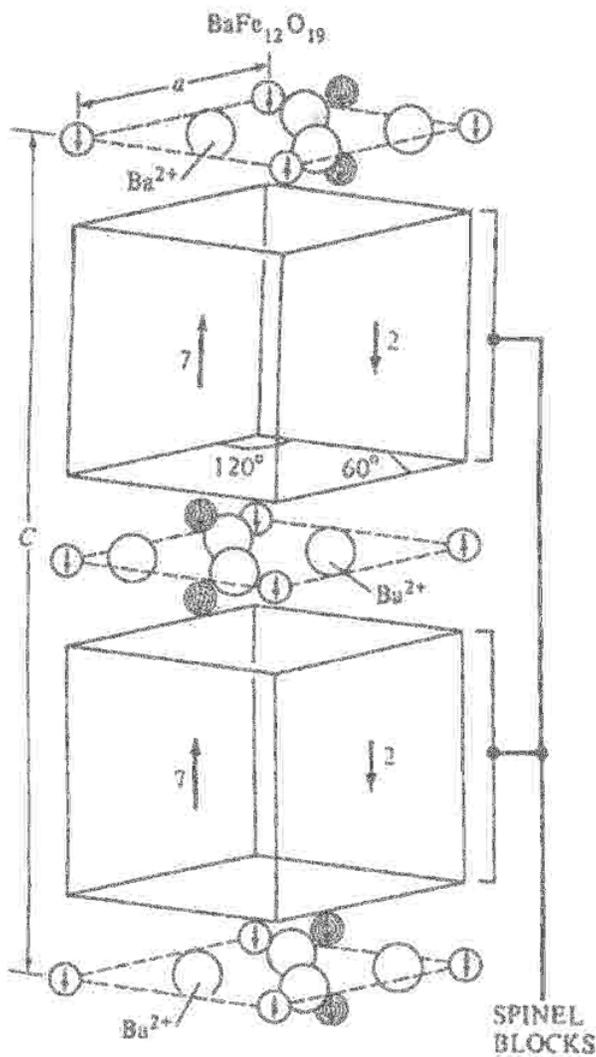


Fig.2 unit cell of barium ferrite($\text{BaFe}_{12}\text{O}_{19}$)

1.3.2. Y-type Hexagonal ferrite - $\text{Ba}_2\text{Me}_2\text{Fe}_{12}\text{O}_{22}$

These are excellent soft ferrites. Y-type hexagonal ferrites have planar magnetic anisotropy. Their cut-off frequency is about an order of magnitude higher than that of spinel ferrites. Y-type hexagonal ferrite exhibits excellent magnetic properties in hyper-frequency. It is anticipated that the Y-type hexagonal ferrite will meet the need of soft magnetic materials for chip components in hyper-frequency.

1.3.3. W-type Hexagonal ferrite - $\text{BaMe}_2\text{Fe}_{16}\text{O}_{27}$

It is a hard ferrite. Increasing attention has been devoted to W-type hexagonal ferrites with the chemical composition $\text{AMe}_2\text{Fe}_{16}\text{O}_{27}$, where A represents a larger divalent metal ion and Me represents a smaller divalent metal ion. This interest derives from their potential application

as permanent magnets for electrical, electronic and automobile devices. The study of the magnetic properties of SrZn₂-W-type hexagonal ferrites indicated the enhancement of the saturation magnetization as much as 18%. [2] The magnetic properties of BaZn₂Fe₁₆O₂₇ ferrites prepared by the co-precipitation method. Many experiments using different magnetic or non-magnetic cations or a combination of both the types of the cations in the substitutions for Me²⁺ were explored in an attempt to improve the thermal stability, saturation magnetization or other intrinsic magnetic properties. e.g. BaO.2MO.6Fe₂O₃ Here M can be Zn or Mg.

