

DEVELOPMENT OF MAGNETODIELECTRIC MATERIALS
TO BE USED IN ADDITIVE MANUFACTURING PROCESSES
FOR HIGH-FREQUENCY APPLICATIONS

by

Paul Emerson Parsons II

A thesis submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Master of Science in Materials Science and Engineering

Winter 2016

© 2016 Paul Parsons
All Rights Reserved

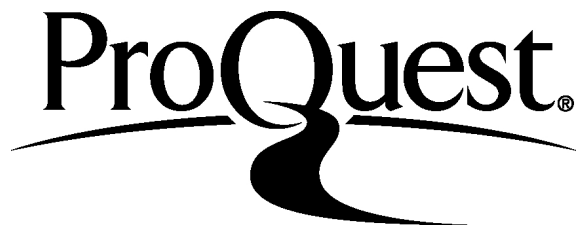
ProQuest Number: 10055518

All rights reserved

INFORMATION TO ALL USERS

The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



ProQuest 10055518

Published by ProQuest LLC (2016). Copyright of the Dissertation is held by the Author.

All rights reserved.

This work is protected against unauthorized copying under Title 17, United States Code
Microform Edition © ProQuest LLC.

ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 - 1346

DEVELOPMENT OF MAGNETODIELECTRIC MATERIALS
TO BE USED IN ADDITIVE MANUFACTURING PROCESSES
FOR HIGH-FREQUENCY APPLICATIONS

by

Paul Emerson Parsons II

Approved: _____
Robert L. Opila, Ph.D.
Co-Professor in charge of thesis on behalf of the Advisory Committee

Approved: _____
Mark S. Mirotznik, Ph.D.
Co-Professor in charge of thesis on behalf of the Advisory Committee

Approved: _____
Darrin Pochan, Ph.D.
Chair of the Department of Materials Science and Engineering

Approved: _____
Babatunde A. Ogunnaike, Ph.D.
Dean of the College of College Engineering

Approved: _____
Ann L. Ardis, Ph.D.
Interim Vice Provost for Graduate and Professional Education

ACKNOWLEDGMENTS

I would like to thank my advisors, Profs. Mark “Big Dog” Mirotznik and Robert Opila, for their direction in this work. I would also like to thank my comrades-in-arms, the degenerates of Evans 135, Austin Good, Zach Larimore, Matthew Mills, and Dr. Peter Pa for supplying me with one of the best lab groups to work with over the past year.

I would specifically like to thank Zach for his contribution by utilizing the nScript to print some amazing devices, and Peter with his guidance regarding HFSS modeling. I would like to thank Matt, S. Garrett, N. Hudak, A. Lu, and M. Malchester for their assistance in synthesizing, washing, and spinning down the materials in the centrifuge, and Robert Schmidt for his help with procuring TEM images.

I would like to dedicate this work to my fiancée, Sarah, who fully encouraged me to walk this path and supported me every step of the way.

TABLE OF CONTENTS

LIST OF TABLES	vi
LIST OF FIGURES	vii
ABSTRACT	xii

Chapter

1	INTRODUCTION	1
1.1	Motivation	1
1.2	Additive Manufacturing	2
1.3	Thesis Outline.....	4
2	MAGNETIC MATERIALS	5
2.1	Magnetism in Materials	5
2.2	Ferrites	7
2.2.1	Spinel Crystalline Structure	7
2.2.2	Soft Magnetic Materials for High-Frequency Applications	10
3	MAGNETODIELECTRIC MATERIALS SYNTHESIS	12
3.1	Synthesis Techniques	12
3.2	Polyol Reduction	15
3.3	Solid-State Ceramics Method.....	20
3.4	Magnetodielectric Composite Materials.....	22
3.5	Magnetodielectric Materials Synthesis Conclusion	23
4	CHARACTERIZATION TECHNIQUES.....	25
4.1	Powder X-Ray Diffraction	25
4.2	Electron Microscopy	28
4.2.1	Scanning Electron Microscopy.....	29
4.2.2	Transmission Electron Microscopy	30
4.3	Vibrating Sample Magnetometry	32
4.4	High-Frequency Electromagnetic Characterization	34
4.4.1	Impedance Analyzer	35
4.4.2	Vector Network Analyzer.....	36
4.5	Characterization Conclusion	40

5	RESULTS AND DISCUSSION.....	41
5.1	X-ray Diffraction	41
5.2	Electron Microscopy	43
5.3	Magnetometry.....	50
5.4	High-Frequency Electromagnetic Properties	58
5.4.1	Materials Properties	58
5.4.2	Demagnetizing Factor of Magnetodielectric Materials	67
5.4.3	Loss Mechanisms of Magnetodielectric Materials.....	70
5.5	Conclusion.....	72
6	ADDITIVELY MANUFACTURED SPIRAL ANTENNA	73
6.1	Antenna Design	73
6.2	Spiral Antenna Fabrication using Additive Manufacturing and Results.	78
6.3	Additively Manufactured Spiral Antenna Conclusion	80
7	CONCLUSION	81
7.1	Summary of Results	81
7.2	Future Work.....	83
	REFERENCES	84
	Appendix	
	CHEMICAL REAGENTS USED IN STUDY	88

LIST OF TABLES

Table 3.1	Categorized synthesis methods of magnetodielectric materials.....	24
Table 5.1	Powder diffraction data of synthesized MDM.	42
Table 5.2	Magnetization data of synthesized MDM.	58
Table 5.3	Averaged high-frequency properties of MDM-composite materials from 50 MHz – 1 GHz.	67
Table 5.4	Demagnetization factors for basic shapes.	69
Table 6.1	MDM-composite material requirements for specified designs of Archimedian Spiral Antenna.	77

LIST OF FIGURES

Figure 1.1	The nScrypt 3Dn-300 micro-dispensing printer.....	3
Figure 1.2	Printing platform of the nScrypt 3Dn-300 with both ink-dispensing (Smart Pump TM) and thermoplastic-dispensing (nFD TM) print heads.	4
Figure 2.1	Magnetic moments indicated by domains in a paramagnet. In (a), the moments are randomly oriented, and in (b), the moments are oriented in the direction of the applied field, adapted from Goldman (2006).....	6
Figure 2.2	Representation of (a) ferromagnetic, (b) antiferromagnetic, and (c) ferrimagnetic structures.	6
Figure 2.3	Representation of (a) mixed spinel (b) octahedral cell with B-site and (c) tetrahedral cell with A-site structures.	8
Figure 2.4	Magnetic moment of $M_xZn_{1-x}Fe_2O_4$, where $M = Ni^{2+}$, Mn^{2+} , and Co^{2+} , where the solid lines represent simulated values and the dots represent measured results.	9
Figure 3.1	Example of a system of (a) monodisperse set of particles and (b) polydisperse particles.	12
Figure 3.2	Nucleation of particles over time in a monodisperse reaction, where all of the particles grow at the same rate.	14
Figure 3.3	Nucleation of particles over time in a polydisperse reaction, where multiple nucleation stages are present, resulting in different growth rates.	14
Figure 3.4	Polyol reduction reaction setup in fume hood.....	15
Figure 3.5	Color change of EG/NaOH solutions where the solution is at (a) room temperature, and (b) reflux.....	16
Figure 3.6	Color change of (a) EG/NaOH/ $FeCl_3$ solution after adding precursor and (b) dried powder.	17
Figure 3.7	Color change of (a) EG/NaOH/Fe-Ni-Zn solution and (b) corresponding powder after drying.	19
Figure 3.8	Color change of (a) DEG/NaOH/Fe-Ni-Zn solution and (b) corresponding powder after drying.	20

Figure 3.9	Solid state ceramics synthesis of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ materials in (a) the precalcined and (b) post-calcined state.	22
Figure 3.10	Stainless steel milling jar and YSZ milling media.	22
Figure 3.11	Disc composite samples of $\text{Fe}_3\text{O}_4/\text{EPON}$ in MDM volume loadings of (a) 0%, (b) 10%, (c) 20%, (d) 30%, and (e) 40%.	23
Figure 4.1	Diffraction of x-rays by a crystal, adapted from Cullity (1967).	26
Figure 4.2	Bruker D8 ADVANCED x-ray diffractometer.	28
Figure 4.3	Resultant scattering from the focused electron bean interacting with sample surface using an SEM.	29
Figure 4.4	JEOL JSM 6330f Field Emission Scanning Electron Microscope.....	30
Figure 4.5	Interaction of electron beam with sample in transmission electron microscopy.	31
Figure 4.6	JEOL JEM-3010 Transmission Electron Microscope.....	32
Figure 4.7	Quantum Design Versalab VSM.....	34
Figure 4.8	Agilent E4991A Impedance Analyzer with 16453A/16454A test fixtures.....	36
Figure 4.9	Agilent E8361C Vector Network Analyzer with 16454A Magnetic Materials Test Fixture coupled to a 16201A 7 mm Terminal Adapter Kit.	37
Figure 4.10	MDM-composite sample to be measured using the magnetic test fixture.	38
Figure 4.11	Reflection Loss Sensitivity as a function of impedance, $ Z_x $, adapted from Agilent Technical Note 1369-2 (2001). As $ Z_x $ deviates from 50 Ω , the sensitivity dramatically decreases.	39
Figure 4.12	Permeability spectra of measurement setup with and without the terminal adapter compared to the impedance analyzer measurement.	40

Figure 5.1	Powder diffraction plot of all MDM synthesized in this thesis, where (a) is the JCPDS 8-324 $M\cdot Fe_2O_4$ standard pattern, (b) is Fe_3O_4 , (c) is EG-reduced $Ni_{0.5}Zn_{0.5}Fe_2O_4$, (d) is DEG-reduced $Ni_{0.5}Zn_{0.5}Fe_2O_4$, and (e) is the conventional solid-state processed $Ni_{0.5}Zn_{0.5}Fe_2O_4$ with corresponding Miller indices.....	42
Figure 5.2	SEM image of Fe_3O_4 sub-micron agglomerates with corresponding scale bar of 1 μm	43
Figure 5.3	TEM image of Fe_3O_4 particles with corresponding scale bar of 20 nm..	44
Figure 5.4	SEM image of EG-reduced $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles with corresponding scale bar of 1 μm	45
Figure 5.5	TEM image of EG-reduced $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles with corresponding scale bar of 20 nm.....	46
Figure 5.6	SEM image of DEG-reduced $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles with corresponding scale bar of 100 nm.....	47
Figure 5.7	TEM image of DEG-reduced $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles with corresponding scale bar of 20 nm.....	48
Figure 5.8	SEM image of solid-state processed $Ni_{0.5}Zn_{0.5}Fe_2O_4$ particles with corresponding scale bar of 1 μm	49
Figure 5.9	SEM image of solid-state processed $Ni_{0.5}Zn_{0.5}Fe_2O_4$ particles after 24 hr of milling with corresponding scale bar of 1 μm	50
Figure 5.10	Magnetization curves of Fe_3O_4 at 300 K and 50 K with corresponding inset displaying differences in coercivities between the two measurements.	51
Figure 5.11	Magnetization curves of EG-reduced $Ni_{0.5}Zn_{0.5}Fe_2O_4$ at 300 K and 50 K.	52
Figure 5.12	Magnetization curves of DEG-reduced $Ni_{0.5}Zn_{0.5}Fe_2O_4$ at 300 K and 50 K.	53
Figure 5.13	Magnetization curves of solid-state ceramics synthesized $Ni_{0.5}Zn_{0.5}Fe_2O_4$ at 300 K and 50 K.	54
Figure 5.14	Magnetization curves of solid-state ceramics synthesized $Ni_{0.5}Zn_{0.5}Fe_2O_4$ at 300 K using the as prepared powder and powder milled after 24 hrs.....	55

Figure 5.15	Dependence of coercivity as a function of particle size for various soft magnetic alloys, adapted from Herzer (1997).	56
Figure 5.16	Magnetization curves comparisons of the various synthesis techniques at 300 K.	57
Figure 5.17	Vector network analyzer measurements the relative permeabilities and magnetic loss tangents of the $\text{Fe}_3\text{O}_4/\text{EPON}$ composites with filler volumetric loadings of 10 – 40 %.	59
Figure 5.18	Impedance analyzer measurements the relative permittivities and dielectric loss tangents of the $\text{Fe}_3\text{O}_4/\text{EPON}$ composites with filler volumetric loadings of 10 – 40 %.	60
Figure 5.19	Vector network analyzer measurements the relative permeabilities and magnetic loss tangents of the EG-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ composites with filler volumetric loadings of 10 – 40 %.	61
Figure 5.20	Impedance analyzer measurements the relative permittivities and dielectric loss tangents of the EG-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ composites with filler volumetric loadings of 10 – 40 %.	62
Figure 5.21	Vector network analyzer measurements the relative permeabilities and magnetic loss tangents of the DEG-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ composites with filler volumetric loadings of 10 – 40 %.	63
Figure 5.22	Impedance analyzer measurements the relative permittivities and dielectric loss tangents of the DEG-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ composites with filler volumetric loadings of 10 – 40 %.	64
Figure 5.23	Vector network analyzer measurements the relative permeabilities and magnetic loss tangents of the Solid-State $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ composites with filler volumetric loadings of 10 – 40 %.	65
Figure 5.24	Impedance analyzer measurements the relative permittivities and magnetic loss tangents of the Solid-State $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ composites with filler volumetric loadings of 10 – 40 %.	66
Figure 5.25	Example of frequency response of dielectric mechanisms, adapted from Agilent Technologies (2005).	72
Figure 6.1	Modeled 585 MHz Archimedean spiral antenna designed using HFSS.	74

Figure 6.2	Simulated Return Loss of modeled 585 MHz Archimedean spiral antenna.....	75
Figure 6.3	Modeled Archimedean spiral antenna designs with variably-loaded magnetic material configurations as (a) inverted spiral, (b) trimmed inverted spiral, (c) 42 mm outer radius trimmed inverted spiral, and (d) 22 mm outer radius trimmed inverted spiral incorporating the MDM/EPON composites in HFSS.....	76
Figure 6.4	Simulated Return Loss of Archimedean spiral antenna with 42 mm outer radius trimmed spiral using HFSS with peak shift to 542 MHz. ...	77
Figure 6.5	Simulated Return Loss comparison of antenna designs using different geometries with the same MDM-composite material.	78
Figure 6.6	Printed Archimedean spiral antenna with MDM/EPON composite material with the (a) bottom and (b) top profiles shown.	79
Figure 6.7	Measured return loss data of MDM/EPON composite-loaded spiral antenna compared to simulated data. The substrate had significant bowing and required flattening.....	80

ABSTRACT

Electrical devices for very-high frequency (VHF, 0.03 – 0.3 GHz) and ultra-high frequency (UHF, 0.3 – 3.0 GHz) are commonly used for communications. However, the wavelengths, λ , of these frequency bands correspond to lengths between 10 and 0.1 m, resulting in prohibitively large devices. Materials with an index of refraction, n , greater than 1 can be used to effectively shrink these devices by a factor of $1/n$. In this thesis, magnetodielectric materials (MDM), where $n \geq 1$, have been made to be used in additive manufacturing processes with strict particle size requirements and were developed using various methods, such as polyol reduction and conventional ceramic solid state processing. These materials were characterized using x-ray diffraction (XRD), scanning and transmission electron microscopy (SEM and TEM), vibrating sample magnetometry (VSM), to determine their crystalline, physical, and direct current (DC) magnetization properties. The techniques used to synthesize the MDM yielded particles that were chemically similar, but had drastically different physical properties which heavily influences their high-frequency electromagnetic properties. These materials were then uniformly dispersed into a non-conducting medium, such as a low-electrical loss polymer or resin, and formed into composite samples with variable volumetric loading. These composite samples were measured using several techniques to characterize the frequency-dependent electromagnetic (EM) properties, such as relative permeability, relative permittivity, and their respective losses. Finite element method (FEM) simulations were performed using these MDM-composites to design a spiral antenna to be used at approximately 585 MHz.

Chapter 1

INTRODUCTION

1.1 Motivation

Magnetic materials, specifically, nanoparticles, are experiencing a surge of interest for a variety of uses pertaining to fields such as biomedicine¹, communications², magnetic recording³, and sensor technologies⁴. These materials are very important for high-frequency applications, specifically in communications, where the materials properties can ultimately help dictate the physical size of these devices. As frequency increases, the corresponding wavelength decreases; however, at microwave frequencies below 3 GHz, the wavelength propagating in air is 10 cm. For devices designed to operate at sub-1 GHz, the corresponding wavelengths are prohibitively large. Some of the efforts to decrease the size of these devices involves manipulating materials properties, such that the index of refraction, n ,

$$n = \sqrt{\mu_r \epsilon_r} \quad (1.1)$$

where μ_r is the relative permeability, and ϵ_r is the relative permittivity and is modified in order to reduce the effective wavelength, λ_{eff} ,

$$\lambda_{\text{eff}} = \frac{c}{fn} \quad (1.2)$$

where c is the speed of light, and f is frequency⁵. Magnetodielectric materials (MDM), where $\mu_r, \epsilon_r < 1$, offer the unique feature by reducing the wavelength, but not necessarily changing the impedance, Z , of the material through the relation:

$$Z = \sqrt{\frac{\mu_r}{\epsilon_r}}. \quad (1.3)$$

These properties can be altered by various means, such as chemical substitution and processing of materials where the physical traits yield different properties.

Composite materials are a class of materials of two or more significantly different properties that form a new material containing some of the properties of its constituents. Through controlled, volumetric loading of MDM into a non-magnetic host, such as a resin or polymer, the electromagnetic (EM) properties of the device can be tailored while meeting additional requirements, such as lighter weight, mechanical stability, or chemical resistance. These multifunctional composite materials offer attractive solutions for certain commercial and defense-oriented applications and will be utilized in additive manufacturing processes to produce devices that are difficult to fabricate using conventional manufacturing methods.

1.2 Additive Manufacturing

Additive manufacturing (AM) is a process where parts are made through successively adding layers of material upon one another to form a specific geometry. It differs from conventional subtractive manufacturing methods in this case, material is added, not removed, greatly reducing the amount of wasted material. Surging in popularity, AM is transitioning from hobbyist kits to an industrially important tools as the technology to produce intricate geometries is becoming more advanced and commercially available. However, as the technology has improved and the capability to print functionalized EM devices has made progress^{6, 7}, many more applications are currently not practical. The main bottleneck to applying AM to more advanced EM devices is materials, specifically, the lack of specialized materials to produce these

devices. In this thesis, we develop materials to enable the printing of advanced EM devices using the nScript 3Dn-300 micro-dispensing printer⁸, seen in Fig. 1.1.



Figure 1.1 The nScript 3Dn-300 micro-dispensing printer.

The nScript printer allows researchers to provide their own material to print, and is a material agnostic platform capable of dispensing materials with a range of viscosities from water to clay. This device has two dispensing heads (Fig. 1.2), capable of printing both custom-made inks and thermoplastics with printed features down to 25 μm with 1 μm spacing.

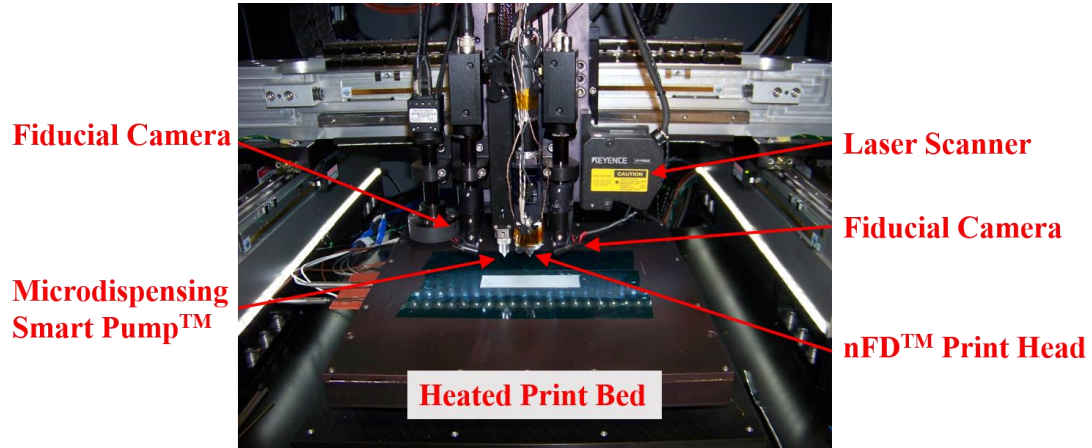


Figure 1.2 Printing platform of the nScript 3Dn-300 with both ink-dispensing (Smart Pump™) and thermoplastic-dispensing (nFD™) print heads.

Using both print heads, it is possible to print multiple materials in a single process. The design requirements of the custom materials are composite materials where particle diameters do not exceed 5 μm , to prevent the dispensing orifice from clogging. MDM-composites materials with tunable electromagnetic properties are to be printed using the nScript 3Dn-300.

1.3 Thesis Outline

In Chapter 2, a background on the mechanisms of magnetism of materials is provided. In Chapter 3, the methods of synthesizing the MDM and MDM-composite materials are provided. Chapter 4 describes the characterization methods, such as x-ray diffraction, magnetometry, microscopy and high-frequency electromagnetics are described. Chapter 5 involves the measurement results and discussion of their significance. In Chapter 6, a spiral antenna was designed, then fabricated using additive manufacturing and results will be discussed. To conclude, Chapter 7 will summarize the work and detail future work.

Chapter 2

MAGNETIC MATERIALS

2.1 Magnetism in Materials

Magnetic properties in materials originates from electron spins, which are unpaired, in valence electrons in individual atoms. The arrangement of these spins allows crystal structures to exhibit a variety of magnetic properties that are useful in different applications. How these crystal structures react to applied magnetic fields, such as magnetizing, or maintaining magnetization also determines suitability for applications. There are typically two main branches of magnetism when referring to classes of materials: diamagnetism and paramagnetism. Diamagnetic materials do not contain intrinsic magnetic moments, and exhibit a negative susceptibility, χ , where:

$$\chi = \frac{M}{H} \quad (2.1)$$

M is the magnetization, and H is the applied field⁹. On the other hand, paramagnets do possess intrinsic magnetic moments and these moments are aligned in a magnetic field, exhibiting a positive χ and are shown in Fig. 2.1. How these moments align, couple, and interact with one another are the branching modes of paramagnetism into ferromagnetism, antiferromagnetism, ferrimagnetism, and superparamagnetism.

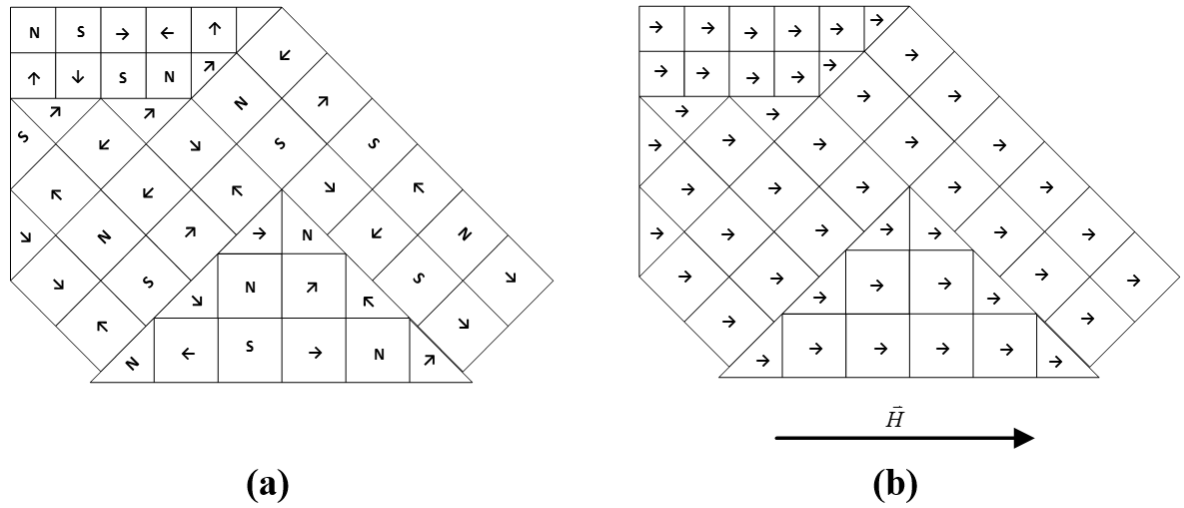


Figure 2.1 Magnetic moments indicated by domains in a paramagnet. In (a), the moments are randomly oriented, and in (b), the moments are oriented in the direction of the applied field, adapted from Goldman (2006).