1.3.4 Z-type Hexagonal ferrite - Ba₃Me₂Fe₂₄O₄₁

It is excellent soft ferrite. It has high performance (high initial permeability, high quality factor, high resonant frequency and low loss tangent) in hyper-frequencies of 300-1000 MHz. Especially, its high cut-off frequencies up to the 3-GHz region, compared with the 300-MHz ceiling encountered with the spinel ferrites, bring it into the hyper-frequency region useful for chip inductors or beads. It is used in MLCI. [3]

1.4 Application of Hexagonal ferrites

- Polycrystalline hexagonal ferrite with the controlled complex permeability are suitable to the improvement in the antenna performance of hand-held cellular telephones. [4]
- In the method of developing electrophotographic images employing a developer having a magnetic carrier component, the improvement comprising the step of using as the carrier a ferrite material in particulate form. An electrophotographic ferrite carrier with substantially spherical shape based on a magnetoplumbite structure of hexagonal ferrite or ferroplana structure derived from the magnetoplumbite structure has a high electrical resistivity and a longer life. [5]
- As a microwave absorber- The hexagonal ferrite powder has been developed by dry attrition and sintering procedure. The developed ferrite powder 60% by weight has been mixed in epoxy resin to form a microwave-absorbing paint. This paint was coated on a conducting aluminum sheet to study the absorption characteristics of a linearly polarized TE wave at X band. The results for single- and two-layer microwave absorbers for different coating thicknesses have been reported. It has been found that it shows the broadband characteristics with minimum absorption of 8 dB from 8 to 12 GHz for a coating thickness of 2 mm. These paints are very useful in

military applications such as RCS reduction, camouflaging of the target and prevention of EMI, etc. [6]

- Hexagonal ferrite is used for a circulator at mm-wave frequencies. No external magnet is needed. The center frequency is 73.5 GHz, the bandwidth over which the isolation is greater than 20 dB is 2.4 GHz, and the insertion loss is 1.1 dB at the center frequency. The tensor permeability in a strong uniaxial field is determined. The dependence of the circulator bandwidth on an applied field is determined to show that the large uniaxial field of hexagonal ferrite contributes to the wideband performance at mm-wave frequencies. [7]
- The ever increasing traffic of the communications medium combined with an urgent need for secure transmission of messages has directed attention to broadcasting at higher frequencies. The lower range of the microwave spectrum has been intensively exploited during the last twenty years. Attention is now focused at the upper microwave and millimeter wave spectrum, 10 to 70 kilomegacycles/sec. Before devices and systems can be designed components must be found that can operate at these higher frequencies. The synthesis of a series of single crystal hexagonal ferrites potentially useful in several different devices at microwave and millimeter wave frequencies . [7]

1.5 Plan of project work.

- Powder synthesis by Citrate gel route
- XRD phase analysis

Chapter 2

LITERATURE REVIEW

2.1.1 Y-type hexagonal ferrite prepared by citrate sol-gel auto-combustion method

Y-type hexagonal ferrite can be sintered under 900 °C. [8] Y-type hexagonal ferrites were prepared by citrate sol-gel auto-combustion method (CSAM). The phase formation process, microstructure and magnetic properties were investigated and compared with those of the samples made by conventional solid-state reaction method (SSRM). The selected material system has stoichiometric composition of $\text{Ba}_2\text{Zn}_{1.2-x}\text{Co}_x\text{Cu}_{0.8}\text{Fe}_{12}\text{O}_{22}$, where x was varied from 0 to 1.2. Phase formation was characterized by powder X-ray diffraction (XRD). The microstructure was observed via scanning electron microscopy (SEM). Frequency spectra of complex permeability were measured via an impedance analyzer. Results reveal auto-combusted powders are about 22 nm and very active. Phase formation temperature and sintering temperature are both 900 °C, much lower than those in SSRM. The sintered samples have fine-grained microstructure. The samples exhibit better magnetic properties in hyper-frequency than those made by SSRM.

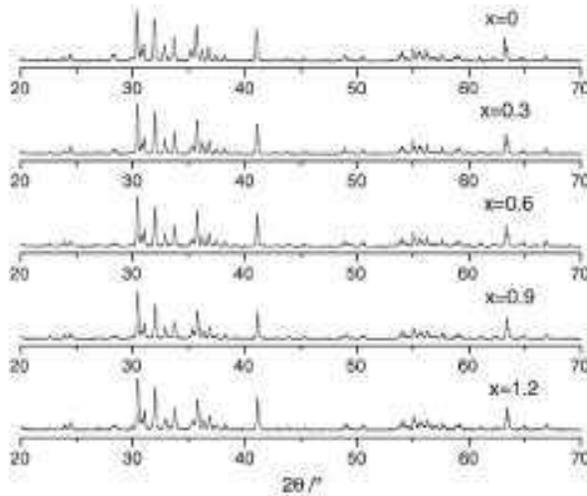


Fig. XRD spectra of the samples with different compositions prepared by CSAM and annealed at 900 °C

2.1.2. High and ultra high resonant frequency.

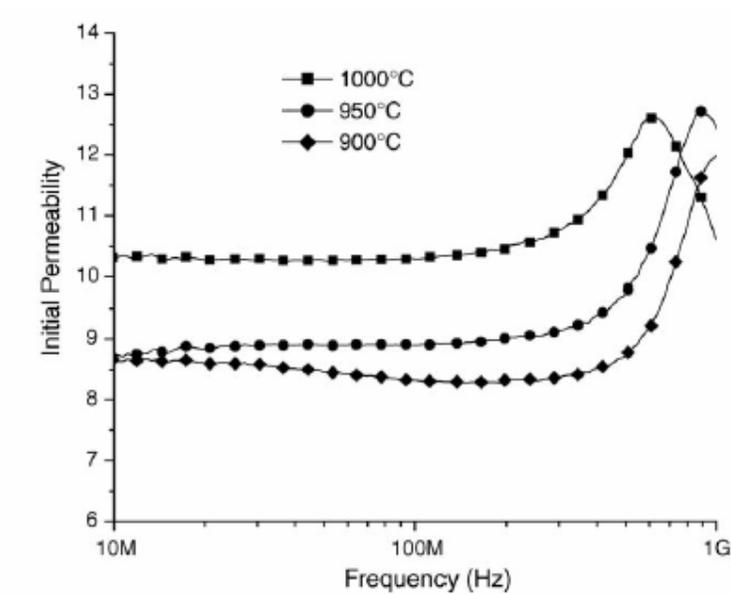


Fig . Frequency spectra of permeability of the sample ($x = 0.3$) prepared by CSAM and [9]sintered at different temperatures.

This fig. shows the frequency spectra of permeability of the sample by CSAM ($x = 0.3$) sintered at different temperatures. Permeability also increases with the rise of sintering temperature.

2.1.3 Influence of stoichiometry and heat treatment conditions on the magnetic properties and phase constitution of Ba-ferrite powders.

The magnetic properties and the microstructure of Ba-ferrite powders prepared by the sol-gel route were investigated. Amorphous gels were processed with a varying Fe/Ba ratio and then powder materials were obtained by heat treating at temperatures between 900 and 1000°C for 1-4 hrs. The results showed that increasing time and temperature was beneficial to the saturation magnetization(M_s), where as the coercivity (H_{ci}) was only slightly affected. The variation of the Fe/Ba ratio led to the formation of different proportions of $BaFe_{12}O_{19}$ and $BaFe_2O_4$. which directly affected the magnetic properties. Transmission electron microscopy(TEM) micrographs showed mainly hexagonal-like grains with crystallite sizes ranging from 50 to 150 nm. [10]