Exchange coupling describes the interaction between neighboring atoms and how these atoms interact through attractive or repulsive forces. The energy of the system will attempt to minimize, resulting in parallel or antiparallel alignments of the spins depending on the distance between atoms, which will give rise to ferro-, anti-ferro-, or ferrimagnetism and these alignments are shown in Fig. 2.2.

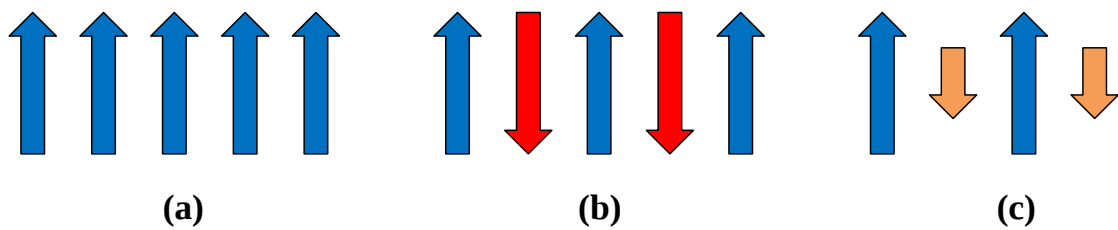


Figure 2.2 Representation of (a) ferromagnetic, (b) antiferromagnetic, and (c) ferrimagnetic structures.

These coupled interactions are quite strong, but can be disrupted by high temperatures¹⁰. If the temperature exceeds the Curie temperature, T_C , of a ferromagnet, the material will transition from a ferromagnetic (where the magnetic domains are ordered) to a paramagnetic material (randomly ordered magnetic domains). The analog for antiferromagnets is the Néel temperature, T_N and both of these temperatures are compositionally specific.

Ferrimagnetism is quite similar to ferromagnetism, despite the anti-parallel spins and is expressed in magnetic metal oxide systems. In spinel ferrites of the $M \cdot Fe_2O_4$ structure, M^{2+} (a metal such as Ni, Zn, Co, Mn, etc.), will occupy a tetrahedral site, where the Fe^{3+} will occupy an octahedral site. Generally, a magnetic moment will not cancel out from the combination of (a) more octahedral sites than tetrahedral sites, and (b) Fe^{3+} will have a larger spin moment which results in a net magnetic moment. Ferromagnetic materials, specifically spinel ferrites will be investigated.

2.2 Ferrites

In this section, the crystalline structure of the ferrites used in this investigation will be discussed, and followed up with the applicability towards high-frequency devices.

2.2.1 Spinel Crystalline Structure

Spinel ferrites are a class of oxide materials that follow the crystalline structure of the $MgAl_2O_4$ natural spinel. Generally, the most commercially important spinels are synthetic, yet historically, one of the most useful magnetic materials is a natural-occurring oxide, Fe_3O_4 . The spinel is composed of neighboring octahedral (B) and tetrahedral (A) sites seen in Fig. 2.3. In these cells, metal cations (8 in A-sites, and 16

in B-sites) are surrounded by O^{2-} anions (32 ions), for a total of 56 ions¹¹. The interstitial sites, A and B, are surrounded by 4 and 6 O^{2-} ions, respectively. For $Ni_xZn_{1-x}Fe_2O_4$ ferrites, these spinels can turn into *normal* spinels or *inverse* spinels based upon the amount of Ni or Zn in the structure.

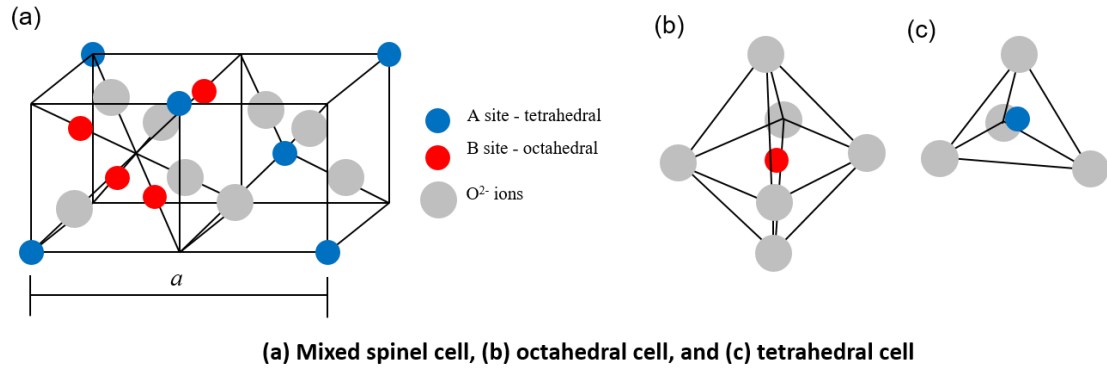


Figure 2.3 Representation of (a) mixed spinel (b) octahedral cell with B-site and (c) tetrahedral cell with A-site structures.

For normal spinel structures, the divalent M^{2+} ion occupies the A site, where trivalent Fe^{3+} occupies the B site¹². However, in inverse spinels, half of the Fe^{3+} ions occupy the A-sites, while the remaining Fe^{3+} and M^{2+} ions occupy the B-sites. In most cases, Zn^{2+} ions prefer the tetrahedral positions and produce normal spinels, while Ni^{2+} ions prefer the octahedral positions and produce inverse spinels¹³. Normal and inverse spinel structures can be combined, resulting in a mixed spinel structure. Controlling the amount of Ni^{2+} ions, we can preferentially tailor the spinel structure to an *inverse* type (Ni-rich) or *normal* type (Zn-rich). It has been shown that by combining mixed ferrites using a non-magnetic oxide, such as Zn ferrite, with an inverse spinel will sometimes result in an increased molar magnetic moment, expressed as:

$$M = \{(1 + x)5 + (1 - x)n\}\mu_B - (1 - x)5\mu_B \quad (2.2)$$

where M is the molar magnetic moment, n is the magnetic moment contribution by M^{2+} , x is the mole fraction, and μ_B is the Bohr magneton. Using the magnetic moments of ions such as Ni^{2+} , Mn^{2+} , and Co^{2+} (2.3, 5 and 3.5 μ_B , respectively), we can see the theoretically predicted values of the magnetic moments of increasing values in Fig. 2.4.

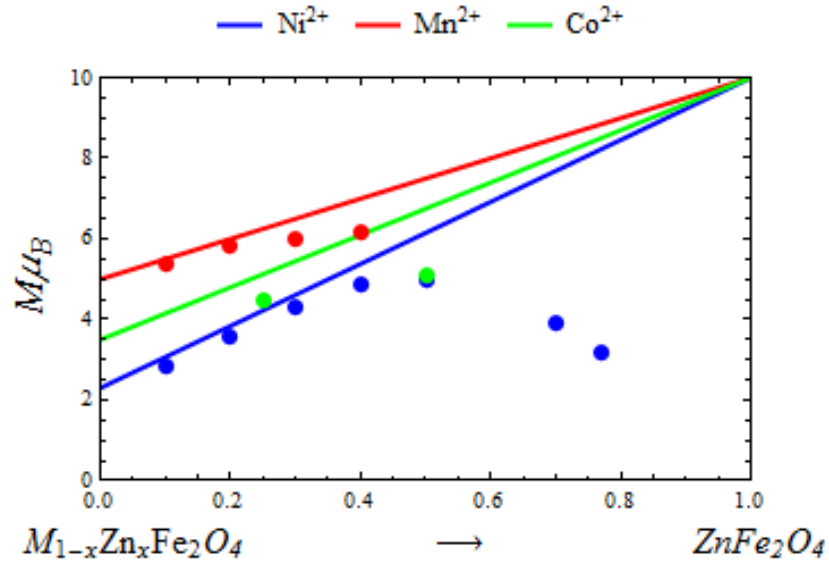


Figure 2.4 Magnetic moment of $M_xZn_{1-x}Fe_2O_4$, where $M = Ni^{2+}$, Mn^{2+} , and Co^{2+} , where the solid lines represent simulated values and the dots represent measured results.

We expect an increasing value of the magnetic moment as x increases; however, it has been experimentally observed that as the solid solution becomes more Zn-rich it becomes more antiferromagnetic, resulting in a decrease of the magnetic moment at high x . This behavior has been explained by Ishikawa as the formation of superparamagnetic spin clusters produced by the breaking of exchange paths by non-magnetic Zn ions¹⁴. It has been shown that the highest magnetic moment of the Ni_xZn_{1-x}

$x\text{Fe}_2\text{O}_4$ system resides approximately at $x = 0.5$ ¹⁵. The magnetization, M , of these materials is related to the permeability, μ , through:

$$M = \chi_m H \quad (2.3)$$

where H is the magnetizing field, and χ_m is the susceptibility, which can be further related to the magnetic flux density, B ,

$$B = \mu H \quad (2.4)$$

This can be rearranged to find the permeability, μ , where,

$$\mu = \frac{B}{H} \quad (2.5)$$

For the complex permeability, this is further expressed by the following relation,

$$\mu^* = \frac{B_0 e^{j(\omega t - \delta)}}{H_0 e^{j\omega t}} = \frac{B_0}{H_0} e^{-j\delta} \quad (2.6)$$

where j is the imaginary unit, δ is the phase delay from B from H , which can be transformed using the Euler relation, to find μ^* ,

$$\mu^* = \mu' - j\mu'' \quad (2.7)$$

2.2.2 Soft Magnetic Materials for High-Frequency Applications

Ferrites have been extensively researched to be used in high-frequency applications due to their high relative permeability and low losses¹⁶. The $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ system is classified as a soft magnetic material due to its low coercivity. Unlike hard magnets, such as NdFeB, where the coercive field strengths are higher than 10k Oe (or 1 T), which makes them suitable for permanent magnets, soft magnet have a much smaller coercivity, up to 100 Oe (or 0.01 T). These coercivities allow for the quick switching of magnetic fields within the material, which lends to the favorable properties of high-frequency, or quickly switching, applications¹⁷. These ferrites can maintain a

relative permeability greater than 1 at frequencies up to 1 GHz, and their high resistivity, contributed by the presence of O^{2-} ions, reduces the effect of eddy currents at these frequencies. For conductive materials, as most magnetic materials are, eddy current are the dominant loss mechanism at high frequencies, which can be attributed to the skin depth, δ ,

$$\delta = \sqrt{\frac{1}{\pi \mu_r \mu_0 f \rho}} \quad (2.8)$$

where μ_r is the relative permeability, μ_0 is the permeability of free space, f is the AC frequency, and ρ is the resistivity of the material. Materials with a high resistivity have a much larger skin depth than materials with a low resistivity at microwave frequencies. There are ferrites that work at frequencies higher than 1 GHz, such as hexaferrites or thin film yttrium-iron-garnet (YIG), but these will not be the subject of this thesis.

Chapter 3

MAGNETODIELECTRIC MATERIALS SYNTHESIS

3.1 Synthesis Techniques

Magnetodielectric nanoparticles (MDMNP) were synthesized using a polyol reduction technique¹⁸⁻²¹. Polyol reduction is also referred to as a forced hydrothermal process, where crystalline complex oxides are formed in aqueous solution at raised temperatures and/or pressures. Aqueous mixtures containing polyols, such as ethylene glycol and higher order glycols (di-ethylene glycol, triethylene glycol, etc.) will allow higher-temperature reactions, rather than solutions without these polyols, which require to be run in a closed reaction vessel. This was one of the procedures selected for study due to the ability to produce monodisperse crystalline nanoparticles.

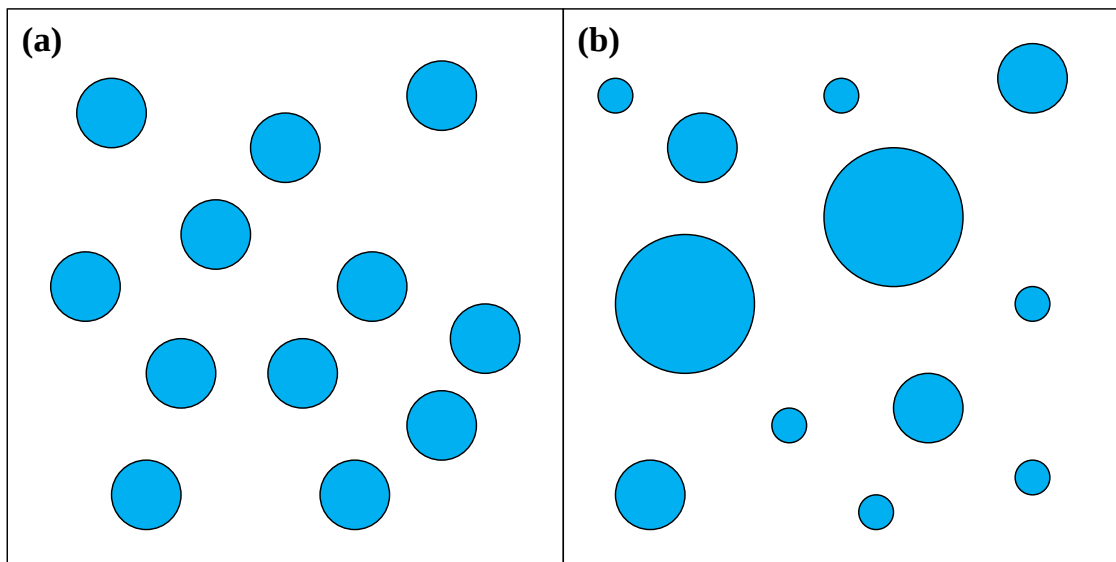


Figure 3.1 Example of a system of (a) monodisperse set of particles and (b) polydisperse particles.

Previous work has been performed using a water-based co-precipitation technique that also produced $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ nanoparticles, but ended up in resulting a highly polydisperse particle distribution, with in an assortment of superparamagnetic particles^{12, 22, 23}. The difference between monodisperse and polydisperse particles is shown in Fig. 3.1, and the mechanism to describe how these particles were formed can be explained by describing how particles are formed by these two techniques. In the polyol reduction reaction, all of the particles are nucleated almost simultaneously, resulting in a steady growth for all crystallites in the solution as shown in Fig. 3.2. This is attributed to the high temperature of the aqueous solution, which approaches the reflux temperature of the polyol/water mix, and is approximately 200 °C. However, in the chemical co-precipitation technique, there are multiple nucleation windows, since it is a much slower reaction, resulting in crystallites forming at different times and growing at different rates is shown in Fig. 3.3. This staggered growth of particles can be attributed to the relatively low temperature of the aqueous solutions, where the temperature is approximately 70 °C, which does not provide enough energy to fully nucleate all particles simultaneously.

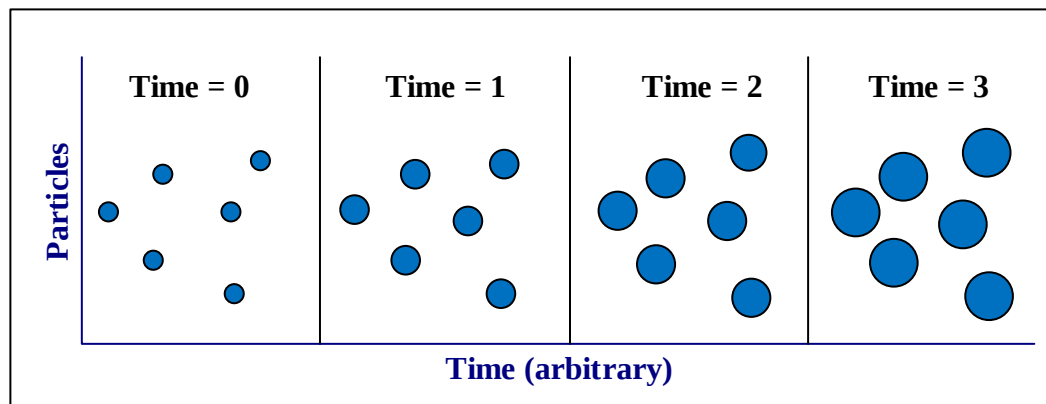


Figure 3.2 Nucleation of particles over time in a monodisperse reaction, where all of the particles grow at the same rate.

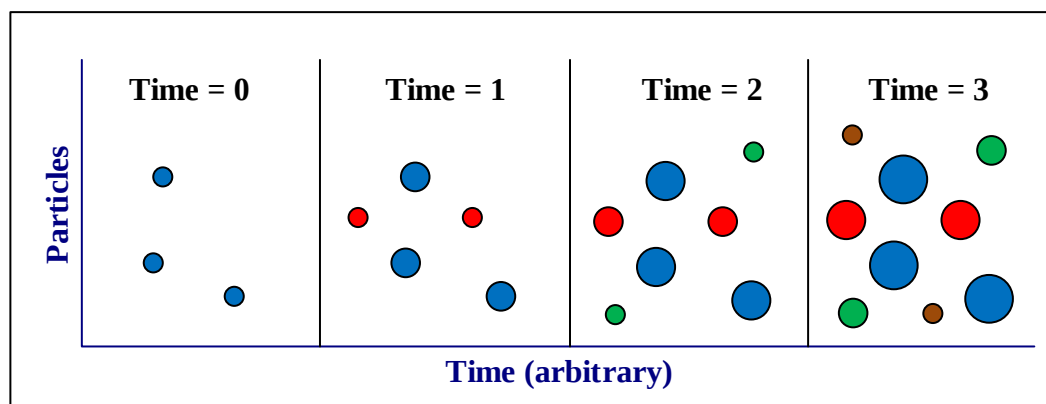


Figure 3.3 Nucleation of particles over time in a polydisperse reaction, where multiple nucleation stages are present, resulting in different growth rates.

While the polyol synthesis resulted in MDM with fine features, the yield of material is not so easy to scale up for applications. Conventional, solid-state ceramics processing was also used to produce MDM with micron-scale features with extremely high yield. In this chapter, the synthesis of the MDM, the formation of the MDM-composites, and their characterization are discussed. All samples were prepared by

either polyol reduction or solid-state ceramics processing, and were characterized using XRD, SEM/TEM for physical properties, and VSM for DC magnetic properties, and MDM-composite samples were fabricated and measured using impedance analysis for high-frequency EM properties.

3.2 Polyol Reduction

The following setup is used to run the hydrothermal processes and is shown in Fig 3.4.

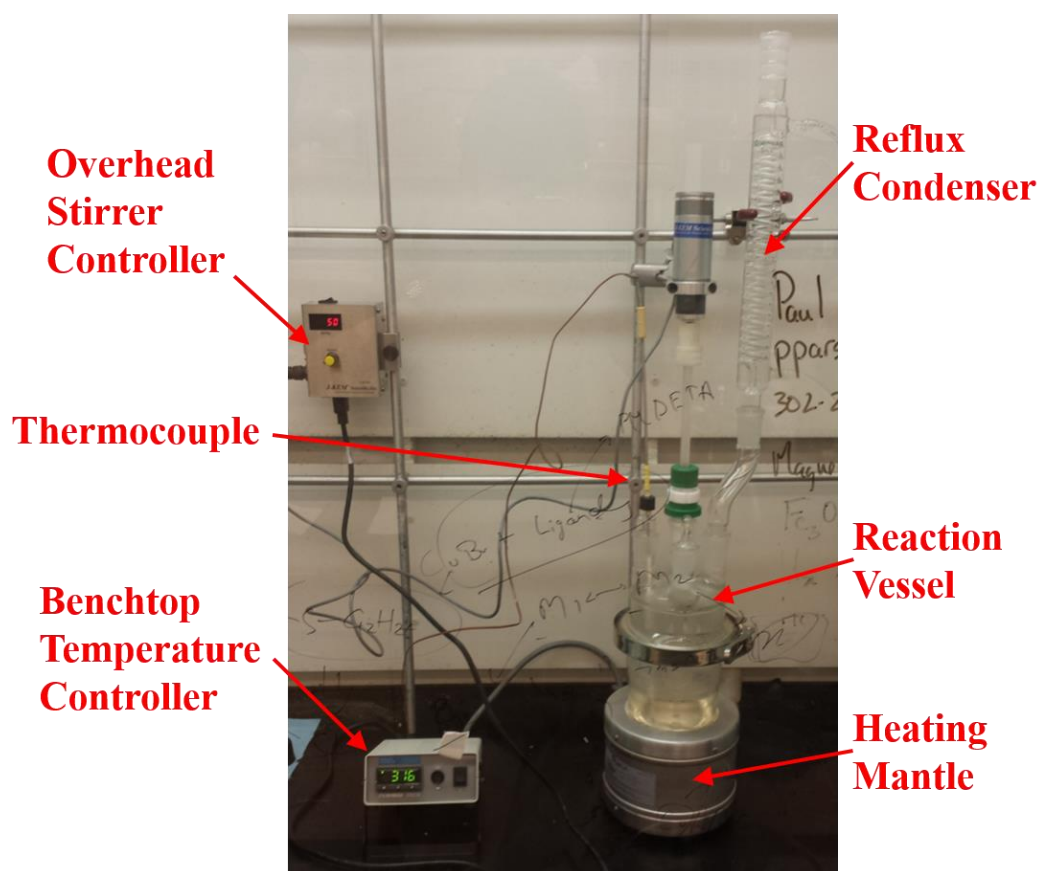


Figure 3.4 Polyol reduction reaction setup in fume hood.

Precursor metal salts (see Appendix A), iron (II) chloride, iron (III) chloride, nickel acetate, and zinc acetate were mixed with ethylene glycol (EG) or diethylene glycol (DEG) with added sodium hydroxide (NaOH) as a reducing agent, then heated to reflux temperature of the medium and agitated at 100 rpm using an overhead stirrer for 30 min²¹ to 6 hr²⁰. Depending on the amount of NaOH added, the reflux temperature of the specified medium would decrease due to formation of H₂O (195 °C → 175 °C for EG and 245 °C → 215 °C for DEG). NaOH would be added to EG before heating, and a transition would occur wherein the solution changes from clear to a dark yellow as the NaOH is fully dissolved into EG as shown in Fig. 3.5.

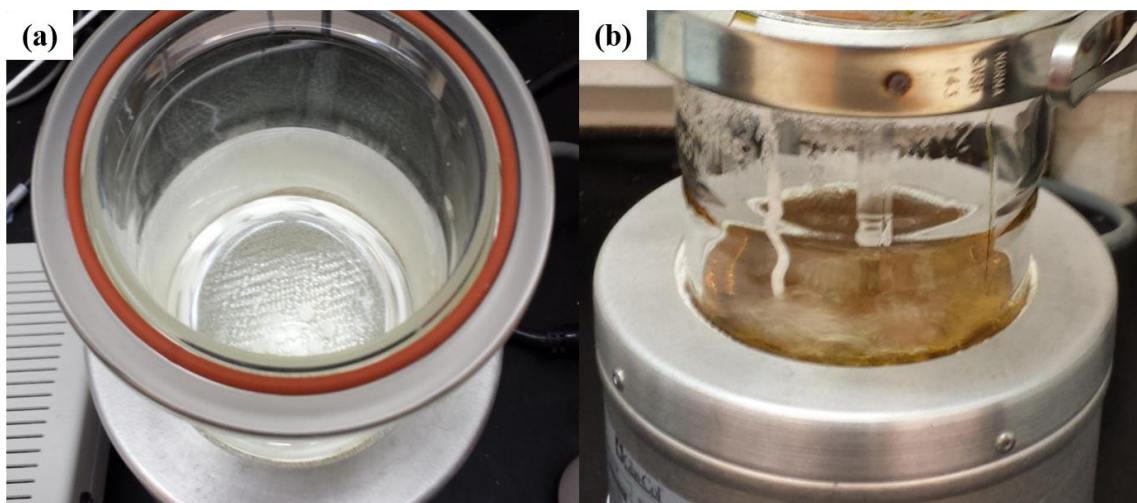


Figure 3.5 Color change of EG/NaOH solutions where the solution is at (a) room temperature, and (b) reflux.