2.1.4. Magnetic studies of Sn²⁺-Sn⁴⁺-substituted barium hexaferrites synthesized by mechanical alloying.

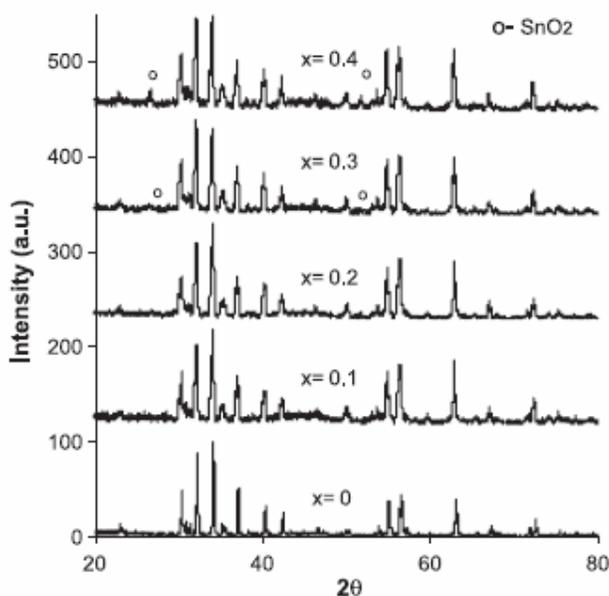


Fig. X-ray diffraction patterns for BaMSn – Sn showing only the magnetoplumbite structure up to x = 0.2.

It was possible to synthesize Sn²⁺-Sn⁴⁺ substituted barium hexaferrites by mechanical alloying. These compounds possess the required micro structure and magnetic properties for high-density magnetic recording applications. The saturation magnetization increased moderately (9%) for small levels of substitution. This enhancement is presumably related to the preferential occupation of Sn²⁺ and Sn⁴⁺ ions in 4f₂ and 4f₁ sites, respectively. By changing the substitution rate x, the coercivity could easily be controlled without a significant reduction of M_s. [11]

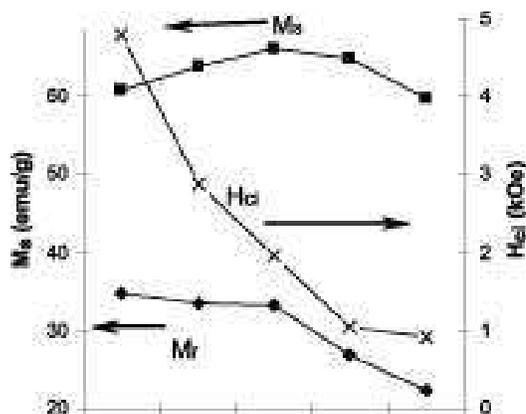


Fig. Saturation (M_s) and remanent (M_r) magnetization and coercivity (H_{ci}) as a function of the substitution.

The magnetic susceptibility (χ) increased with the substitution x , which is believed to relate to the disappearance of some superexchange interactions among the iron ions. The rapid increase in the magnetic susceptibility as well as the large reduction in saturation magnetization at $x > 0.3$ could suggest that a noncollinear magnetic structure occurs due to spin canting. Our results suggest that the Sn^{2+} - Sn^{4+} substitution can be a promising candidate for magnetic recording applications. [12]

2.1.5 Effects of pH and calcination temperatures on the formation of citrate-derived hexagonal barium ferrite particles

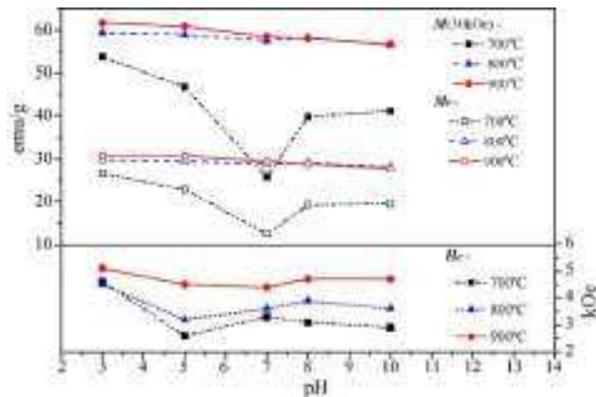


Fig. The magnetizations measured at 30 kOe, the remanence magnetizations, and the coercive forces for the specimens derived from the solutions of different pH values, at three calcination temperatures

The pH of the aqueous solution, being adjusted by NH_4OH addition and containing $\text{Ba}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$ and $\text{C}_3\text{H}_4(\text{OH})(\text{COOH})_3$ in a ratio of 1:12:19, affected the formation temperatures and the magnetic properties of the citrate-derived $\text{BaFe}_{12}\text{O}_{19}$. Without NH_4OH addition, pure barium hexaferrite was not able to form, even at 900 °C. By using the solutions of $\text{pH} > 8$, the nanoparticles with single crystalline barium hexaferrite phase can be obtained at temperatures as low as 650 °C. For the solid precursor prepared from the solution of pH 3, 700 °C was required to form pure barium hexaferrite but the $\text{BaFe}_{12}\text{O}_{19}$ so obtained had better morphological development of its crystallites and exhibited better magnetic properties than those obtained at other pH conditions. Increasing the calcination temperatures

of the solid precursors can increase the purity and crystallinity of $\text{BaFe}_{12}\text{O}_{19}$ and enhance magnetic properties of the resultant $\text{BaFe}_{12}\text{O}_{19}$ nanoparticles. [13]

2.2 Summary

The hexagonal ferrites have been widely studied as potential materials for perpendicular magnetic recording and microwave absorption. For these applications, high saturation magnetization, a suitable coercivity and low temperature coefficients of coercivity and remanence are desired. To obtain good quality of barium ferrite materials, various methods have been used for their preparation and a large number of investigations have been carried out to modify the magnetic parameters by replacing Fe^{3+} with different cationic combination. In order to obtain hexagonal ferrites with improved characteristics for applications in the field of magnetic recording, several substitutions have been done.

Ferrites are the main materials to produce multilayer chip inductors (MLCI) that are the most important passive surfaces mounting devices (SMD) in modern electronic industry. However, the traditional ferrites are far from meeting the requirements of high performance, miniaturization size, light weight and low cost. Recently, there has been a growing interest in Co_2Z ferrite, which is considered an ideal candidate for MLCI, because Co_2Z has high performance (high initial permeability, high quality factor, high resonant frequency and low loss tangent) in hyper-frequencies of 300-1000 MHz. Especially, its high cut-off frequencies up to the 3-GHz region, compared with the 300-MHz ceiling encountered with the spinel ferrites, bring it into the hyper-frequency region useful for chip inductors or beads. [14]

Chapter 3

EXPERIMENTAL WORK

3.1 Introduction

Hexagonal ferrites were prepared by citrate sol-gel auto-combustion method (CSAM). The phase formation process, microstructure and magnetic properties were investigated and compared with those of the samples made by conventional solid-state reaction method (SSRM). The selected material system has stoichiometric composition of $Ba_2Zn_{1.2-x}Co_xCu_{0.8}Fe_{12}O_{22}$, where x was varied from 0 to 1.2. Phase formation was characterized by powder X-ray diffraction (XRD). Frequency spectra of complex permeability were measured via an impedance analyzer. Results reveal auto-combusted powders are about 22 nm and very active. [15] Phase formation temperature and sintering temperature are both 900 °C, much lower than those in SSRM. The sintered samples have fine-grained microstructure. The samples exhibit better magnetic properties in hyper-frequency than those made by SSRM. As zinc content increases, the permeability is enhanced and the cut-off frequency drops. The magnetic properties are also correlated with the sintering temperature and microstructure. Permeability increases with the rise of sintering temperature.

3.2 Synthesis :

3.2.1. Synthesis technique & Experimental procedure

Hexagonal ferrites were prepared by CSAM. Unlike conventional SSRM, analytic reagent grade nitrates, $Fe(NO_3)_3 \cdot 9H_2O$, $Zn(NO_3)_2$ and $Ba(NO_3)_2$, were selected as raw materials. Citrate was slowly added to the mixed solution of nitrates as a chelator. Concentrated ammonia solution was dropped into the solution until the solution was neutral or slightly alkaline (pH 7-8). Then the solution became homogeneous stable sol. The gel was dried in an oven at 120 °C. With the aid of a little amount of ethanol, the obtained dried gel was ignited in an open container. The dry gel was burnt in a self-propagating combustion manner. During auto-combustion, the burning gel expanded rapidly in volume and grew as a dendritic structure. Loose powders were finally formed. The auto-combusted powders were annealed at 900 °C in the air, before ball milled in a ball mill for 24 h using stainless-steel balls and alcohol as media. The resulting powders were pressed in a stainless-steel die under a pressure of 5 MPa with 5 wt.% polyvinyl alcohol as binder-lubricant. The pressed pallets (10 mm diameter, about 3 mm thickness) were kept for sintering in the temperature range of 850-1000 °C for 4h in air . [16]