For the formation of Fe₃O₄ nanoparticles, 0.01 mol FeCl₃·6H₂O was added to the combined solution of 0.05 mol NaOH in 200 mL of EG at reflux. Almost

immediately the solution changed color to a very dark green, almost black as shown in Fig. 3.6.

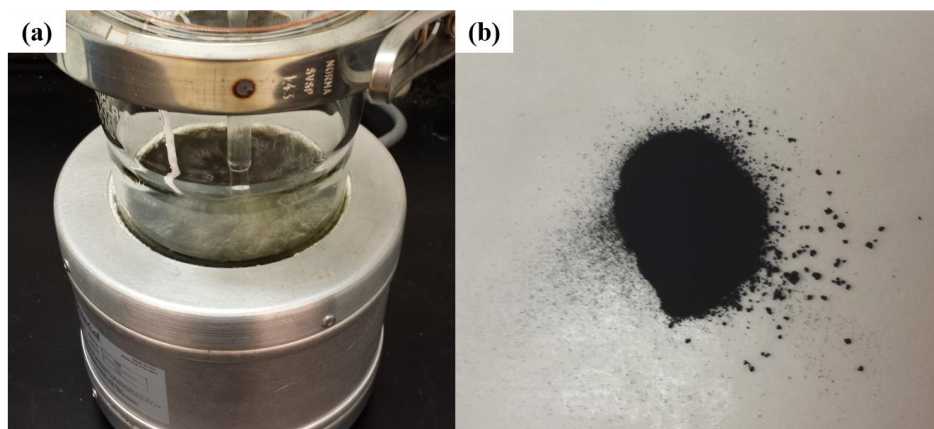
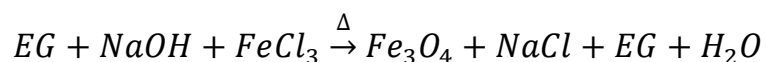


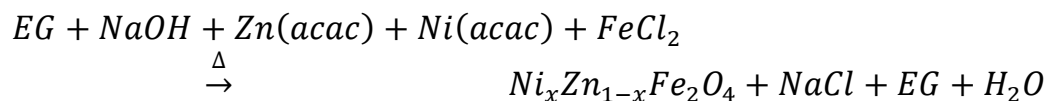
Figure 3.6 Color change of (a) EG/NaOH/FeCl₃ solution after adding precursor and (b) dried powder.

The following reaction occurred, where:



After the specified reaction time of 6 hr, the solution was cooled to room temperature and washed with de-ionized (DI) water to separate the EG byproducts, in this case, NaCl from the magnetic nanoparticles. This material was very easy to separate by using an NdFeB magnet, indicating that the crystallinity of the material is good enough to support room temperature magnetization. The particles were then dried overnight in an oven at 60 °C in air to produce black powder and were crushed using an agate mortar and pestle. This synthesis method would yield approximately 1.0 g of powder. The materials were characterized using XRD, SEM, and VSM.

For the formation of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles in EG, 0.02 mol $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$, 0.01 mol $\text{NiC}_4\text{H}_6\text{O}_4 \cdot 4\text{H}_2\text{O}$, and 0.01 mol $\text{ZnC}_4\text{H}_6\text{O}_4 \cdot 2\text{H}_2\text{O}$ was combined with 0.10 mol NaOH in 300 mL EG and heated to 180 °C. The solution took on a very dark color as shown in Fig. 3.7, where the following reaction occurs:



After a reaction time of 3 hr, the solution was cooled to room temperature and washed with DI water to separate the EG byproducts, in this case, NaCl from the magnetic nanoparticles. Unlike the Fe_3O_4 , this material was not immediately able to be separated using an NdFeB magnet, requiring a centrifuge to be used. The materials were spun down at 5k rpm at 15 min intervals at room temperature. The supernate was decanted off, and the particles were washed using DI water and spun down several more times to remove the EG and NaCl byproducts, resulting in a clear fluid. The particles were then separated magnetically and dried overnight in an oven at 60 °C in air to produce black powder and were crushed using an agate mortar and pestle. This synthesis method would yield approximately 1.0 g of powder. The materials were characterized using XRD, SEM, and VSM.

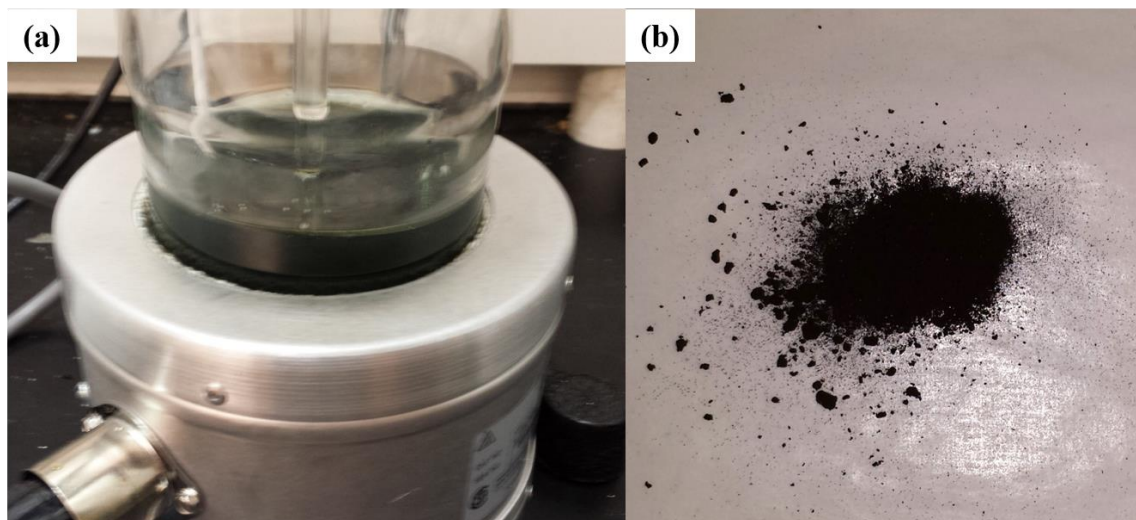
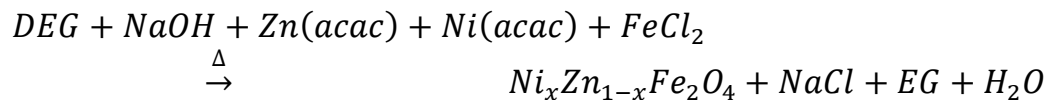


Figure 3.7 Color change of (a) EG/NaOH/Fe-Ni-Zn solution and (b) corresponding powder after drying.

DEG was also used as a reaction medium, since it is chemically similar to EG and can reflux at a higher temperature, up to 245 °C for pure DEG. For the formation of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles using DEG, 0.02 mol $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$, 0.01 mol $\text{NiC}_4\text{H}_6\text{O}_4 \cdot 4\text{H}_2\text{O}$, and 0.01 mol $\text{ZnC}_4\text{H}_6\text{O}_4 \cdot 2\text{H}_2\text{O}$ was combined with 0.10 mol NaOH in 300 mL DEG, and heated to reflux (200 °C in this case) with the resulting color change shown in Fig. 3.8. The following reaction occurs, where:



After running the reaction for 3 hr, the heater was turned off and the solution allowed to cool to room temperature overnight. After cooling, the nanoparticle solution is dark and somewhat viscous and requires washing to separate nanoparticles from solution.

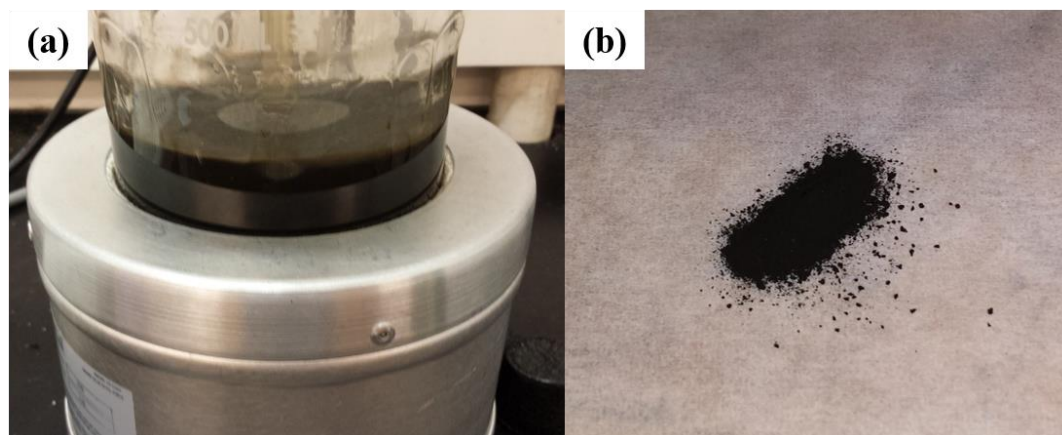


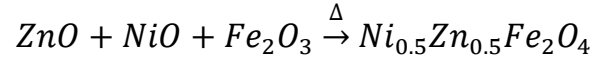
Figure 3.8 Color change of (a) DEG/NaOH/Fe-Ni-Zn solution and (b) corresponding powder after drying.

The materials were spun down in a centrifuge at 5000 rpm for 15 minute intervals, where the supernatant is discarded and remaining nanoparticles are thoroughly washed with deionized (DI) water. This process is repeated until most of the NaOH and DEG byproducts are washed away, resulting in magnetic nanoparticles that can eventually be pulled out of aqueous solution using an NdFeB magnet. The particles are dried in an oven at 60 °C overnight, turning into fine powders. This synthesis method would yield approximately 1.0 g of powder. These powders are then ground into a finer powder using an agate mortar and pestle and then characterized using XRD, TEM, SEM, and VSM.

3.3 Solid-State Ceramics Method

As an alternative to the relatively low-yield nanoparticle synthesis, a conventional solid-state ceramics processing method was also used to develop $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ particles and give yields up to kilograms of material at a time. Oxide precursors of 0.05 mol NiO, 0.05 mol ZnO, 0.10 mol and Fe_2O_3 were mixed together

using water to form a slurry and then dried. This oxide powder mixture was finely ground using an agate mortar and pestle, then placed in an Al₂O₃ crucible and calcined at 1000 °C for 2 hrs with a 2.5 °C/min ramp rate in a tube furnace. The following reaction occurs, where:



After cooling down to room temperature, it is immediately apparent that some of the powders sintered together and formed aggregate that are sub-millimeter in size, with a slight reduction of mass (approximately ~15 %) and are shown in Fig. 3.9. These particle sizes are unacceptable for printing, as the aggregate diameter exceeds the orifice diameter of the print heads on the nScrypt 3dn-300 micro-dispensing printer. The material was ground using an agate mortar and pestle, but unfortunately did not reach our size threshold and required additional grinding via milling machine. A stainless steel jar and yttria-stabilized zirconia (YSZ, purchased from Inframat Advanced Materials) 5.0 x 5.0 mm cylinders as milling media were selected due to the relative hardness of the materials and are shown in Fig. 3.10. The MDM were added into the jar with a powder (g): media (g) ratio of 1:10 and put onto a tumbler mill for 24 hr. The tumbler mill was selected due to the relatively low kinetic energy resulting in gentle grinding of the media without contamination from the milling jar, as opposed to a planetary mill or high-speed shaker mill, where the extremely high kinetic energy would undoubtedly contaminate the MDM with excess Fe, which could potentially increase conductivity and result in detrimental high-frequency loss characteristics. Following the milling procedure, the particles were filtered using stainless steel sieve, and the MDM were characterized using XRD, SEM, and VSM.

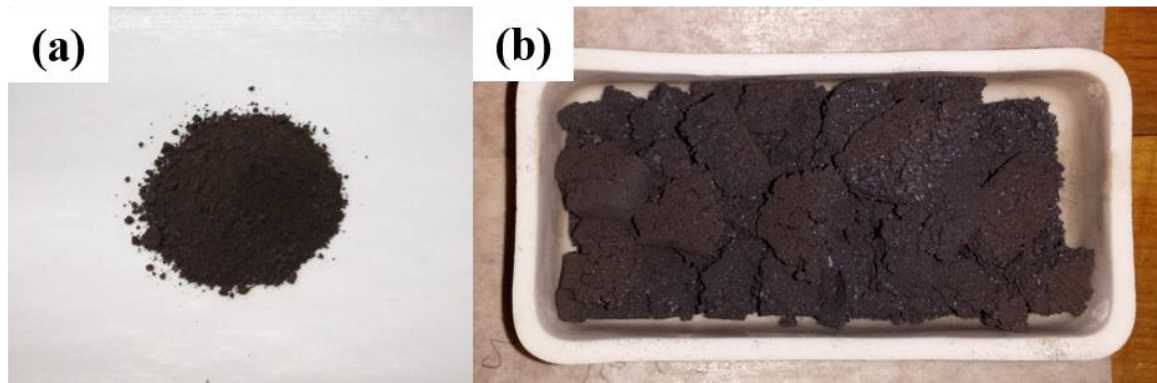


Figure 3.9 Solid state ceramics synthesis of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ materials in (a) the precalcined and (b) post-calcined state.



Figure 3.10 Stainless steel milling jar and YSZ milling media.

3.4 Magnetodielectric Composite Materials

A resin-based MDM-composite was fabricated using the synthesized MDM's as a filler material combined with EPON™ 8132 and EPIKURE™ 3140 resin system. The resin was selected for its EM properties ($\epsilon_r \approx 2.5$, and $\tan\delta \approx 0.001$) and capability or high volumetric loading. Samples of $\text{Fe}_3\text{O}_4/\text{EPON}$ and $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ were

created by adding MDM's to the resin in order to make volumetric loaded fractions of 10 – 40 % composite samples with favorable electromagnetic and mechanical properties (i.e, high permeability and permittivity, low loss tangent, high flexibility). The samples were mixed using a shear-mixing apparatus to promote uniform particle distribution and then poured into sample molds and cured at 100 °C for two hours. Discs samples with a dimensions of 20 mm in diameter, and 2 mm thickness were made, shown in Fig. 3.11, to measure the high-frequency complex permittivity and dielectric loss tangents using an impedance analyzer. After these measurements were made, a center hole was drilled out to make a one-turn inductor, where the frequency dependent complex reflection coefficient, Γ , was measured using the vector network analyzer.

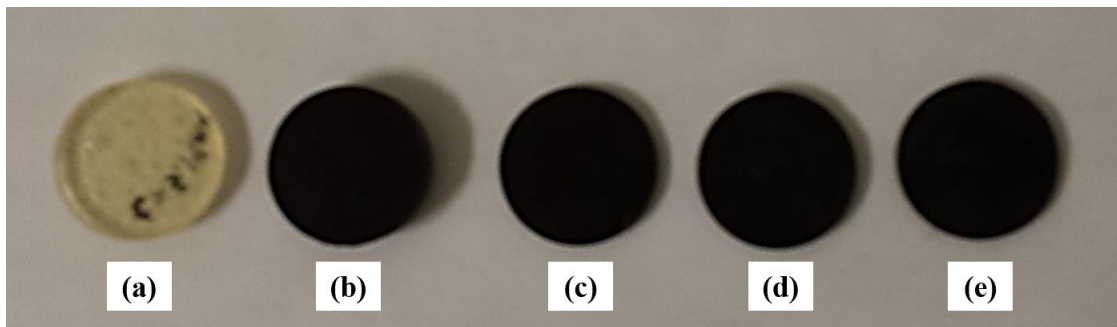


Figure 3.11 Disc composite samples of $\text{Fe}_3\text{O}_4/\text{EPON}$ in MDM volume loadings of (a) 0%, (b) 10%, (c) 20%, (d) 30%, and (e) 40%.

3.5 Magnetodielectric Materials Synthesis Conclusion

MDM were synthesized using the following methods, polyol reduction, which results in a relatively monodisperse and small crystal structures and a conventional solid-state ceramics processing technique, which yields larger, polydisperse crystal structures. While each method produces the same compound chemically, the physical

properties of the materials are quite different, which will have a profound effect on the high-frequency electromagnetic properties. All synthesized materials are summarized in Table 3.1.

Table 3.1 Categorized synthesis methods of magnetodielectric materials.

Sample	Synthesis technique	Expected Size	Proposed Uniformity	Post-processing Required
Fe_3O_4	EG polyol	Nanometer	Monodisperse	No
$\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$	EG polyol	Nanometer	Monodisperse	No
$\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$	DEG polyol	Nanometer	Monodisperse	No
$\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$	Solid-state	Micrometer	Polydisperse	Yes

Chapter 4

CHARACTERIZATION TECHNIQUES

In this chapter, I will discuss the variety of instruments used to characterize the MDM and MDM composite materials. Phase identification, and crystalline structure were performed using powder x-ray diffraction (XRD). Particle size and shape were measured using electron microscopy. If the particles were expected to be quite small, a transmission electron microscope (TEM) was used. If the particles were expected to be sub-micron, a scanning electron microscope (SEM) was used. DC magnetization was measured at both room and cryogenic temperatures using a vibrating sample magnetometer (VSM). For the high-frequency EM properties such as complex permeability, complex permittivity and their respective loss tangents, samples were measured using both an impedance analyzer (IA) and a customized setup using a vector network analyzer (VNA).

4.1 Powder X-Ray Diffraction

Powder x-ray diffraction (XRD) is a technique that has multiple uses. Primarily, it is used as a means of identification of the crystalline structure of materials²⁴. Additionally, it can be used as a means to estimate the size of crystalline grains within a powder sample. X-rays of a known wavelength are emitted from a source that passes through a set of metal slits, which focuses the beam path to a sample. These x-rays will penetrate the surface of the sample and then diffract and scatter according to Bragg's Law,

$$2d \sin \theta = n\lambda \quad (4.1)$$

where d is the spacing between crystal planes, θ is the angle of the incident wave, n is the order of reflection, and λ is the known wavelength of the x-ray. It is essential for this

condition to be met in order for diffraction to occur. As diffraction is mainly a scattering phenomenon, the long-range order of atoms in a periodic crystalline lattice have a phase relation that results in either destructive or constructive interference. As the x-ray source and detector rotate, these interference patterns result in peaks indicative of crystalline planes in as a function of 2θ as seen in Fig. 4.1. This is particularly useful as a means to identify crystalline materials since these patterns are reproducible, regardless of sample orientation due to the nature of scattering. The data sets of many crystalline materials have been documented for easy reference and matching of samples to well-known powder pattern standards.

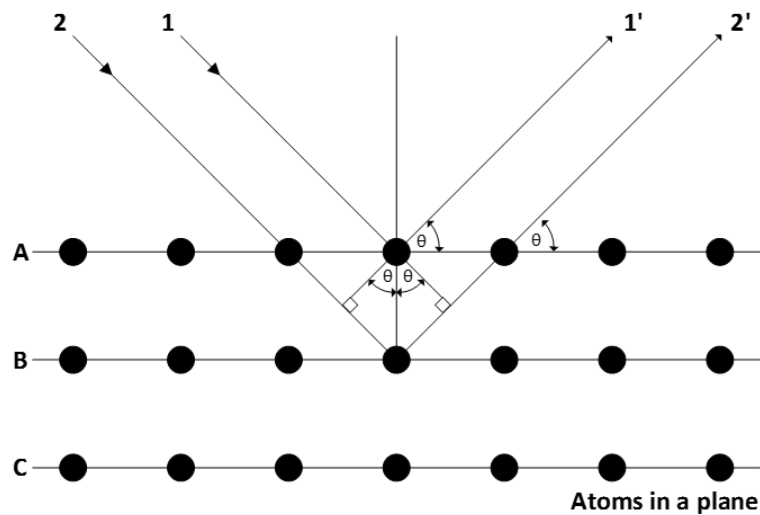


Figure 4.1 Diffraction of x-rays by a crystal, adapted from Cullity (1967).

Additionally, XRD can be used to estimate the grain size of crystalline materials, and is referred to as the Scherrer estimate²⁵:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (4.2)$$

where, D is the mean size of the crystal domains, K is the shape factor of the crystallites, λ is the wavelength of the x-ray, β is the full-width at half-maximum intensity of the peak in radians, and θ is the Bragg angle. This is an estimate only, as it heavily relies on the geometry of the grains and uniformity of size of these grains within a sample. If a sample volume contained one large grain surrounded by several smaller grains, the diffraction pattern would be dominated by the large grain, resulting in an inaccurate representation of the majority of the sample. It is still a useful tool in helping to determine if the sample is amorphous or crystalline by examining these peaks. If the peaks were broad, it would indicate short-range or amorphous order, and if the peaks are sharp and narrow, this indicates a high degree of crystallinity.

The Bruker D8 ADVANCED x-ray diffractometer, seen in Fig. 4.2, was used to measure the crystalline characteristics of all synthesized magnetodielectric materials. All measurements were made at room temperature with a 2θ from $20 - 80^\circ$, and measurements were pattern-matched using the DIFFRAC.SUITE Commander Software package.



Figure 4.2 Bruker D8 ADVANCED x-ray diffractometer.

4.2 Electron Microscopy

To confirm both size and geometry of the MDM's, electron microscopes were utilized in this work. Electrons are accelerated to form a focused beam, which acts as the source of illumination of the sample. The wavelengths of these accelerated electrons are much shorter than the wavelength of emitted visible light photons, which lend the higher resolving power to electron microscopes in general. With the nanoscale features of the synthesized MDM, electron microscopes are required to observe the size and shape of these particles. Two types of microscopes were used, a scanning electron microscope (SEM) and transmission electron microscope (TEM).

4.2.1 Scanning Electron Microscopy

An SEM was used to collect information about the sample's surface topography. Additional information can be collected about the sample based upon the type of measurement, such as chemical composition from back-scattered electrons²⁶. When a focused beam of electrons strike the surface of a sample, secondary electrons, back-scattered electrons, Auger electrons and even x-rays of the sample are emitted and is seen in Fig. 4.3.

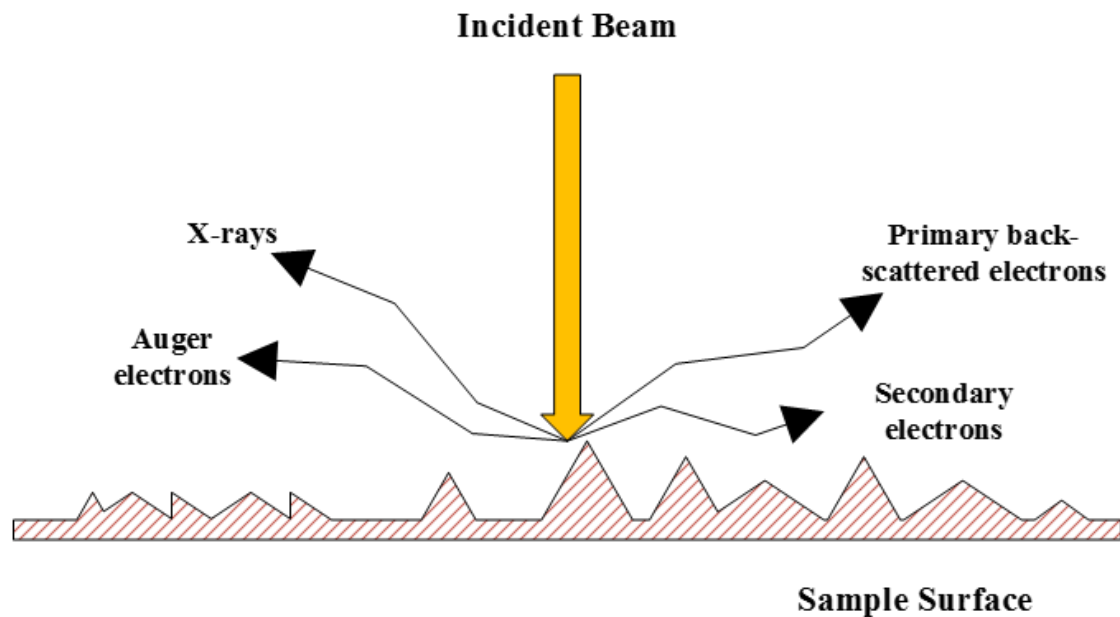


Figure 4.3 Resultant scattering from the focused electron beam interacting with sample surface using an SEM.