Calculations for batch composition

3.3.3.1 M-Type Barium hexaferrite

Mol.formula- $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$

Starting raw material- $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Ba}(\text{NO}_3)_2$

Batch composition for 10 gms of $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ --

Mol.wt. of $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3 = 1111.494$

Mol.wt. of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} = 404$

Mol.wt. of $\text{Ba}(\text{NO}_3)_2 = 261.32$

Amount of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ required = $12 \cdot 10 \cdot 404 / 1111.494 = 43.6169$ gm

Amount of $\text{Ba}(\text{NO}_3)_2$ required = $10 \cdot 261.32 / 1111.494 = 2.351$ gm

Since Metal : citrate = 1:1 (mole ratio)

Moles of citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) = 0.1169

Amount of citric acid = mol.wt * moles = $210.148 \cdot 0.1169 = 24.576$ gms.

3.3.3.2 Y- Type Barium hexaferrite

Mol.formula- $2\text{BaO} \cdot 2\text{ZnO} \cdot 6\text{Fe}_2\text{O}_3$

Starting raw material- $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2$ and $\text{Ba}(\text{NO}_3)_2$

Batch composition for 10 gms of $2\text{BaO} \cdot 2\text{ZnO} \cdot 6\text{Fe}_2\text{O}_3$ --

Mol.wt. of $2\text{BaO} \cdot 2\text{ZnO} \cdot 6\text{Fe}_2\text{O}_3 = 1427.66$

Mol.wt. of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} = 404$

Mol.wt. of $\text{Zn}(\text{NO}_3)_2 = 189.4$

Mol.wt. of $\text{Ba}(\text{NO}_3)_2 = 261.32$

Amount of $\text{Zn}(\text{NO}_3)_2 = 2.6533$ gm

Amount of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ required = 33.9578 gm

Amount of $\text{Ba}(\text{NO}_3)_2$ required = 3.6608 gm

Moles of citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) = moles of (Ba+Fe+Zn) = 0.098063

Amount of citric acid = 20.63245 gms.

3.3.3.3 W- Type Barium hexaferrite

Mol.formula- $2\text{BaO} \cdot 2\text{ZnO} \cdot 6\text{Fe}_2\text{O}_3$

Starting raw material- $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2$ and $\text{Ba}(\text{NO}_3)_2$

Batch composition for 10 gms of $2\text{BaO} \cdot 2\text{ZnO} \cdot 6\text{Fe}_2\text{O}_3$ --

Mol.wt. of $\text{BaO} \cdot 2\text{ZnO} \cdot 8\text{Fe}_2\text{O}_3 = 1593.73$

Mol.wt. of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} = 404$

Mol.wt. of $\text{Zn}(\text{NO}_3)_2 = 189.4$

Mol.wt. of $\text{Ba}(\text{NO}_3)_2 = 261.32$

Amount of $\text{Zn}(\text{NO}_3)_2 = 2.3768185$ gm

Amount of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ required = 40.559014 gm

Amount of $\text{Ba}(\text{NO}_3)_2$ required = 1.6396785 gm

Moles of citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) = moles of (Ba+Fe+Zn) = 0.1192174

Amount of citric acid = 25.083341 gms.

3.3.3.4 Z-Type Barium hexaferrite

Mol.formula- $3\text{BaO} \cdot 2\text{ZnO} \cdot 12\text{Fe}_2\text{O}_3$

Starting raw material- $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2$ and $\text{Ba}(\text{NO}_3)_2$

Batch composition for 10 gms of $2\text{BaO} \cdot 2\text{ZnO} \cdot 6\text{Fe}_2\text{O}_3$ --

Mol.wt. of $\text{BaO} \cdot 2\text{ZnO} \cdot 8\text{Fe}_2\text{O}_3 = 2539.19$

Mol.wt. of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} = 404$

Mol.wt. of $\text{Zn}(\text{NO}_3)_2 = 189.4$

Mol.wt. of $\text{Ba}(\text{NO}_3)_2 = 261.32$

Amount of $\text{Zn}(\text{NO}_3)_2 = 1.4917$ gm

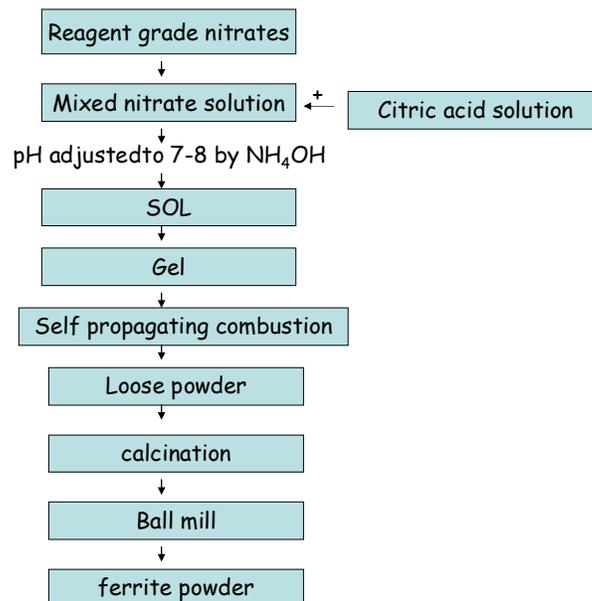
Amount of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ required = 19.0914 gm

Amount of $\text{Ba}(\text{NO}_3)_2$ required = 3.0872 gm

Amount of citric acid = 24.0281 gms.

Powder X-ray diffraction (XRD) was applied to characterize the phase composition of the powder samples (raw and calcined) treated under different conditions using a X-ray diffractometer equipped with Cu K α radiation ($\lambda = 0.15405$ nm). [17]

Flow chart of synthesis of raw powder.



3.3 General characterization

3.3.1 Phase formation process

A series of XRD patterns show the phase formation process of the ferrite samples prepared by CSAM. After auto-combustion, the main phases of resulting powders are simple compounds, such as spinel ferrites and BaCO_3 . That indicates that Y-type phase cannot be formed directly after auto-combustion due to its complex crystal structure. According to the compositions, spinel ferrites include ZnFe_2O_4 , CuFe_2O_4 , CoFe_2O_4 and Fe_3O_4 . With the rise of annealing temperature, BaCO_3 reacts with Fe_3O_4 to form BaFe_2O_4 . After annealed at $750\text{ }^\circ\text{C}$, BaCO_3 disappears and BaFe_2O_4 become one of the main phases in the samples. While the temperature more increases, BaFe_2O_4 react with other spinel ferrites to form complex compound, Y-type hexaferrite. When the annealing temperature rises to $800\text{ }^\circ\text{C}$, Y-type hexagonal ferrite begins to form. Some BaFe_2O_4 and spinel ferrites do not react completely and remain in the samples. The results show that well-defined Y-type phase is formed at $900\text{ }^\circ\text{C}$. Fig. 2 indicates that there is a pure Y-type hexagonal ferrite crystalline phase for each composition in the samples. CSAM lowers the phase formation temperature of Y-type ferroplana markedly whereas Y-type phase was formed over $1000\text{ }^\circ\text{C}$ in SSRM. [18]

3.3.2 Particle size

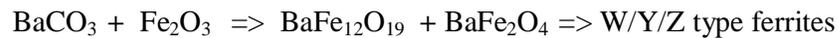
The particle size of the powders was calculated according to Scherrer equation. The auto-combusted powders have average size of about 22 nm . After annealed, the granularity will augment with the rise of temperature and prolongation of annealing time. Highly active powders can be obtained by controlling the annealing process strictly. The particle size of the sample annealed at $800\text{ }^\circ\text{C}$ is about 72 nm , while that of the sample annealed at $900\text{ }^\circ\text{C}$ is about 88 nm . Large surface energy endows the nano sized powders with high activity so that the phase formation temperature and sintering temperature are much lower than those in SSRM. [19]

Chapter 4

RESULTS AND DISCUSSION

4.1 Results and Discussion

As fig. shows M-type ferrite contains mainly iron oxide Fe_2O_3 & other three ferrites contains iron oxide as well as BaCO_3 , where as Z-type ferrite shows very little amount of phase formation. when material is calcined at 900°C for 4 hrs, the XRD Analysis shows that M-type ferrite phase formation is nearly completed as shown in fig. The W, Y and Z type ferrites shows the presence of M-type ferrite and Barium ferrite. Amount of barium ferrite increase gradually in W, Y and Z type ferrites respectively. So it can be concluded that W, Y and Z type ferrites forms via the following reaction route.