The most common mode of SEM's are to use the signals produced by secondary electron detectors to produce a high-resolution topographical image. The SEM has excellent resolution in the micron-scale, but has difficulty in imaging materials that are resistive

and very small (< 10 nm). A JEOL JSM 6330f Far Field Scanning Electron Microscope (Fig. 4.4) was used to produce the surface topography of the MDM's.



Figure 4.4 JEOL JSM 6330f Field Emission Scanning Electron Microscope

4.2.2 Transmission Electron Microscopy

When materials are too small to be detected with an SEM or have poor resolution, a transmission electron microscope (TEM) is used. Like an SEM, a TEM utilizes a focused beam of accelerated electrons to interact with the specimen. Unlike the SEM, the electrons in a TEM pass through the specimen (Fig. 4.5) where the

unscattered (or absorbed) electrons form a bright field image. The contrast between the scattered and unscattered electrons is the driving force behind the image.

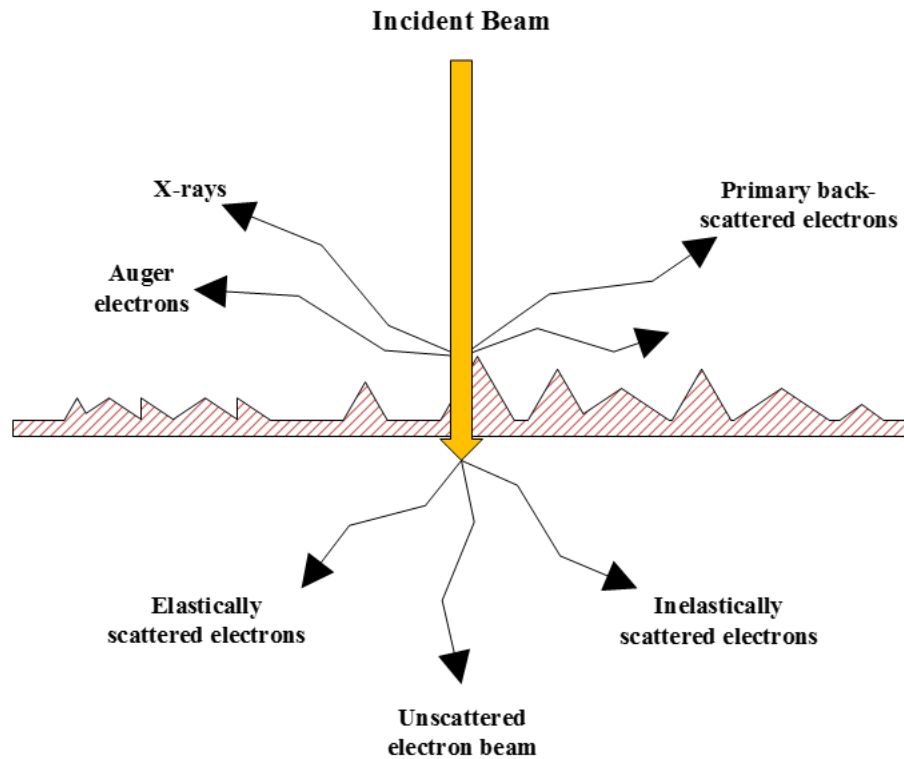


Figure 4.5 Interaction of electron beam with sample in transmission electron microscopy.

If a material is too thick, most of the electrons will be absorbed and there will be poor resolution. A JEOL JEM 3010 TEM (Fig. 4.6) was used to image particles too small to be resolved using an SEM.

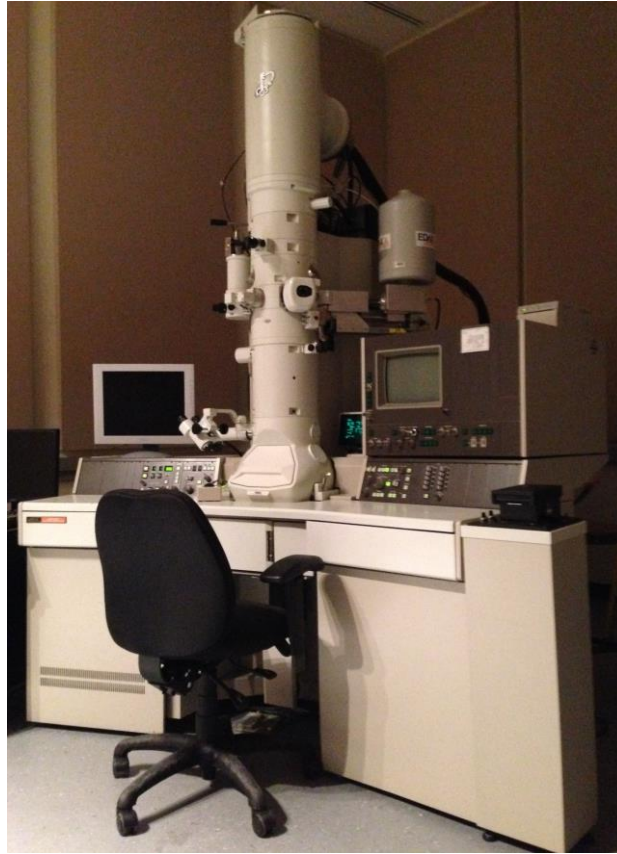


Figure 4.6 JEOL JEM-3010 Transmission Electron Microscope

4.3 Vibrating Sample Magnetometry

A vibrating sample magnetometer (VSM) is an instrument that can measure DC magnetization of a material at a variety of temperatures. While not as sensitive as a superconducting quantum interference device (SQUID), the VSM is capable of obtaining the saturation magnetization and hysteresis curve of a material. A VSM operates using Faraday's law of induction, wherein a time varying magnetic field across a conductor will induce an electromotive force, or the parallel where a generated force moving a conductor will induce a time varying magnetic field. What brings these two ideas together is the idea of a change in magnetic flux.

In the VSM, a small sample on a rod is placed between two pickup coils that are in the presence of a magnetic field (upwards of 7 T). Depending on the sample, such as a ferro-or ferrimagnetic material, it will become magnetized and generate a magnetic field of its own. At this time, the sample is vibrated quite rapidly in a transverse configuration to that of the electromagnet. If the frequency and amplitude of the vibration are known and kept constant, the modulation of the magnetic field will result in an electric field to be measured in the pickup coils. This field can be written as²⁷:

$$U_{ind} = -\delta\Phi/\delta t = -n_w A \delta\vec{B}/\delta t \quad (4.3)$$

Where Φ is the magnetic flux, n_w , is the number of windings and A is the area of the pickup coil. The magnetic flux density, $\vec{B}$ will then become:

$$\vec{B} = \mu_0(\vec{H}_0 + \vec{M}) \quad (4.4)$$

where $\vec{H}_0$ is the constant magnetic field, and $\vec{M}$ is the magnetization, written as:

$$\vec{M} = \int d\vec{m}/dV dV \quad (4.5)$$

where $\vec{m}$ is the magnetic moment per volume when the sample is in the presence of $\vec{H}_0$.

With equations 2 and 3, we find that:

$$\delta\vec{B}/\delta t = \delta\vec{M}/\delta t \quad (4.6)$$

and this describes how the change in magnetic flux originates from the vertical sample movement of relative to the coils. This change in flux is proportional to the change in magnetization of the sample which is influenced by the induction generated.

In this study, we used a Quantum Design Versalab VSM as shown in Fig 4.7. We performed measurements at 300 K and 50 K, with fields up to 3 T to determine the magnetization and coercivity of the MDM's.



Figure 4.7 Quantum Design Versalab VSM

4.4 High-Frequency Electromagnetic Characterization

To measure the high-frequency characteristics of these composite materials, two instruments were used up to 1 GHz. An impedance analyzer (IA), Agilent E4991A, equipped with a 16453A Dielectric Materials Test Fixture was used to determine the complex permittivity, ϵ , where:

$$\epsilon = \epsilon' + j\epsilon'' \quad (4.7)$$

The dielectric loss tangent, $\tan\delta_e$, can then be expressed in terms of ϵ , where:

$$\tan\delta = \frac{\epsilon''}{\epsilon'} \quad (4.8)$$

This term is used to express how “lossy” a material is and describes how the material will inherently dissipate electromagnetic energy, usually in the form of heat.

The complex permeability, μ , is similar in form to that of ϵ , where:

$$\mu = \mu' + j\mu'' \quad (4.9)$$

with corresponding magnetic loss tangent, $\tan\delta_m$, expressed in terms of μ , where:

$$\tan\delta = \mu' / \mu'' \quad (4.10)$$

A custom solution to measure the complex permeability had to be developed to perform these measurements in-house. Using a vector network analyzer (VNA), Agilent E8361C with the a fixture to measure the impedance of a one-turn inductor (16454A Magnetic Materials Test Fixture) and a terminal adapter to help properly match impedances and reduce reflections at high frequencies (16201A 7 mm Terminal Adapter Kit), the reflection coefficient, $\Gamma = S_{11}$, could be measured and used with a series of relations to extract the complex permeability.

4.4.1 Impedance Analyzer

The IA used in this study was the Agilent E4991A, seen in Fig. 4.8. To measure the complex permittivity, the 16453A Dielectric Materials Test Fixture is used in a parallel plate capacitor setup. The MDM-composite samples, in the form of discs, are placed between two conducting pins on the fixture, where the parallel capacitance, C_p , parallel resistance, R_p , are measured as a function of frequency. It is important to note that the IA houses the software to take into account the fixture impedance and apply corrections to solve for the complex permittivity, which can be expressed through the measured relations²⁸:

**E4991A
Impedance
Analyzer**



**16453A Dielectric
Materials Test
Fixture**

**16454A Magnetic
Materials Test Fixture**

Figure 4.8 Agilent E4991A Impedance Analyzer with 16453A/16454A test fixtures.

$$\epsilon_r^* = \left(\frac{C_p}{C_0} - j \frac{1}{\omega R_p C_0} \right) \quad (4.11)$$

where C_0 is the capacitance of air, and ω is angular frequency. This relation can be further broken down into the respective real and imaginary components:

$$\epsilon_r' = \left(\frac{t C_p}{A \epsilon_0} \right) \quad (4.12)$$

where t is the thickness of the sample, and A is the area of the sample, and,

$$\epsilon_r'' = \left(\frac{t}{\omega R_p A \epsilon_0} \right) \quad (4.13)$$

where ϵ_0 is the permittivity of free space.

4.4.2 Vector Network Analyzer

In in-house solution was developed to provide the capability of measuring the components to calculate the complex permeability and the device setup is shown in Fig

4.9. Using information referenced using²⁹, the complex impedance could be acquired as a set of reflection coefficients, Γ , and then converted into permeability through a set of equations through a VNA measurement:

$$Z_s = Z_0 \left(\frac{1+\Gamma}{1-\Gamma} \right) \quad (4.14)$$

Where Z_s is the impedance of the sample, Z_0 is the characteristic impedance of the system, in this case, 50Ω . The measurement is performed by placing the toroid sample, shown in Fig. 4.10, in the 16454A Magnetic Material Test Fixture, which is then mounted onto the 16201A 7 mm Terminal Adapter Kit. The terminal adapter is connected to the ruggedized 2.92 mm VNA cable using a series of N-type 50Ω connectors.

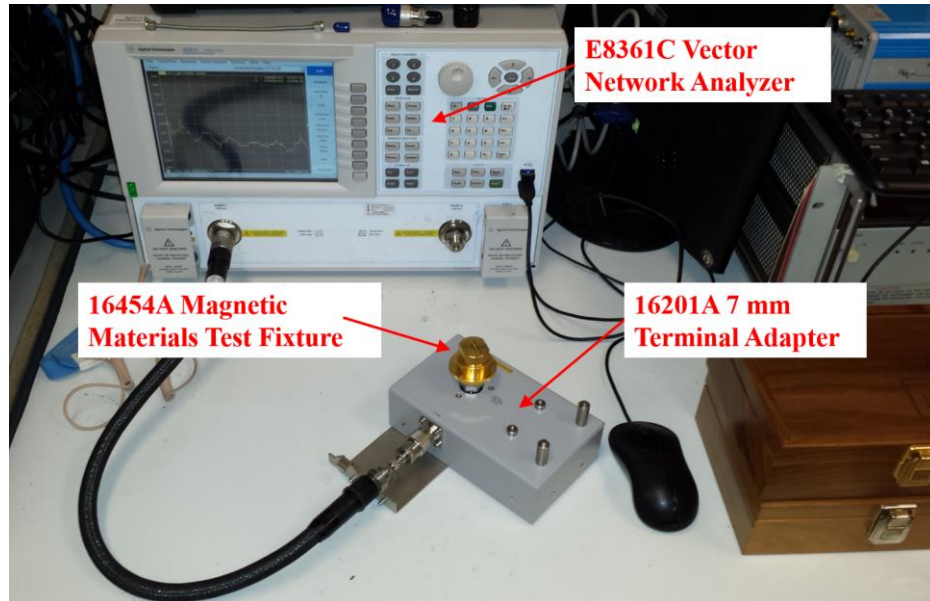


Figure 4.9 Agilent E8361C Vector Network Analyzer with 16454A Magnetic Materials Test Fixture coupled to a 16201A 7 mm Terminal Adapter Kit.

Measurements are also made using an empty cavity, resulting in the complex impedance of air, Z_a . Using these parameters, one could calculate the complex components of the permeability using²⁸:

$$\mu = 1 + \frac{(Z_s - Z_a)}{j f \mu_0 h \ln(c/b)} \quad (4.15)$$

where f is the frequency, μ_0 is the permeability of free space, h is the height of the sample, c is the outer diameter of the sample, and b is the inner diameter of the sample. The permeability can be split up into its respective real and imaginary components, where the magnetic loss tangent, $\tan \delta_m$, can be determined.

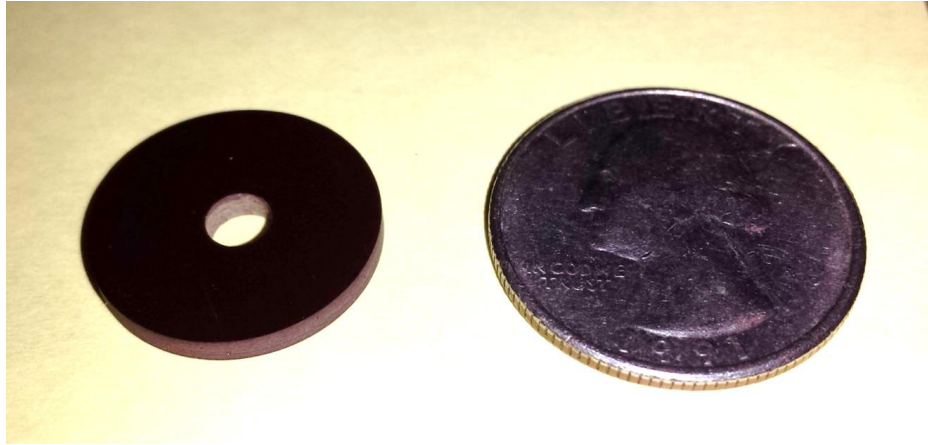


Figure 4.10 MDM-composite sample to be measured using the magnetic test fixture.

It is important to note that the 7 mm terminal adapter is quite necessary to correctly match the impedance of the test fixture to the VNA. Even when a one-port calibration is made with simply the 16454A and VNA, there are additional reflections at lower-frequencies due to an impedance mismatch and is shown in Fig. 4.11.

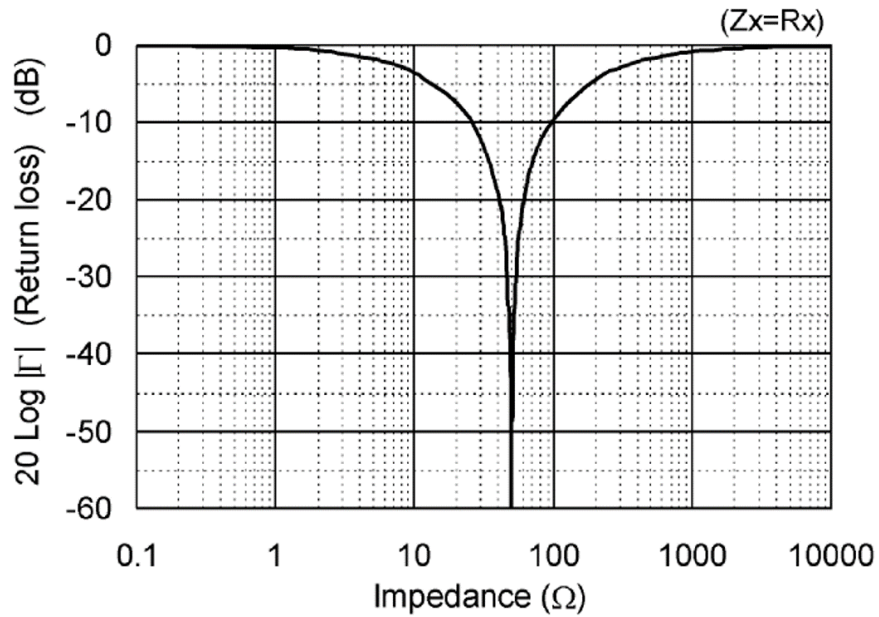


Figure 4.11 Reflection Loss Sensitivity as a function of impedance, $|Z_x|$, adapted from Agilent Technical Note 1369-2 (2001). As $|Z_x|$ deviates from 50 Ω , the sensitivity dramatically decreases.

This can be described in³⁰, where the measurement sensitivity varies due to the impedance of the sample not being properly matched. High-permeability materials tend to provide very small impedance values, where $|Z| \leq 50 \Omega$, at lower frequencies. As the frequency increases, the materials exhibit better matching and this is illustrated in Fig. 4.12. The design of an in-house low-frequency complex dielectric parameters using a VNA method is currently under development.

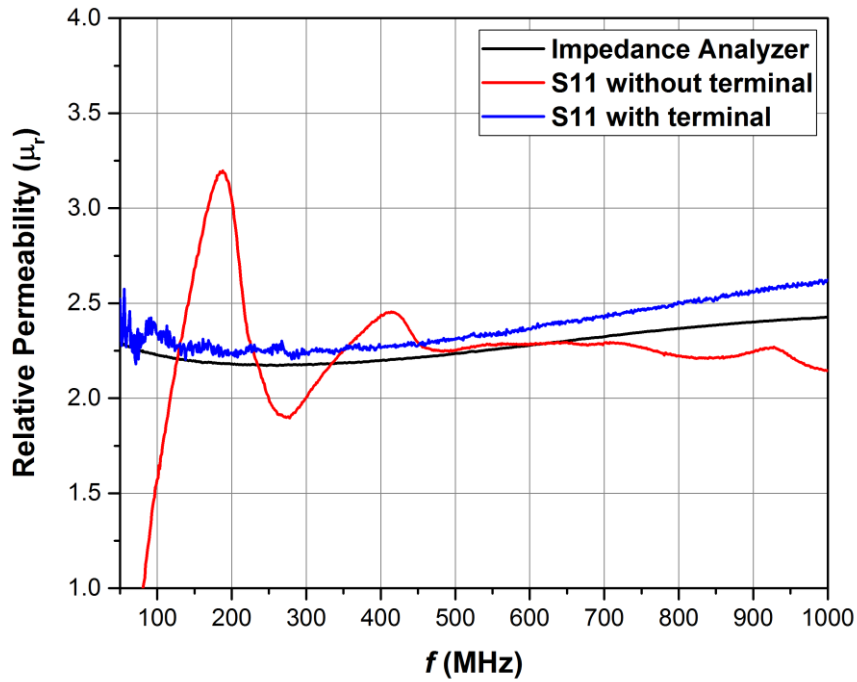


Figure 4.12 Permeability spectra of measurement setup with and without the terminal adapter compared to the impedance analyzer measurement.

4.5 Characterization Conclusion

The characterization methods used in this thesis were outlined in this chapter. For physical properties such as crystal identification, estimated grain size, particle size and shape, an XRD and SEM/TEM were used, respectively. For DC magnetization properties at room and cryogenic temperatures, 300 K and 50 K, respectively, a VSM was used. To measure the high-frequency electromagnetic properties such as relative permeability, relative permittivity and their respective loss tangents, both an impedance analyzer and vector network analyzer were used between 50 MHz – 1 GHz.

Chapter 5

RESULTS AND DISCUSSION

In this chapter, the results from characterizing the synthesized materials, using the techniques outlined in Chapter 4, will be presented and discussed.

5.1 X-ray Diffraction

Using the Bruker D8 ADVANCED x-ray diffractometer, powder MDM samples were characterized using a source of Cu-K α_1 ($\lambda = 0.154056$ nm) and identified using the DIFFRAC.SUITE Commander Software package.

In Fig. 5.1, the powder diffraction plots of the various synthesized MDM are presented. All patterns are compared to the JCPDS 8-324 standard crystalline powder pattern of M·Fe₂O₄ (where M is a metal cation) spinel, and match very well, so the spinel structure of the MDM's are confirmed. The Fe₃O₄, and solid-state ceramics processed Ni_{0.5}Zn_{0.5}Fe₂O₄ indicate a high degree of crystallinity, due to the sharp peaks. However, the degree of crystallinity of the polyol-reduced Ni_{0.5}Zn_{0.5}Fe₂O₄ (both EG and DEG), are not nearly as sharp, which indicates an increased concentration of very small, amorphous particles in the sample. The presence of these amorphous particles could degrade the magnetic properties of the sample. The grain size, D , was estimated using the Scherrer equation, where the shape factor $k = 0.9$ is used (for spherical-like particles), and $\lambda = 0.154056$ nm. The estimated grain size of all synthesized MDM are below 50 nm in diameter, and are presented in Table 5.1.

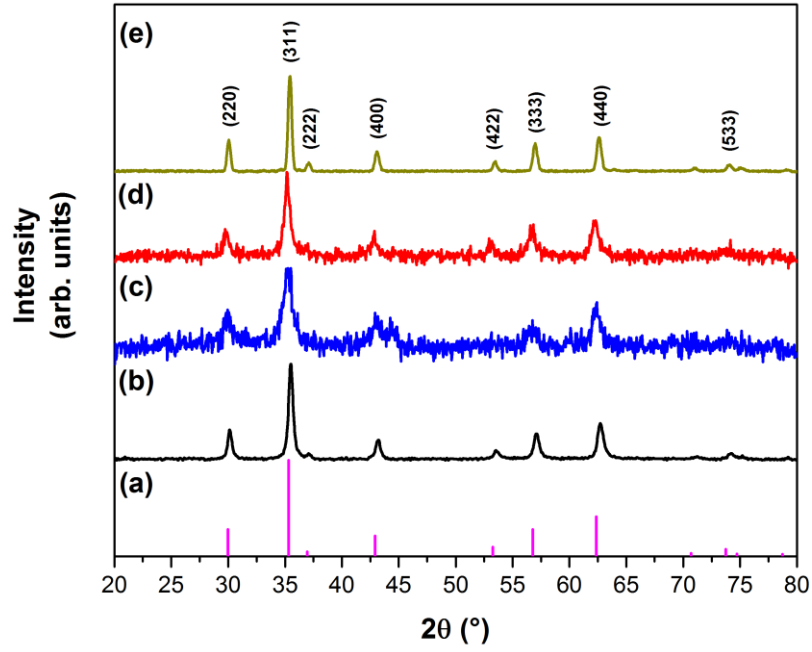


Figure 5.1 Powder diffraction plot of all MDM synthesized in this thesis, where (a) is the JCPDS 8-324 $M \cdot \text{Fe}_2\text{O}_4$ standard pattern, (b) is Fe_3O_4 , (c) is EG-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$, (d) is DEG-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$, and (e) is the conventional solid-state processed $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ with corresponding Miller indices.

Table 5.1 Powder diffraction data of synthesized MDM.