Chapter 5

CONCLUSION AND REFERENCES

CONCLUSION:

- (1) The auto-combusted powders are nano-sized and highly active. After annealed at 900 °C, pure Y-type hexagonal ferrite can be formed, while the phase formation temperature of Y-type phase by SSRM is 1000 °C.
- (2) The samples fabricated by CSAM can be sintered well under 900 °C without any addition, about 100 °C lower than that by SSRM.
- (3) As Co^{2+} content rises, saturation magnetization decreases and magnetic planar anisotropy increases. That determines the decrease of permeability // with rise of Co concentration. The cut-off frequency is in inverse proportion to permeability according to Snoek's Law.
- (4) For the same composition, the samples made by SSRM exhibit higher permeability than those via CSAM.
- (5) Permeability increases with the rise of sintering temperature.

Y-type hexagonal ferrites obtained by sol-gel auto-combustion method have low sintering temperature (equal to or less than 900 °C). It meets the need of LTCC technique to co-fire with Ag electrode without any addition. They exhibit excellent magnetic properties, such as high permeability and high cut-off frequency, in hyper-frequency. It is suitable to fabricate high quality multi-layer chip device for hyper-frequency.

During preparation of Z-type hexaferrite by conventional ceramic processing methods other types (M,Y,& W) forms,so sol-gel method is suggested to form single phase Z-type hexaferrite.

REFERENCES

- [1] Jen-Yan Hsu, IEEE Trans. Magn. 30 (1994) 4096.
- [2] J. Smit, H.B.J. Wijn, Ferrites, Cleaver-Hume Press, London, 1959.
- [3] Y. Bai, J. Zhou, Z. Gui, L. Li, J. Magn. Magn. Mater. 246 (2002) 140.
- [4] S.G. Lee, S.J. Kwon, J. Magn. Magn. Mater. 153 (1996) 279.
- [5] A. Nakono, Proc. ICF-6 (1995) 1225.
- [6] Hongguo Zhang, Zhenwei Ma, Ji Zhou, Zhenxing Yue, Zhilun Gui (1995) 225
- [7] Y Bai, J. Zhou, Z. Gui, L. Li, Mater. Lett. 58 (2004) 1602.

- [8] T. Gonzalez-Carreno, M.P. Morales, C.J. Serna, Mater. Lett. 43 (2000)
- [9] J. Huang, H. Zhuang, W. Li, Mater. Res. Bull. 38 (2003) 149
- [10] J. Magn. Magn. Mater. 140-144 (1995) 2209.
- [11] W. Lee, T. Fang, J. Mater. Sci. 30 (1995) 4349
- [12] J. Lipka, A. Gruskova, M. Michalikova, M. Miglierini, J. Slama, I. Toth

- [13] H. Kojima, in: E.P. Wohlfarth (Ed.), Ferromagnetic Materials, vol. 3, North-Holland, New York, 1982 (Chapter 5).
- [14] G. Pouillard, M.S. Alam, M.C. Trinel-Dufour, P. Perrot, J. Chem. Res. Symp. 5 (1981) 136.
- [15] T. Gonzalez-Carrefio, M.P. Morales, C.J. Serna, Mater. Lett. 43 (2000) 97.
- [16] W. Zhong, W.P. Ding, N. Zhang, J.M. Hong, QJ. Yan, YW. Du, J. Magn. Magn. Mater. 168 (1997) 196.
- [17] K. Haneda, C. Miyakawa, H. Kojima, J. Am. Ceram. Soc. 57 (1974) 354.
- [18] R.H. Arendt, J. Solid State Chem. 8 (1973) 339.
- [19] M.L. Wang, Z.W. Shih, J. Crystal Growth 114 (1991) 435.