Sample ID	Estimated Grain Size of (311) peak
Fe_3O_4	18.2 nm
$\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ (EG)	10.3 nm
$\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ (DEG)	15.5 nm
$\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ (solid state)	21.4 nm

5.2 Electron Microscopy

Using the JEOL JSM 6330f Field Emission Scanning Electron Microscope (SEM) and JEOL JEM-3010 Transmission Electron Microscope (TEM), the particle sizes and shapes of all synthesized MDM were determined. In most cases, an SEM is adequate to determine size, shape and degree of agglomeration; however, when the particle size was too small to be resolved using an SEM, a TEM was used instead.

The spherical-like Fe_3O_4 nanoparticles were measured using SEM and TEM, and are shown in Figs. 5.2 and 5.3, respectively. There is a high degree of aggregation, and the individual particles cannot be easily resolved using SEM and these agglomerations are approximately 500 nm in diameter. This size is much greater than the estimated grain size using the Scherrer approximation (18.2 nm in this case), and indicates that multiple particles and magnetic domains occupy the large aggregate.

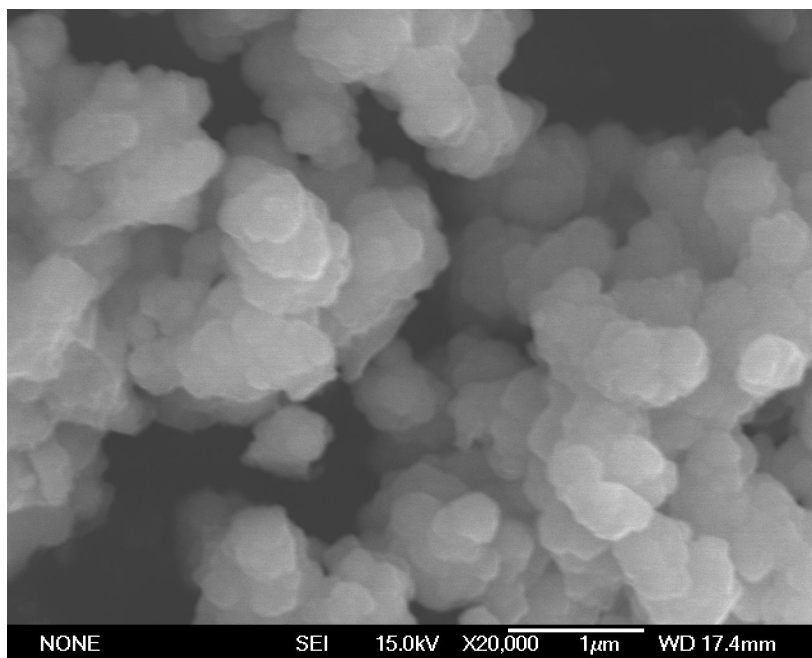


Figure 5.2 SEM image of Fe_3O_4 sub-micron agglomerates with corresponding scale bar of 1 μm .

In Fig 5.3, the TEM image of the Fe_3O_4 particles are presented. A high degree of agglomeration is seen, but the particle sizes and shapes are better resolved. In the following image, single domain and multiple domains particles are seen. The clusters of material containing multiple crystal domains and can vary in size from 20 – 50 nm in diameter, which is approximately 1 to 2.5 times the estimated grain size using the Scherrer equation.

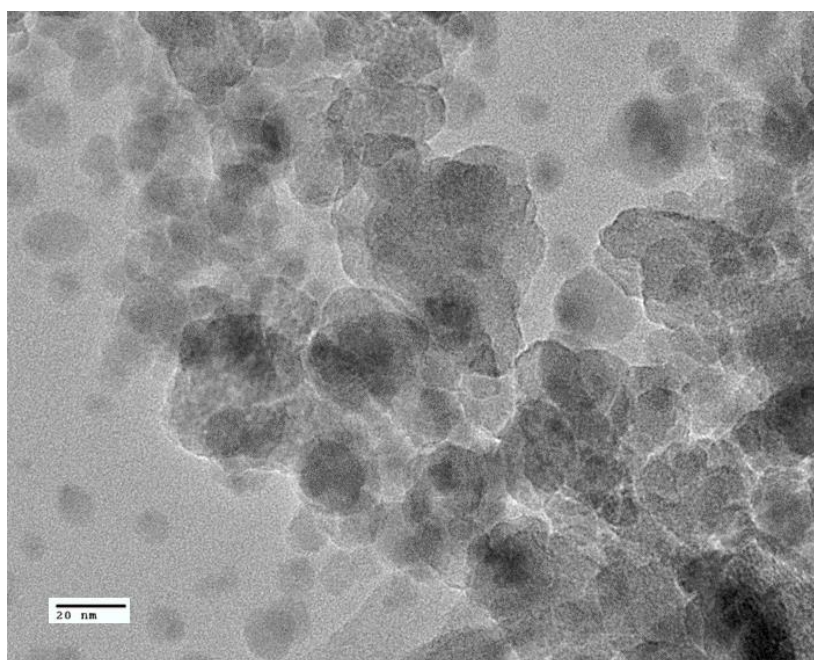


Figure 5.3 TEM image of Fe_3O_4 particles with corresponding scale bar of 20 nm.

The EG-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ were measured using SEM and are shown in Fig. 5.4. As with the Fe_3O_4 samples, there is a high degree of aggregation, but it can plainly be shown that there are nanometer sized inclusions.

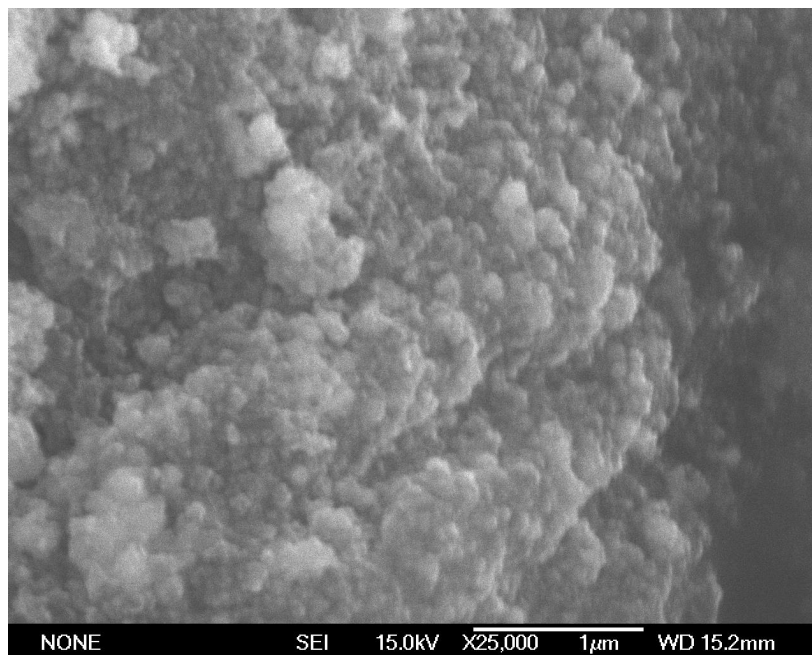


Figure 5.4 SEM image of EG-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles with corresponding scale bar of 1 μm .

There is difficulty in resolving these particles using an SEM, so a TEM was used and the corresponding image is used in Fig. 5.5. The particles are more uniform than the Fe_3O_4 particles, with single domains shown having diameters between 10-15 nm. These sizes correspond to 1 to 1.5 times the estimated grain size using the Scherrer equation.

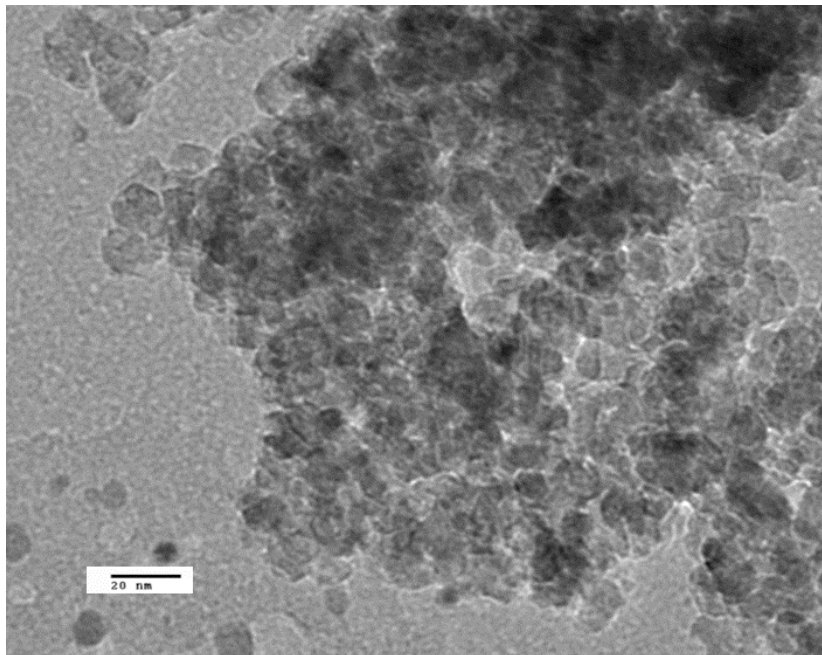


Figure 5.5 TEM image of EG-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles with corresponding scale bar of 20 nm.

The DEG-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles were measured using SEM and are shown in Fig. 5.6. These particles exceed the ability of the SEM to resolve extremely fine features, as the sizes are well below 100 nm. What we do see is that these particles are not aggregating together into large clusters, but to determine their relative size, a TEM has to be used.

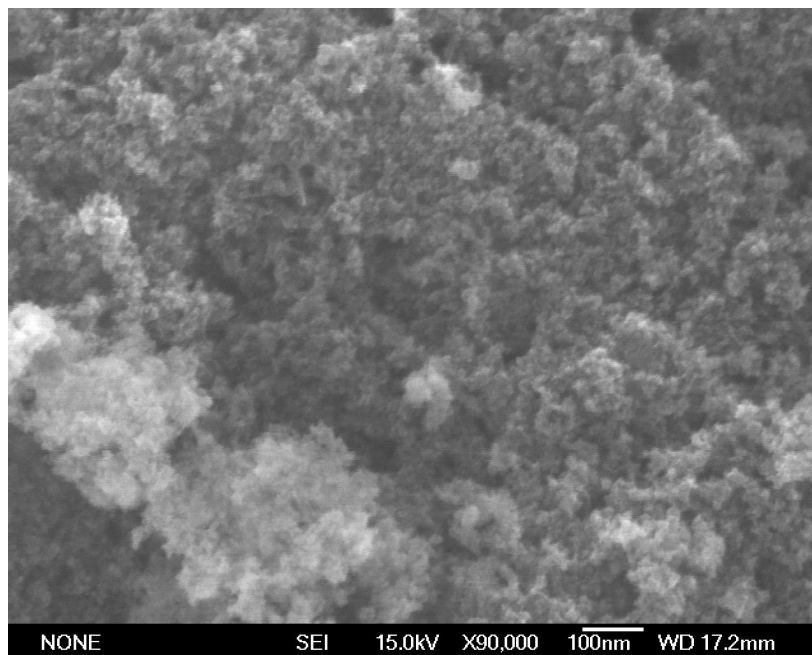


Figure 5.6 SEM image of DEG-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles with corresponding scale bar of 100 nm.

A TEM image of the DEG-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ are shown in Fig. 5.7. There is a high degree of symmetry in all axes, resulting in a very spherical particle of approximately 15 nm. This value almost exactly corresponds to the Scherrer approximation, 15.5 nm, indicating that these particles are typically single domain particles.

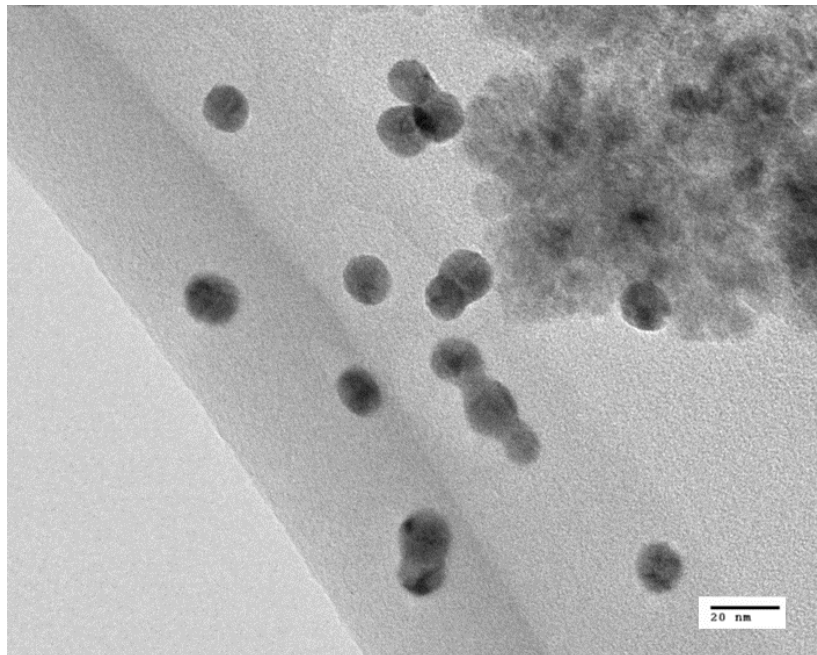


Figure 5.7 TEM image of DEG-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles with corresponding scale bar of 20 nm.

The solid-state processed $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ were measured using SEM and are shown in Fig. 5.8. It is obvious that the particles are experienced sintering and some have fused together via “necking”, to form very large particles. In some cases, upwards of 5-10 μm , and greatly exceed the Scherrer approximation (21.4 nm) by several orders of magnitude indicating that many grains occupy the particle. These particles do not have such a high degree of symmetry and have distinct edges, close to a cubic shape.

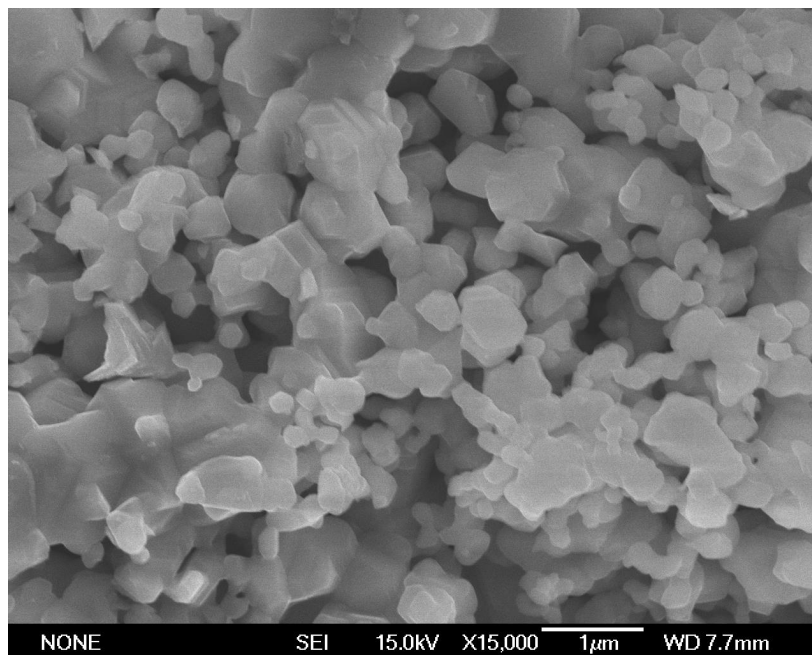


Figure 5.8 SEM image of solid-state processed $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ particles with corresponding scale bar of 1 μm .

The solid-state processed materials were processed in a stainless steel milling jar with yttria-stabilized zirconia, (YSZ, $\text{Y}_2\text{O}_3\cdot\text{ZrO}_2$) for 24 hrs to reduce the particle size to meet the micro-dispensing orifice requirements ($< 5 \mu\text{m}$). These milled materials were also imaged using an SEM and are shown in Fig. 5.9. The particles have been broken apart to reach an average size of 1-2 μm , reaching our micro-dispensing requirement.

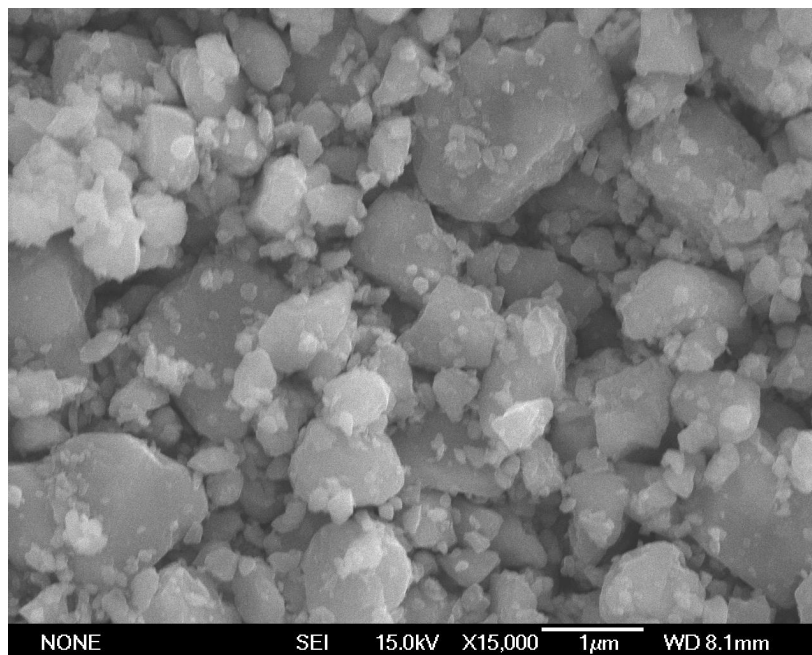


Figure 5.9 SEM image of solid-state processed $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ particles after 24 hr of milling with corresponding scale bar of 1 μm .

5.3 Magnetometry

Small pellets of MDM were formed and placed on the sample-bearing rod, then placed into the vented chamber where the pickup coils are located. Measurements were run at room temperature (300 K) and cryogenic temperatures (50 K) with a ramping rate of 10 K/min.

In Fig. 5.10, we see the magnetization curves of the polyol-reduced Fe_3O_4 particles. This material does not fully saturate with the magnetic fields present, but can be approximated to be saturated at approximately 3 T for the 300 K and 50 K measurement.

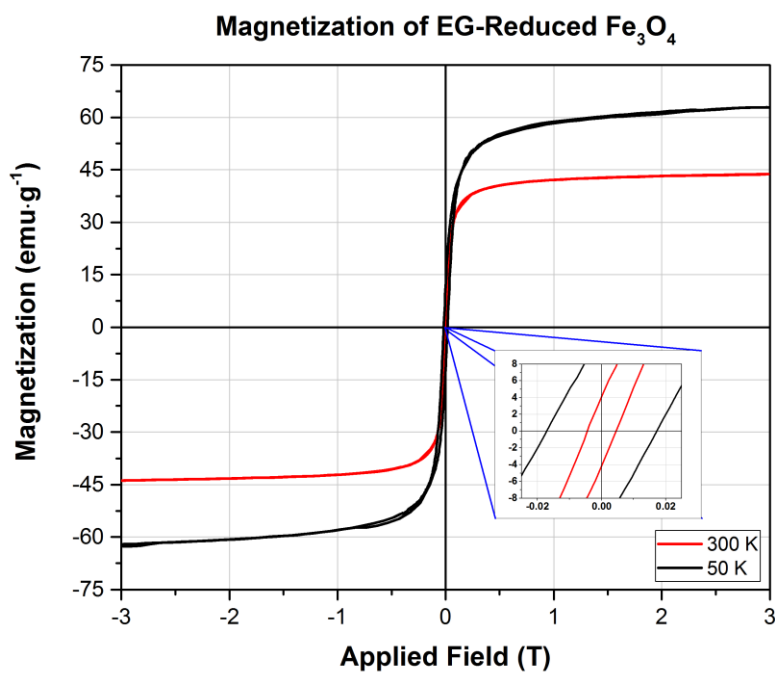


Figure 5.10 Magnetization curves of Fe_3O_4 at 300 K and 50 K with corresponding inset displaying differences in coercivities between the two measurements.

These values correspond to $43.74 \text{ emu}\cdot\text{g}^{-1}$ and $62.19 \text{ emu}\cdot\text{g}^{-1}$ for the 300 K and 50 K samples, respectively. This is approximately 50% of the bulk magnetization of Fe_3O_4 and can be described by the surface chemistry, where the number of nearest neighbor oxygen atoms in octahedral iron is reduced in this scheme, potentially leading to a shift in hybridization orbitals, resulting in a reduced magnetization³¹. The measured coercivities are 0.0045 T and 0.0172 T for the 300 K and 50 K samples, respectively. These coercivities indicate a magnetically soft material³³.

In Fig. 5.11, the magnetization curves of EG-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ particles are presented. There is an increased room temperature magnetization over the Fe_3O_4 particles due to the effects of cation substitutions of ferromagnetic Ni and diamagnetic

Zn atoms for the Fe atoms. These measured magnetizations of these materials corresponds to $58.77 \text{ emu}\cdot\text{g}^{-1}$ and $80.80 \text{ emu}\cdot\text{g}^{-1}$ and measured coercivities are 0.0011 T and 0.0003 T for the 300 K and 50 K samples, respectively.

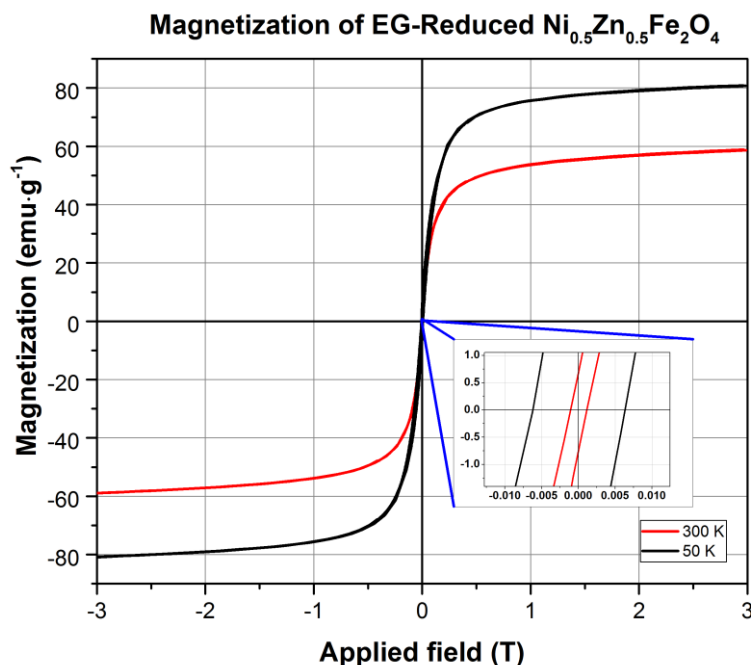


Figure 5.11 Magnetization curves of EG-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ at 300 K and 50 K .

In Fig. 5.12, the magnetization curves of DEG-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles are presented. These materials also do not fully saturate in the applied field and measure a magnetization of $57.15 \text{ emu}\cdot\text{g}^{-1}$ and $82.17 \text{ emu}\cdot\text{g}^{-1}$ for the 300 K and 50 K samples, respectively. These values match quite well to the EG-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ particles. The measured coercivities are 0.0012 T and 0.0001 T for the 300 K and the 50 K samples, respectively, indicating a magnetic soft material. From a

DC-magnetization standpoint, there is little difference between the room temperature properties between the EG and DEG-reduced ferrites, despite the reaction temperatures (180 °C vs. 200 °C).

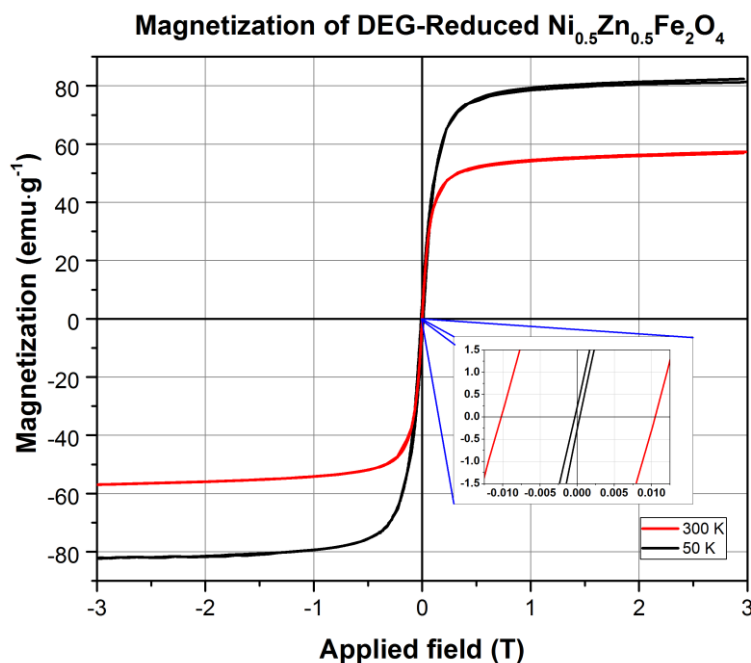


Figure 5.12 Magnetization curves of DEG-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ at 300 K and 50 K.

In Fig. 5.13, the magnetization curves of the solid-state ceramics processed MDM are presented. Unlike the polyol-reduced MDM particles, this material is easily synthesized in large quantities. The measured magnetization at 3 T is 66.03 $\text{emu}\cdot\text{g}^{-1}$ and 107.67 $\text{emu}\cdot\text{g}^{-1}$ for the 300 K and 50 K samples, respectively. This is really close to the reported bulk magnetization values of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$. The measured coercivities are 0.0014 T and 0.0023 T for the 300 K and 50 K samples, respectively.

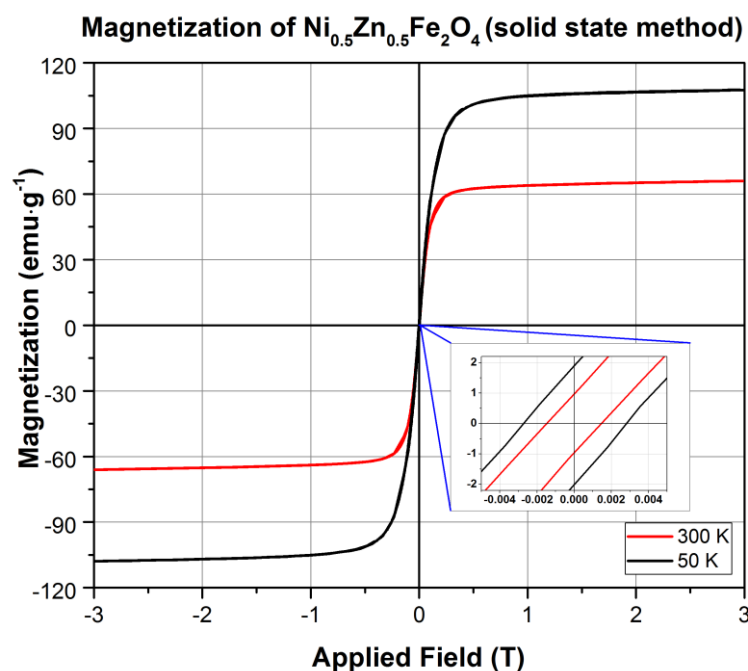


Figure 5.13 Magnetization curves of solid-state ceramics synthesized $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ at 300 K and 50 K.

Despite the increased magnetization over the DEG and similar magnetization to the EG-reduced MDM, the particle size was too large to be effectively used in micro-dispensing and required milling to break down the particles into 1-2 μm particles. After milling for 24 hr, the materials were measured again to see how the deformation of particles affected the magnetic properties. In Fig 5.14, the magnetization curves of the milled materials compared to the calcined MDM is shown. There is some degradation in performance as the magnetization has been reduced to $62.16 \text{ emu}\cdot\text{g}^{-1}$ with a coercivity of 0.0144 T. This translates to a 5.9 % reduction in room temperature magnetization, with almost a 1000 % increase in coercivity. While still technically very soft magnetically, the increase in coercivity can be attributed to the presence of fractured

magnetodielectric pieces from milling. As the milling process continues, the number of fractured, and small, possibly single-domain particles increases. The occupied volume consists of a mixture of large and small particles, and when the number of small particles increases, the number of larger particles decrease, leading to a greater contribution to the coercivity by these smaller particles.

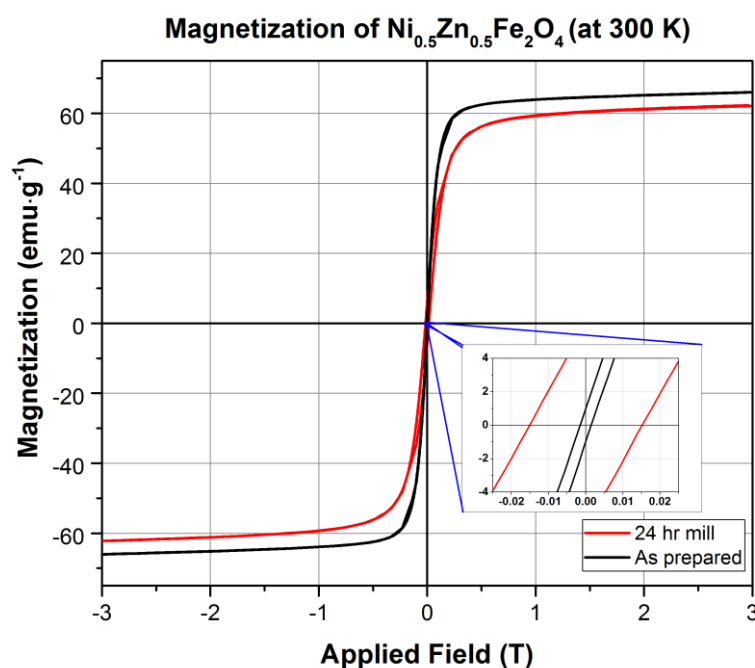


Figure 5.14 Magnetization curves of solid-state ceramics synthesized $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ at 300 K using the as prepared powder and powder milled after 24 hrs.

The dependence of coercivity on particle size for several magnetic alloys³³ is illustrated in Fig. 5.15 and similarly describes the behavior of the synthesized MDM. When a particle is very small, it is generally superparamagnetic and has a very low

coercivity. As the particle gradually increases in size, the coercivity also increases and reaches a maximum value. Regarding the milled MDM, as the concentration of smaller particles increases, due to the fracturing of larger particles, these small particles could potentially contribute to an increased coercivity of the system.

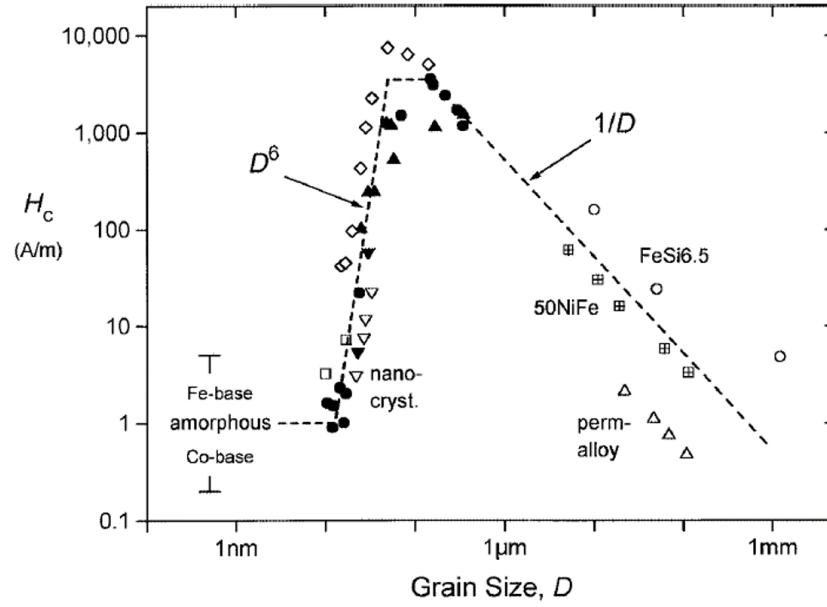


Figure 5.15 Dependence of coercivity as a function of particle size for various soft magnetic alloys, adapted from Herzer (1997).

In the Fig. 5.16, magnetization loops of all the samples at 300 K are presented for comparison, and the magnetization data of all samples is listed in Table 5.2. The solid-state processed $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ have the highest room temperature magnetization, followed closely by the DEG and EG-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ and can explained by the substitution of Ni and Zn for Fe. The Fe_3O_4 particles have a moderate magnetization compared to the aforementioned $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ materials. This is expected as Fe^{3+} ions

occupy all the tetrahedral and octahedral lattice positions, resulting in an overall reduced magnetization.

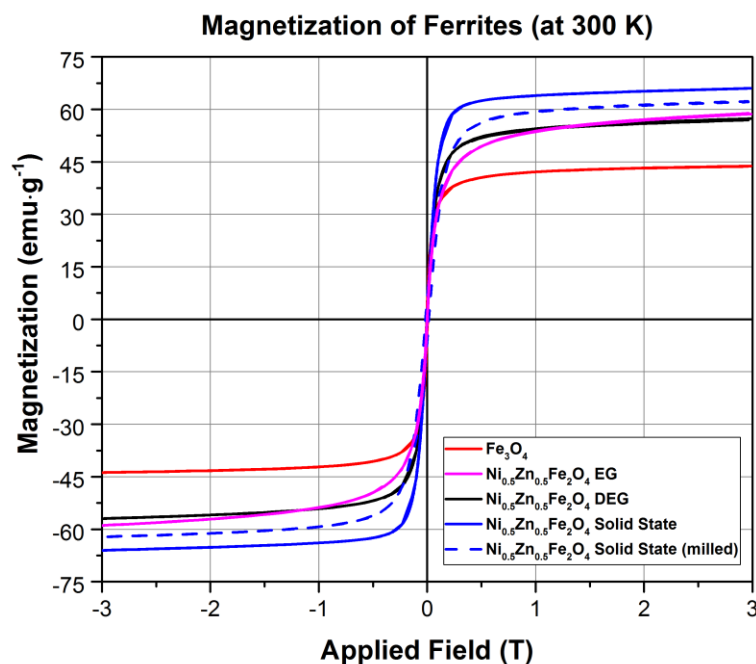


Figure 5.16 Magnetization curves comparisons of the various synthesis techniques at 300 K.

The coercivities of all samples are quite low, which enables the rapid magnetization switching at high frequency. The polyol-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ particles have the lowest coercivity at 300 K, approximately $1/10^{\text{th}}$ that of the solid-state processed ferrites.

Table 5.2 Magnetization data of synthesized MDM.

Sample ID	M_s (emu·g ⁻¹)	H_c (T)	T (K)
Fe ₃ O ₄	43.74	0.0045	50
Fe ₃ O ₄	62.19	0.0172	300
Ni _{0.5} Zn _{0.5} Fe ₂ O ₄ (EG)	80.80	0.0064	50
Ni _{0.5} Zn _{0.5} Fe ₂ O ₄ (EG)	58.77	0.0011	300
Ni _{0.5} Zn _{0.5} Fe ₂ O ₄ (DEG)	82.17	0.0001	50
Ni _{0.5} Zn _{0.5} Fe ₂ O ₄ (DEG)	57.15	0.0012	300
Ni _{0.5} Zn _{0.5} Fe ₂ O ₄ (solid state)	107.67	0.0023	50
Ni _{0.5} Zn _{0.5} Fe ₂ O ₄ (solid state)	66.03	0.0014	300
Ni _{0.5} Zn _{0.5} Fe ₂ O ₄ (solid state) 24 hr mill	62.16	0.0144	300

5.4 High-Frequency Electromagnetic Properties

In this section, the high-frequency EM properties of the materials were measured using an impedance analyzer for relative permittivities (ϵ_r) and dielectric loss tangents ($\tan\delta_e$) for all samples, and the relative permeabilities (μ_r) and magnetic loss tangents ($\tan\delta_m$) of the Fe₃O₄/EPON composites from 50 MHz – 1 GHz. All Ni_{0.5}Zn_{0.5}Fe₂O₄/EPON composites were measured using vector network analysis to determine μ_r and $\tan\delta_m$ from 50 MHz – 1 GHz. A short-open-load (S-O-L) calibration was performed on both devices prior to measurements. The materials under test (MUT) were composite samples of MDM filler into resin where the volumetric loading of filler has been controlled from 10 – 40 %. The averaged measurements of these materials throughout the frequency range are presented in Table 5.3. Afterwards, the demagnetizing effects and loss mechanisms for the MDM composite materials will be discussed.

5.4.1 Materials Properties

The magnetic properties of the Fe₃O₄/EPON composites are shown in Fig. 5.17, and the dielectric properties are shown in Fig. 5.18. As the volumetric loading increases,

all relevant parameters (μ_r , $\tan\delta_m$, ϵ_r , $\tan\delta_e$) increase and this behavior is expected of all samples and material types. The permeabilities are relatively constant throughout the frequency range and exhibit a $\mu_r > 1$ at all volumetric loadings, and ϵ_r demonstrate the similar behavior, where the permittivity remains constant, but has higher values (up to 6.2) than μ_r .

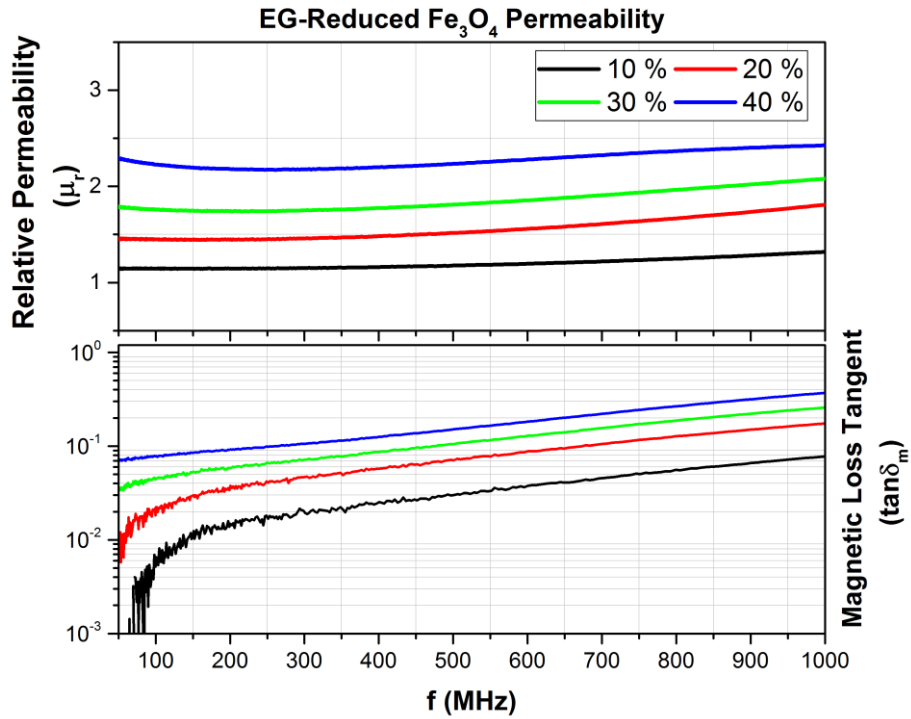


Figure 5.17 Vector network analyzer measurements the relative permeabilities and magnetic loss tangents of the $\text{Fe}_3\text{O}_4/\text{EPON}$ composites with filler volumetric loadings of 10 – 40 %.

The magnetic and dielectric loss tangents also increase as the amount of filler increases, but $\tan\delta_m$ and $\tan\delta_e$ operate via different mechanisms and do not necessarily behave linearly. At lower frequencies, $\tan\delta_m$ is low, less than 10^{-1} , but increases beyond

10^{-1} as frequency and loading increase. With respect to $\tan\delta_e$, both the 10 % and 20 % compositions show very little loss at the frequency range, but increases and stabilizes to 10^{-2} for 30 % and greater than 10^{-1} for 40 % loadings.

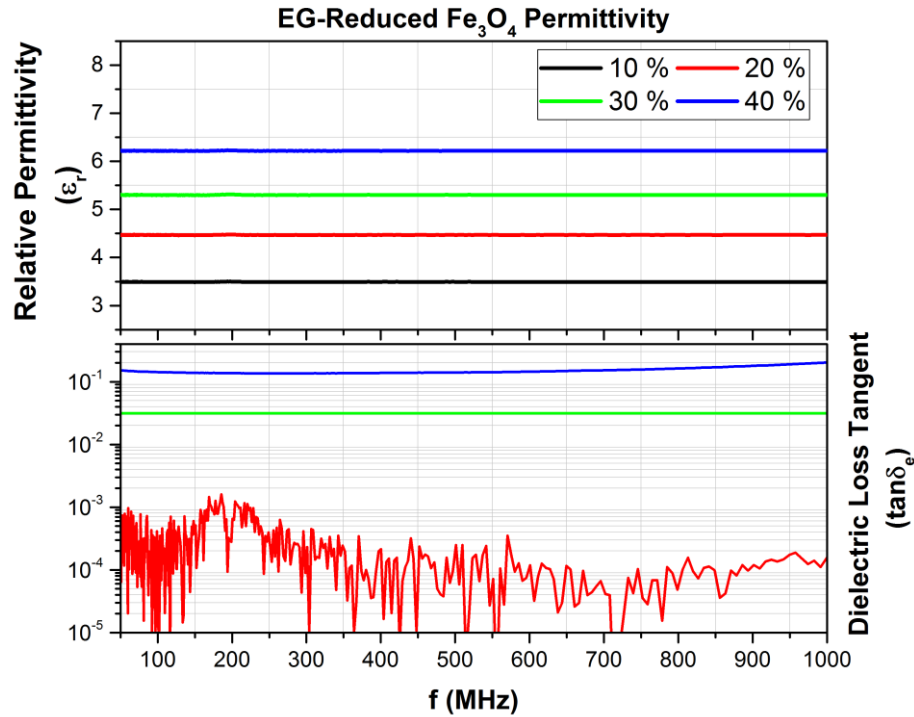


Figure 5.18 Impedance analyzer measurements the relative permittivities and dielectric loss tangents of the $\text{Fe}_3\text{O}_4/\text{EPON}$ composites with filler volumetric loadings of 10 – 40 %.

The EG-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ composites in Fig. 5.19 have more promising results regarding μ_r , particularly at lower frequency bands. Below 250 MHz, $\mu_r \geq 3$, but decreases to approximately 2.25 at 1 GHz demonstrating an undesired dispersion relation. The magnetic loss tangent is minimized between 100 – 300 MHz, where it reaches 10^{-1} and increases as frequency increases. The loss tangent is

considerably higher at the frequencies < 100 MHz which can be attributed to sensitivity of the measurement system. At lower frequencies, the impedance, $|Z_{MUT}|$, of these materials does not quite match the impedance of the instrument, 50Ω and leads to some deviation in data, but is corrected at higher frequencies.

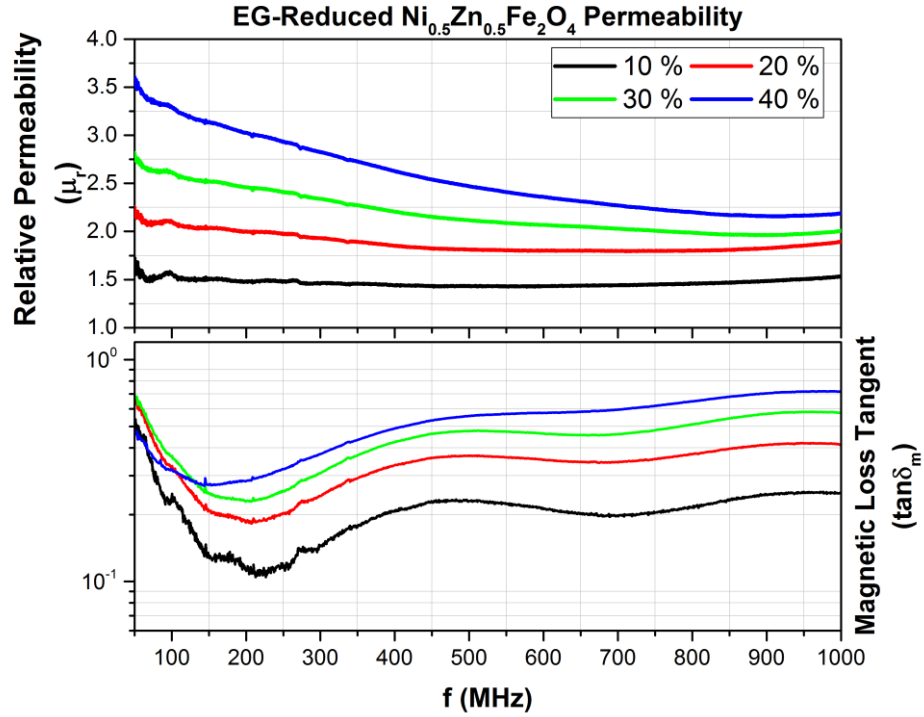


Figure 5.19 Vector network analyzer measurements the relative permeabilities and magnetic loss tangents of the EG-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ composites with filler volumetric loadings of 10 – 40 %.

The dielectric properties of the EG-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ composites are shown in Fig. 5.20. Unlike the $\text{Fe}_3\text{O}_4/\text{EPON}$ composites, ϵ_r is much higher at all loadings, up to an averaged value of $\epsilon_{\text{avg}} \approx 21$ throughout the frequency range. However, it does not appear to be as stable as the $\text{Fe}_3\text{O}_4/\text{EPON}$ composite material and decreases

to 17.5 at 1 GHz. The dielectric loss tangents are in the 10^{-2} range at lower frequencies and increase to above 10^{-1} at 1 GHz.

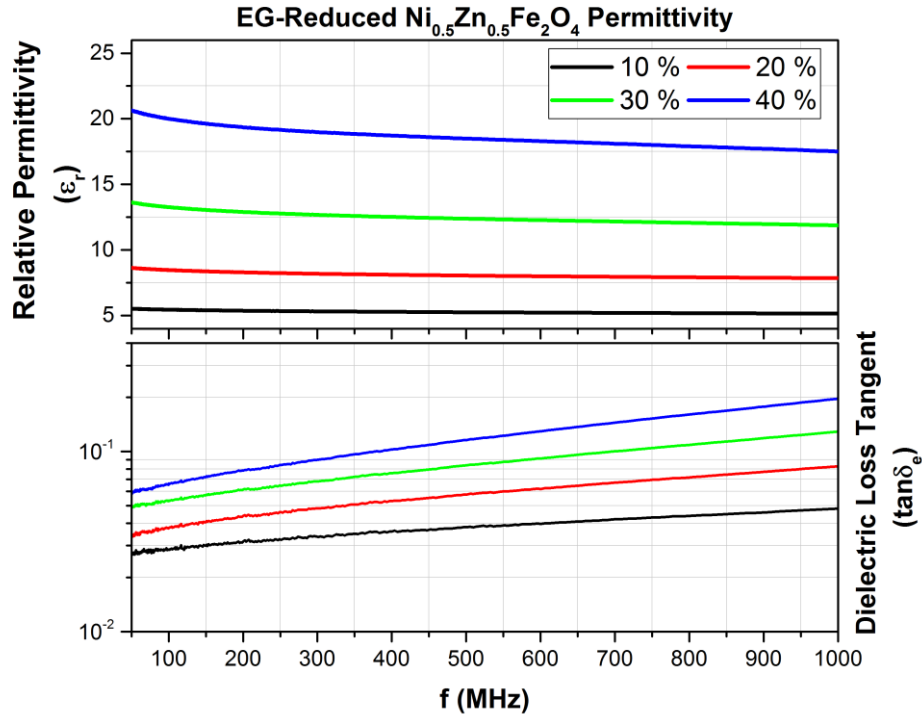


Figure 5.20 Impedance analyzer measurements the relative permittivities and dielectric loss tangents of the EG-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ composites with filler volumetric loadings of 10 – 40 %.

In Fig. 5.21, μ_r and $\tan\delta_m$ of the DEG-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ composites are shown. Out of all of the materials measured, these nanoparticles maintained the highest permeabilities, where $\mu_r \geq 3$ at frequencies up to approximately 650 MHz while maintaining a $\tan\delta_m$ similar to that of the EG-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ composites, which is still considered to be quite a lossy material.

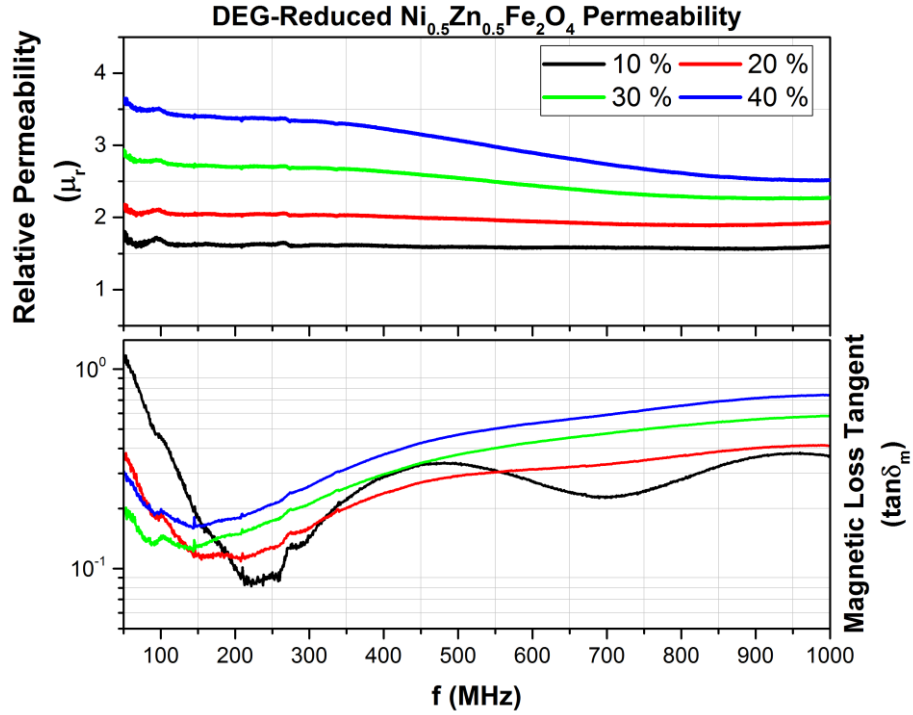


Figure 5.21 Vector network analyzer measurements the relative permeabilities and magnetic loss tangents of the DEG-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ composites with filler volumetric loadings of 10 – 40 %.

In Fig. 5.22, the corresponding ϵ_r and $\tan\delta_e$ of the DEG-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ composites are shown. While these values are also quite high, compared to the $\text{Fe}_3\text{O}_4/\text{EPON}$ composites ($\epsilon_{\text{avg}} \approx 6.2$), they are not nearly as high as the EG-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ composites ($\epsilon_{\text{avg}} \approx 21$). Additionally, the dielectric loss tangents of these materials ($\tan\delta_e \approx 0.04$) are more favorable to that of the EG-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ composites ($\tan\delta_e \approx 0.07$).

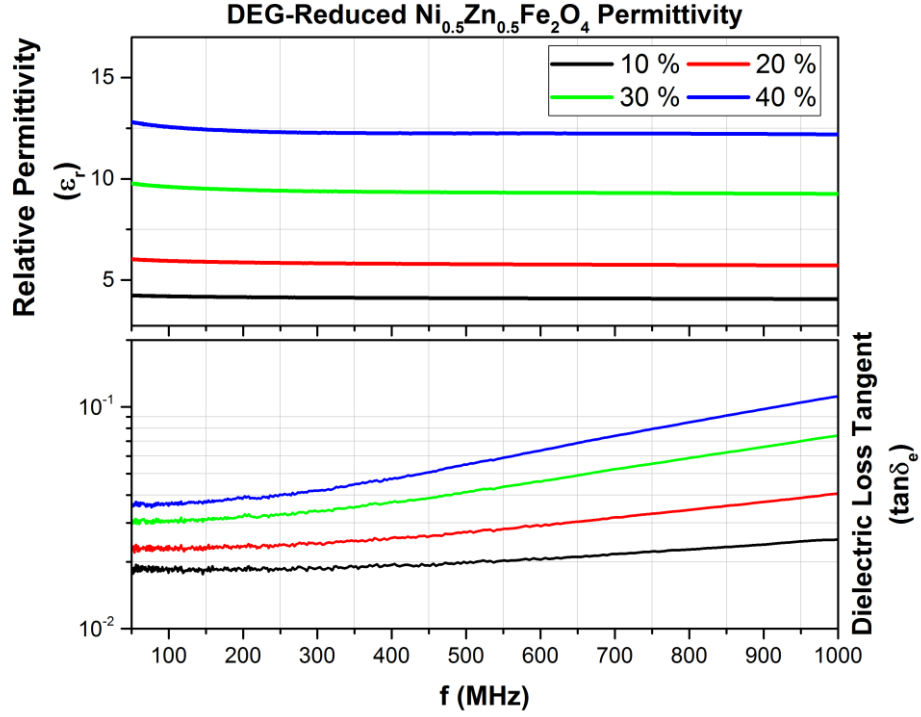


Figure 5.22 Impedance analyzer measurements the relative permittivities and dielectric loss tangents of the DEG-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ composites with filler volumetric loadings of 10 – 40 %.

In Fig. 5.23, μ_r and $\tan\delta_m$ of the solid-state processed $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ composites are shown. These materials have stable permeabilities throughout the frequency range, owing to the large size of the crystallites. However, the value is smaller compared to that of the DEG and EG-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ composites. Additionally, these materials contain the lowest magnetic loss characteristics of the $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ composites, which is in direct contrast to expected results and will be discussed later in this chapter.

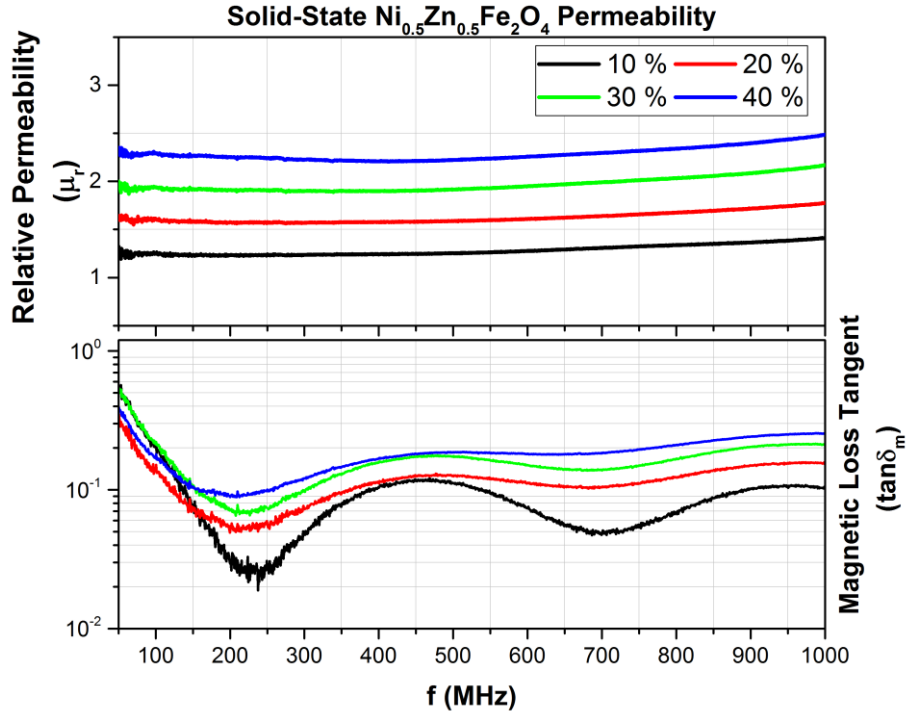


Figure 5.23 Vector network analyzer measurements the relative permeabilities and magnetic loss tangents of the Solid-State $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ composites with filler volumetric loadings of 10 – 40 %.

In Fig. 5.24, the corresponding ϵ_r and $\tan\delta_e$ of the solid-state processed $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ composites are shown. Unlike the DEG and EG-reduced composites, these values are much lower, and resemble the $\text{Fe}_3\text{O}_4/\text{EPON}$ composite materials. Despite being compositionally similar to the DEG and EG-reduced materials, the lower relative permittivity can be attributed to the difference in particle size. Regarding the dielectric loss tangents, the solid-state materials have the least-dispersive and lowest values for all volumetric loadings of the $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ composites.

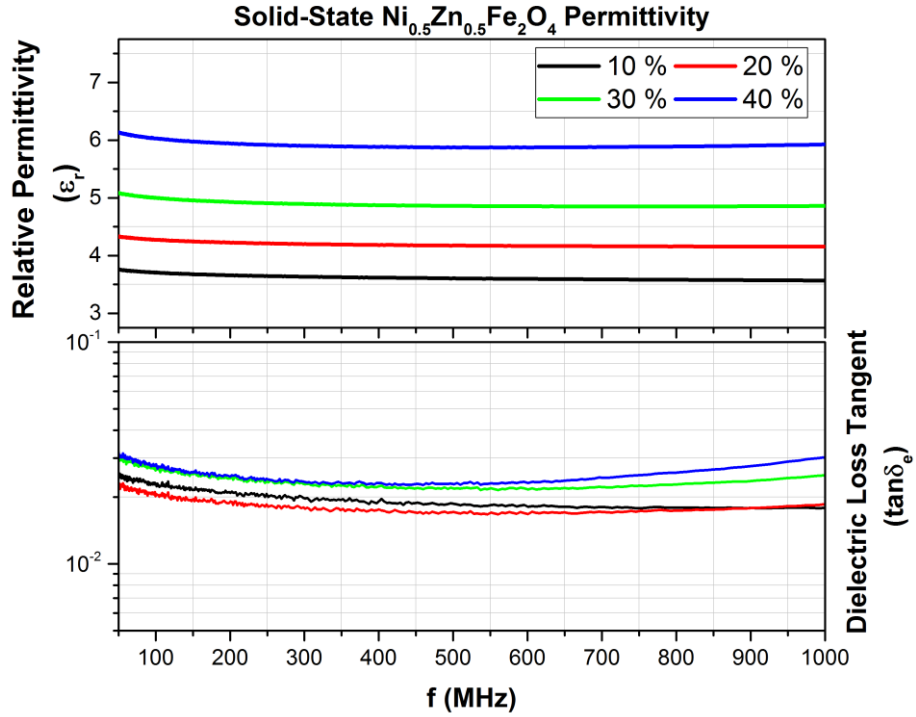


Figure 5.24 Impedance analyzer measurements the relative permittivities and magnetic loss tangents of the Solid-State $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ composites with filler volumetric loadings of 10 – 40 %.

The particle size and particle shape heavily influence the high-frequency magnetic and dielectric properties. In the following sections, demagnetizing effects, which reduce the effective permeability, and mechanisms to describe magnetic and dielectric losses will be discussed.

Table 5.3 Averaged high-frequency properties of MDM-composite materials from 50 MHz – 1 GHz.

Sample ID	vol. loading	μ_r	$\tan\delta_m$	ϵ_r	$\tan\delta_e$
Fe ₃ O ₄ /EPON	10 %	1.12	0.01	3.49	0.001
	20 %	1.44	0.05	4.47	0.001
	30 %	1.79	0.08	5.30	0.04
	40 %	2.24	0.10	6.22	0.17
(EG) Ni _{0.5} Zn _{0.5} Fe ₂ O ₄ /EPON	10 %	1.48	0.21	5.61	0.03
	20 %	1.88	0.34	8.73	0.04
	30 %	2.17	0.45	13.89	0.06
	40 %	2.53	0.54	21.03	0.07
(DEG) Ni _{0.5} Zn _{0.5} Fe ₂ O ₄ /EPON	10 %	1.60	0.29	4.28	0.02
	20 %	1.97	0.29	6.10	0.03
	30 %	2.49	0.38	9.94	0.04
	40 %	2.96	0.48	13.08	0.04
(Solid State) Ni _{0.5} Zn _{0.5} Fe ₂ O ₄ /EPON	10 %	1.30	0.09	3.82	0.03
	20 %	1.64	0.12	4.30	0.03
	30 %	1.99	0.16	5.10	0.03
	40 %	2.31	0.19	6.10	0.04

5.4.2 Demagnetizing Factor of Magnetodielectric Materials

In magnetic materials, the presence of an external magnetic field induces an internal magnetic field that is directed opposite to the magnetization¹¹. This demagnetizing field, H_d , is proportional to the magnetization:

$$H_d = NM \quad (5.1)$$

where, N is the directionally-dependent demagnetizing factor, and M is the magnetization. The magnitude of the effective field, H_{eff} ; that acts within the specimen is smaller than the applied field external field, H_{ex} , such that:

$$H_{eff} = H_{ex} - H_d. \quad (5.2)$$

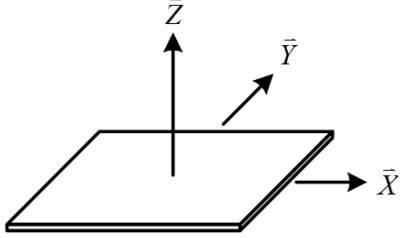
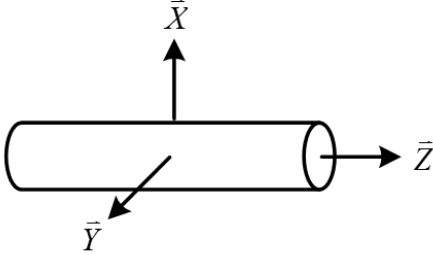
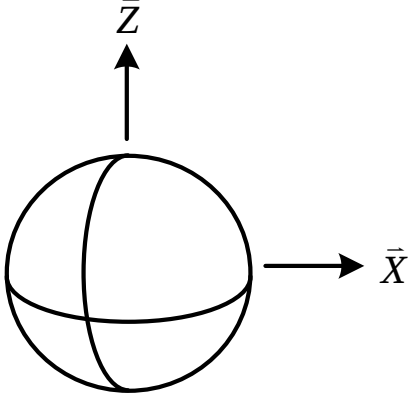
The synthesized ferrite particles are sphere-like in shape, providing high levels of symmetry; therefore, the demagnetizing factor of the particles is approximately $N = \frac{1}{3}$ (since $N_x + N_y + N_z = 1$)² and the N values for different geometries are shown in Table 5.4. This demagnetization effect also affects the measured permeability (apparent permeability, μ_{app}). Assuming there is no strong exchange interaction among ferrite inclusions, the apparent permeability is related to the true permeability of material through³⁴:

$$\mu_{app} = \frac{\mu}{[1+N(\mu-1)]} \quad (5.3)$$

For $\mu \gg 1$ and $N = \frac{1}{3}$ leads to $\mu_{app} \leq 3$.

Due to the high level of symmetry of these materials, it is unlikely that μ_{app} will exceed 3; but is considered isotropic and act as $\mu_{app} \approx 3$ in all directions with proper loading. To enhance the permeability further, we have to investigate anisotropic materials, preferably thin disk, plate, or high-aspect ratio geometries that will have a maximum permeability in two directions and a minimized permeability in the third direction. Hexagonal ferrites can fit this role, but aligning the particles in a preferential direction by applying magnetic fields is a focus for investigation.

Table 5.4 Demagnetization factors for basic shapes.

Shape	N_x	N_y	N_z
<u>Thin disk or plate</u> 	0	0	1
<u>Thin rod</u> 	$\frac{1}{2}$	$\frac{1}{2}$	0
<u>Sphere</u> 	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$

Adapted from Pozar (2005)

5.4.3 Loss Mechanisms of Magnetodielectric Materials

Generally, three different components are attributed to the magnetic loss of the material³⁵,

$$P_{loss} = P_h + P_{ec} + P_{anom} \quad (5.4)$$

The total loss, P_{loss} , is the cumulative losses of the hysteretic loss, P_h , the eddy current loss, P_{ec} , and anomalous losses, P_{anom} . Hysteretic losses are related to amplitude of the magnetization and are important in the low-frequency region as they are linearly dependent to the frequency estimated from the product of the area of the hysteresis loop, A , times the frequency, f , such that

$$P_h = Af. \quad (5.5)$$

The eddy current losses, P_{ec} , are related on the resistivity of the sample, the dimensions of the material with respect to the axis of magnetization, the density of the material, and are proportional to the square of the frequency. Eddy current losses for spherical particles are expressed as³⁶

$$P_{ec} = \frac{\pi B_m^2 d^2 f^2}{20\rho} \quad (5.6)$$

where B_m is the amplitude of magnetic induction, d is the diameter of the particle, f is the frequency, and ρ is the resistivity. In the frequency region of interest to RF applications, hysteretic and eddy current losses are the relevant factors to the magnetic loss behavior of this material, and anomalous losses do not contribute significantly. To minimize hysteretic losses, the coercivity of the material, H_c , needs to be minimized. The eddy current losses can be reduced with the material having a high resistivity, which is native to NiZn ferrite. Further, uniformly small dimensions, inherent to nanoparticles, also lead to reduced contributions from eddy currents. Surprisingly, the largest particles, the solid-state prepared $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ composites have some of the best

magnetic loss characteristics, where the DEG and EG-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ composites, which contain much smaller particles (approximately $\sim 100\times$ smaller) are significantly higher. A much smaller value for magnetic loss would be expected for the DEG and EG-reduced composites and can possibly be explained by the onset of ferrimagnetic resonance¹⁰. This resonance limits the frequencies at which the magnetic materials can effectively be used, and it has been observed that the higher the permeability, the lower the frequency that ferrimagnetic resonance occurs.

Regarding the dielectric loss tangent, it is observed that the dispersion and onset of resonances are tied to both the structure of the material and frequency³⁷. At lower frequencies, ionic and dipolar (or rotational) polarizations dominate, where atomic and electronic polarizations will become the dominating dielectric response factors at higher frequencies. In the frequencies of interest, dipolar interactions are the existent interactions and the permittivities and loss tangents resemble the behavior as shown in Fig. 5.25. These frequencies are far below the Debye relaxation frequencies, which is indicated by higher and relatively stable values of ϵ_r and low $\tan\delta_e$. If the Debye relaxation frequencies were reached, ϵ_r would rapidly decrease.

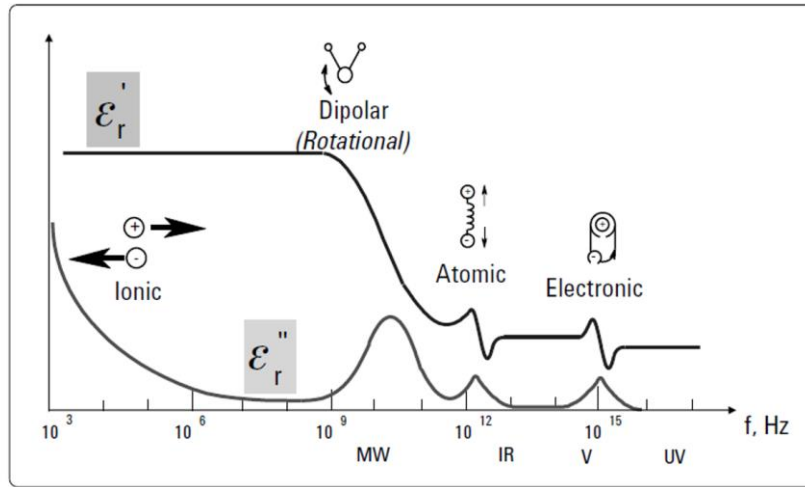


Figure 5.25 Example of frequency response of dielectric mechanisms, adapted from Agilent Technologies (2005).

5.5 Conclusion

The synthesized materials were identified using XRD, and characterized using microscopy and magnetometry revealing spinel-phase nano and micron-sized particles. The NiZn materials had much higher magnetizations than the Fe₃O₄ materials. Composite materials were characterized for their high-frequency properties using impedance and vector network analysis. The relative permeabilities of the NiZn materials were higher than the Fe₃O₄ materials, but did not exceed 3 at high frequencies. The magnetic loss tangents of all materials were $\leq 10^{-1}$ at high frequencies, which can be attributed to the onset of ferrimagnetic resonance, where the imaginary component of the permeability intersects the real component. The relative permittivities of all materials were relatively stable in the frequency range; however, the DEG and EG-reduced materials exhibited very high values. The dielectric loss tangents were quite low, between 10^{-2} - 10^{-1} which can be attributed to the materials in this range not quite reaching the Debye relaxation frequency.

Chapter 6

ADDITIVELY MANUFACTURED SPIRAL ANTENNA

In this chapter, the methods used to design a low-frequency antenna will be discussed. Afterwards, MDM-composites will be added to adjust antenna performance through means of size reduction (via shifting to lower frequency) by simulating various geometries. An antenna was fabricated using additive manufacturing technology and measured at the targeted frequencies.

6.1 Antenna Design

Using the Ansys High-Frequency Structural Simulator (HFSS), a commercial finite element method (FEM) solver, an Archimedean Spiral antenna was designed to operate at 585 MHz. Spiral antennas are generally considered to have wide bandwidth, but relatively low gain³⁸. These types of antenna have a constant spacing between adjacent arms with an outer radius defined through the relation:

$$r = r_0 e^{\alpha(\psi+\delta)} \quad (6.1)$$

Where r_0 is the inner radius, α is an expansion coefficient term, ψ is the pitch angle, and δ is the offset angle. Additional arms are added by simply rotating the first arm by an angle, in this case for a second arm, 180° around the origin.

Software that is commercially available, such as the Ansys HFSS Antenna Design Kit (ADK), greatly simplifies basic antenna designs, prompting the user to specify frequencies of operation and generates designs based on these criteria. Unfortunately, when ADK is used to design low-frequency spiral antennas, the program runs into issues such as a very high number of turns of the spiral, enormous inner radius (which would prove to be difficult to connect), resulting in a very large footprint.

Through tailoring of the design parameters, a bottom-fed Archimedean spiral antenna was designed to operate at 585 MHz, and while the return loss characteristics at the specified frequency is quite good it does not quite follow the description of ultra-wideband (in this case, $BW \approx 60$ MHz), and is shown in Fig. 6.1 with corresponding return loss in Fig. 6.2. This antenna has no MDM-composite material and the conductive arms are simulated using DuPont CB-028 Conductive Silver Paste ($\sigma \approx 10^7 \frac{S}{m}$) onto a polycarbonate substrate ($t = 1.1$ mm, substrate width = 110 mm, substrate length = 110 mm, $\epsilon_r = 2.9$, and $\tan\delta_e = 0.001$).

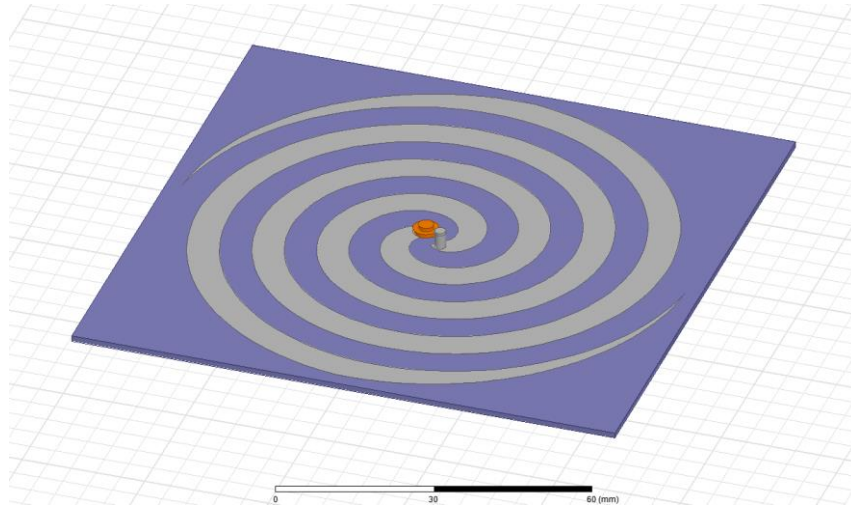


Figure 6.1 Modeled 585 MHz Archimedean spiral antenna designed using HFSS.

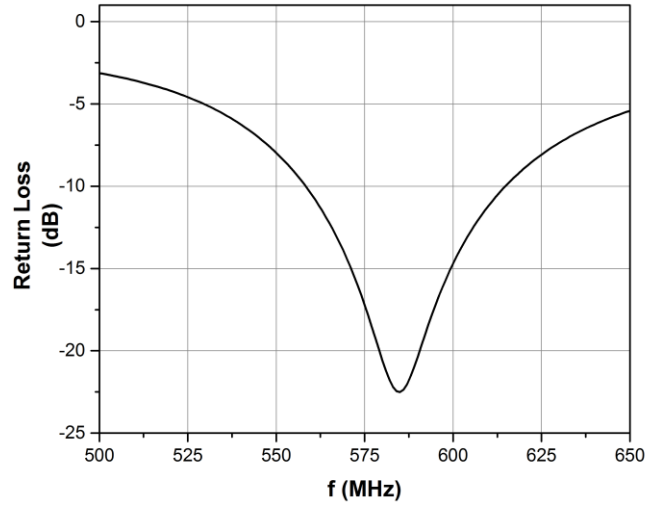


Figure 6.2 Simulated Return Loss of modeled 585 MHz Archimedean spiral antenna.

Using the $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ composite material, the frequency of operation can be reduced, acting as antenna size reduction, and potentially result in increased bandwidth. For this work, the solid-state processed $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ composite at 30 % volumetric loading was used as a material layer placed on top of the antenna, with a thickness of 1.0 mm. To utilize the power of additive manufacturing, specific geometries of the material is to be printed that would be exceptionally difficult using conventional manufacturing processes. These model geometries are outlined in Fig. 6.3, where the magnetodielectric-composite material is printed in between the conductive spiral arms with specified inner and outer diameters.

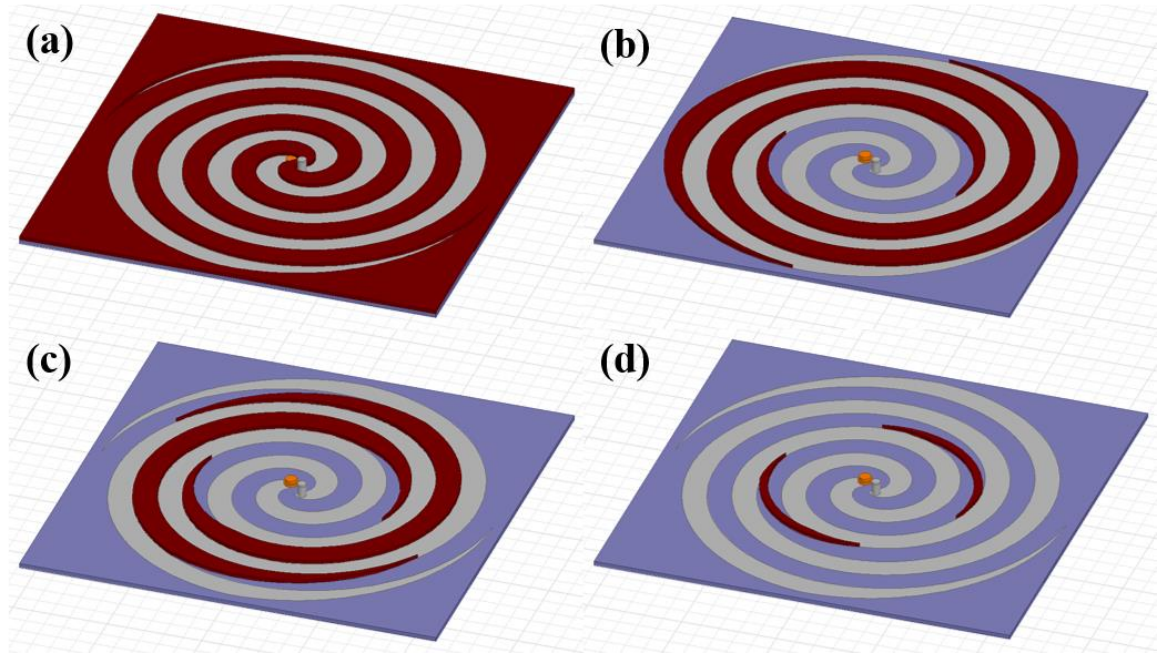


Figure 6.3 Modeled Archimedean spiral antenna designs with variably-loaded magnetic material configurations as (a) inverted spiral, (b) trimmed inverted spiral, (c) 42 mm outer radius trimmed inverted spiral, and (d) 22 mm outer radius trimmed inverted spiral incorporating the MDM/EPON composites in HFSS.

Through tailoring the geometry of the MDM-composite, the amount of material can be reduced while still resulting in frequency-reduction. It is in our best interest to reduce the amount of material needed while still seeing a noticeable shift in frequency. Parametric analyses were run, where the outer radius diameter of the MDM-composite changed from 28 – 52 mm using a constant inner radius, with the results shown in Fig. 6.4. In Table 6.1, the amounts of material required for specified model geometries is presented and it is shown that using a fraction of material, compared to the 1 mm-thick full slab of MDM-composite, still results in a noticeable frequency shift.

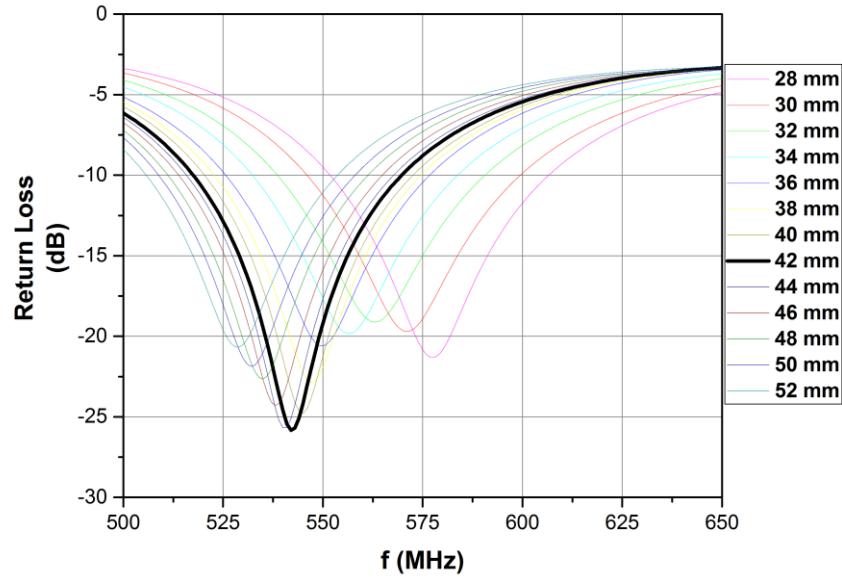


Figure 6.4 Simulated Return Loss of Archimedean spiral antenna with 42 mm outer radius trimmed spiral using HFSS with peak shift to 542 MHz.

Table 6.1 MDM-composite material requirements for specified designs of Archimedian Spiral Antenna.

Antenna Model	Material Volume (cm ³)	Volume reduction	Operating Freq. (MHz)	$\Delta_{585 \text{ MHz}}$ shift (MHz)
Full Slab	12.091	-	474	111
Inverted Spiral	7.854	35.0 %	512	73
Trimmed Inverted Spiral	3.186	73.7 %	529	56
Trimmed Inverted Spiral (42 mm outer radius)	1.709	85.9 %	542	43
Trimmed Inverted Spiral (28 mm outer radius)	0.170	98.6 %	578	7

In Fig. 6.5, the comparisons between simulated antenna models using the different geometries are shown. As a proof of concept, the 42 mm model was selected to be built for this study to demonstrate the complex additive manufacturing process using the

nScript microdispenser, which would be very difficult to manufacture using conventional processes.

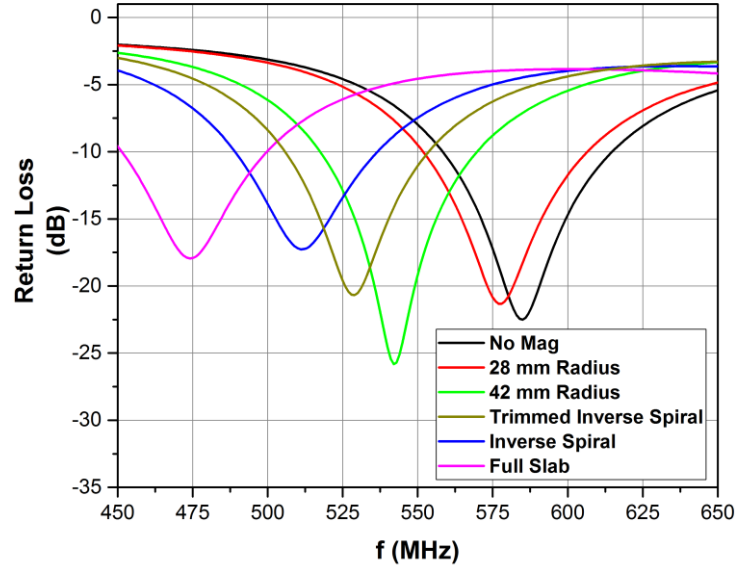


Figure 6.5 Simulated Return Loss comparison of antenna designs using different geometries with the same MDM-composite material.

6.2 Spiral Antenna Fabrication using Additive Manufacturing and Results

Silver paste was dispensed onto a polycarbonate substrate and then cured in place according to vendor specifications. With the substrate still in place, $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ composite was dispensed between the conductive spiral arms using the HFSS geometries as the toolpath, and then cured using the nScript's heated platen until the composite cured. Conductive vias were drilled into the antenna and bottom-fed using SMA connectors and electrically connected using a silver epoxy compound. After final curing, the antenna was checked for electrically conductivity and

ready to be measured using a vector network analyzer. In Fig. 6.6, the finished antenna assembly is shown with both bottom, and top profiles.

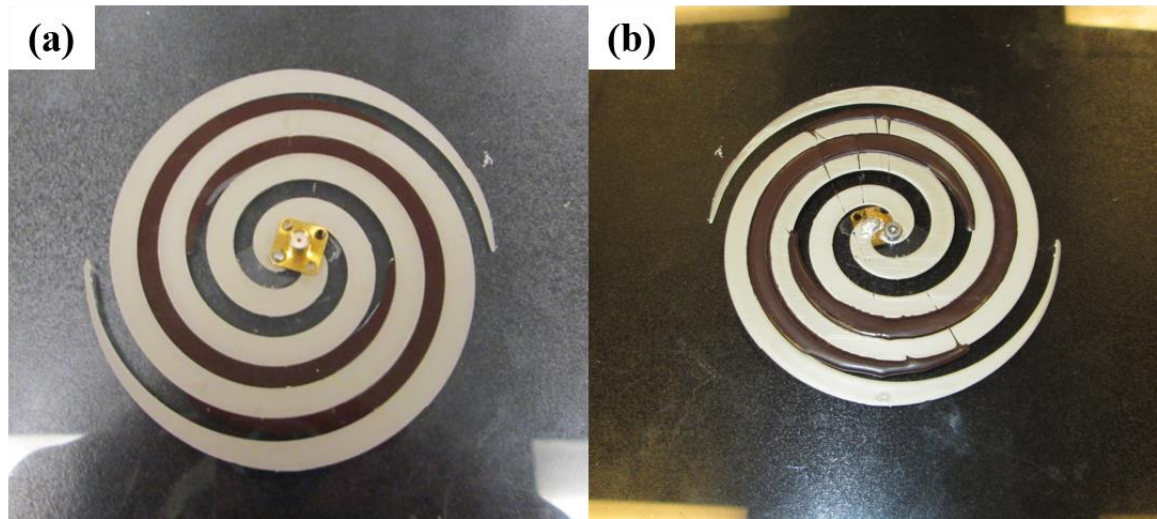


Figure 6.6 Printed Archimedean spiral antenna with MDM/EPON composite material with the (a) bottom and (b) top profiles shown.

In Fig. 6.7, the measured antenna is presented with overlapping simulated data. The substrate was quite bowed, which definitely affected radiation patterns of the antenna. This could have been caused during the curing where the silver paste heats up and sinters during this process, possibly deforming the substrate slightly in the process. The measurement of the bowed substrate did not prove to be very effective, but when the substrate was flattened and re-measured, the return loss peak at ~ 540 MHz is prominent, although not nearly as attenuated as the simulation results, which operate as a “best case” scenario. Despite this, the antenna could still effectively work at 540 MHz with a return loss of -12 dB.

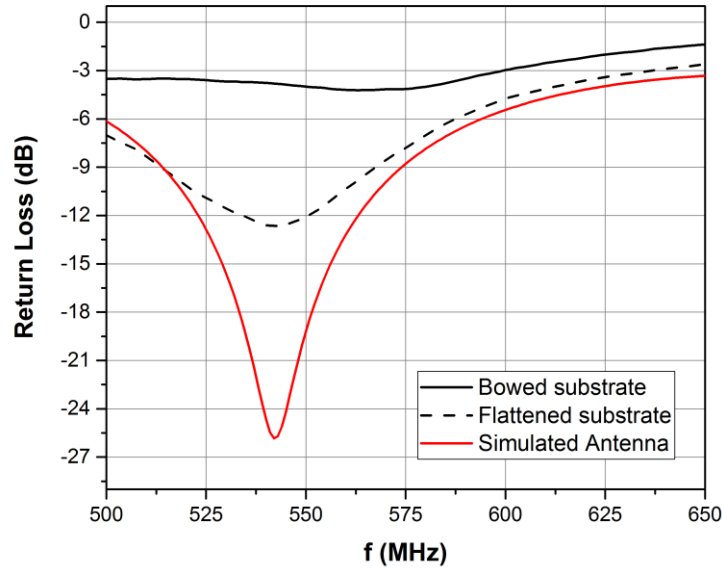


Figure 6.7 Measured return loss data of MDM/EPON composite-loaded spiral antenna compared to simulated data. The substrate had significant bowing and required flattening.

6.3 Additively Manufactured Spiral Antenna Conclusion

An Archimedean spiral antenna was designed using HFSS to operate at 585 MHz. Adding MDM-composite, which has both a μ and ϵ greater than 1 was added to the simulation between spiral arms to reduce the operating frequency. Through adjusting the amount of MDM-composite, a shift towards lower frequencies was observed and the amount of material required could be regulated. By using only 14 % of the material compared a 1 mm-thick, full slab of MDM-composite, the designed antenna was able to operate at 40 % of the predicted frequency shift and was verified by an additively manufactured device. Further improvements can be made in the development of materials properties and antenna design to result in a more effective antenna.

Chapter 7

CONCLUSION

7.1 Summary of Results

Magnetodielectric materials to be used in additive manufacturing, such as micro-dispensing, were developed and then characterized for their physical and high-frequency properties. There were some requirements of the materials for additive manufacturing, such as small particle diameter, high relative permeability, high relative permittivity and low loss tangents.

The materials were synthesized using a variety of methods, such as polyol reduction involving two reaction mediums: ethylene glycol and diethylene glycol, and a solid state ceramics process, which involves the diffusion of metal oxide precursors into the final crystalline product. The method of synthesis resulted in compositionally similar materials, but their particle size and degree of crystallinity varied significantly which affected both DC magnetic and high-frequency electromagnetic properties. The DC magnetizations of the polyol-reduced and solid-state processed $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ were very similar to bulk values ($M_s \approx 58 - 60 \text{ emu}\cdot\text{g}^{-1}$), and the polyol-reduced Fe_3O_4 materials had lower magnetizations, due to the lack of substitutions of Ni^{2+} and Zn^{2+} ions. The coercivities of all materials are very low, indicating that these materials are soft magnets and can rapidly switch at high frequencies. The polyol-reduced methods yielded sphere-like $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles that were perfectly suitable to be used in micro-dispensing due to their size. The solid-state processing method yielded sphere-like micron-sized particles that were easy to make in large batches. Unfortunately, for these materials to be used in micro-dispensing, the materials needed to be mechanically milled to reach a target particle diameter $\leq 5 \text{ }\mu\text{m}$.

MDM-composite materials were fabricated using the synthesized materials coupled with the EPON epoxy system in various volumetric filler loadings of 10 – 40 %. These materials were characterized for their high-frequency electromagnetic properties from 50 MHz – 1 GHz. The polyol-reduced $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ composites had the highest ϵ_r , μ_r , values and the highest respective loss tangents. It was expected that spherical, nanoparticle systems would maintain relatively low loss tangents, but the onset of ferrimagnetic resonance could potentially explain this behavior. The solid state $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ composites, which was easy to make in large batches had comparable permeabilities, but a much lower permittivity and, surprisingly, the lowest loss tangents. The $\text{Fe}_3\text{O}_4/\text{EPON}$ composites had very similar electromagnetic properties to the solid-state processed $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ composites in terms of ϵ_r , μ_r , and $\tan\delta$. From a high-frequency standpoint, these composite materials meet all of the requirements where ϵ_r , and μ_r , were both greater than 1, particle size smaller than the orifice diameter of the micro-dispenser, resulting in a very good material to be used in additive manufacturing processes.

An Archimedean spiral antenna was designed in HFSS to operate at 585 MHz. MDM-composite material was then simulated in various geometries to determine the frequency shift towards a lower value, ultimately reducing the size of the antenna. Commercially available conductive silver paste was used to print a two-arm spiral onto a thin polycarbonate substrate. Then solid-state $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{EPON}$ composites loaded at 30% was selected to be printed in a concentric circle between the conductive spiral arms, with an inner radius of 26 mm and an outer radius of 42 mm at 1 mm thickness. The simulated shift specified that this would result in a shift from 585 MHz $\rightarrow$ 542 MHz by only using a relatively small amount of material, resulting in materials

savings that could equate to lowering manufacturing costs. This antenna was measured at the frequency range, and after flattening out the substrate, yielding a return loss peak of ≤ -12 dB at 542 MHz. Through manipulation of design parameters, the frequency can be shifted to an even lower frequency at the expense of using more material.

7.2 Future Work

More work is currently under investigation to improve materials properties for additive manufacturing of devices for high-frequency applications. To increase the permeability, or the operating frequency, anisotropic materials such as hexaferrites, where the particle geometry resembles a hexagonal plate, as opposed to an isotropic sphere, are actively being studied. The demagnetization factor for spherical particles limits the effective permeabilities at high frequency due to the high levels of symmetry of spheres generated from the demagnetizing field. High-aspect ratio materials do not have these levels of symmetry and will exhibit the maximum permeability in two directions, at the expense of a minimized permeability in the third. Work will need to be done to properly align the particles in the composite during the dispensing process to generate the anisotropic medium to attain this maximum permeability.

Additionally, high-dielectric, low-loss materials are also actively being investigated to be used as device substrates at frequencies between 18 – 40 GHz. These materials will deviate from the resin-based composite system and incorporate thermoplastics so rigid structures, such as gradient-index optics (GRIN), passive beam-steering devices, and a variety of lenses, can be developed using only additive manufacturing methods. In all cases, it is the development of materials that will enable all of these devices to be produced and complement conventional manufacturing processes.

REFERENCES

1. L. Harivardhan Reddy, J. Arias, J. Nicolas and P. Couvreur, "Magnetic Nanoparticles: Design and Characterization, Toxicity, Biocompatibility, Pharmaceutical and Biomedical Applications," *Chemical Reviews*, vol. 112, no. 11, pp. 5818-5878, 2012.
2. D. Pozar, *Microwave Engineering*, Hoboken, NJ: John Wiley & Sons, Inc., 2005.
3. N. Frey and S. Sun, "Magnetic Nanoparticle for Information Storage Applications," in *Inorganic Nanoparticles: Synthesis, Applications, and Perspectives*, Boca Raton, FL, CRC Press, 2011, pp. 33-68.
4. J. Philip, V. Mahendran and L. Felicia, "A Simple, In-Expensive and Ultrasensitive Magnetic Nanofluid Based Sensor for Detection of Cations, Ethanol and Ammonia," *Journal of Nanofluids*, vol. 2, no. 2, pp. 112-119, 2013.
5. R. Garg, P. Bhartia, I. Bahl, and A. Ittipiboon, *Microstrip Antenna Design Handbook*, Artech House, Norwood, MA, 2000.
6. JJ. Adams, E.B. Duoss, T.F. Malkowski, M.J. Motala, B.Y. Ahn, R.G. Nuzzo, J.T. Bernhard, and J.A. Lewis, "Conformal Printing of Electrically Small Antennas on Three-Dimensional Surfaces," *Advanced Materials*, vol. 23, no. 11, pp. 1335-1340, 2011.
7. M.S. Mannoer, Z. Jiang, T. James, Y.L. Kong, K.A. Malatesta, W.O. Soboyejo, N. Verma, D.H. Gracias, and M.C. McAlpine, "3D Printed Bionic Ears," *Nano Letters*, vol 13, no. 6, pp. 2634-2639, 2013.
8. nScrypt, Inc., nScrypt, Inc., 2015. [Online]. Available: nscrypt.com. [Accessed 2015].
9. R. Valenzuela, *Magnetic Ceramics*, Cambridge University Press, Cambridge, 1994.
10. A. Goldman, *Modern Ferrite Technology*, Springer Science, New York, 2006.
11. S. Chikazumi, *Physics of Ferromagnetism*, Oxford University Press, New York, 2009.

12. P. Parsons, K. Duncan, S. P. Karna and J. Xiao, "Tailored Electromagnetic Properties of NiZn Nanocomposite Materials," in *IEEE International Conference on Nanotechnology*, Toronto, 2014.
13. M. Sorescu, L. Diamandescu, R. Peelamedu, R. Roy, and P. Yadoji, "Structural and magnetic properties of NiZn ferrites prepared by microwave sintering." *J. Magn. Magn. Mater.*, 293, 2004.
14. Y. Ishikawa, "Superparamagnetism in the ZnFe_2O_4 - NiFe_2O_4 System," *J. Phys. Soc. Japan*, vol. 17, 1962.
15. E.W. Gorter, "Saturation Magnetization and Crystal Chemistry of Ferrimagnetic Oxides," *Philips Research Reports*, vol. 9, no. 4, 1954.
16. Smit, J., and Wijn, H.P.J., *Ferrites*, Philips Technical Library, Eindhoven, 1959.
17. Coey, J.M.D., *Magnetism and Magnetic Materials*, Cambridge University Press, New York, 2009.
18. J. Chun, S. Seo, G. Jung and J. Lee, "Easy access to efficient magnetically recyclable separation of histidine-tagged proteins using superparamagnetic nickel ferrite nanoparticle clusters," *Journal of Materials Chemistry*, vol. 16, pp. 6713-6717, 2011.
19. S. Chkoundali, S. Ammar, N. Jouini, F. Fievet, P. Molinie, M. Danot, F. Villain and J.-M. Greneche, "Nickel ferrite nanoparticles: elaboration in polyol medium via hydrolysis, and magnetic properties," *Journal of Physics: Condensed Matter*, vol. 21, pp. 4357-4372, 2004.
20. N. Ballot, F. Schoenstein, S. Merccone, T. Chauveau, O. Brinza and N. Jouini, "Reduction under hydrogen of ferrite MFe_2O_4 (M: Fe, Co, Ni) nanoparticles obtained by hydrolysis in polyol medium: A novel route to elaborate CoFe_2 , Fe and Ni_3Fe nanoparticles," *Journal of Alloys and Compounds*, vol. 536S, pp. S381-S385, 2012.
21. A. Giri, G. Hirsh, K. Duncan, S. Karna and C. Dennis, "Magnetic distributions of iron-(nickel zinc ferrite) nanocomposites from first order reversal curve analysis," *Journal of Applied Physics*, vol. 113, p. 173908, 2013.

22. P. Parsons, K. Duncan, A. Giri, J. Xiao and S. Karna, "NiZn Ferrite Nanoparticles and their Polymer Composites for Antenna Miniaturization," in *IEEE International Conference on Nanotechnology*, Birmingham, 2012.
23. P. Parsons, K. Duncan, A. Giri, J. Xiao and S. Karna, "Electromagnetic properties of NiZn ferrite nanoparticles and their polymer composites," *Journal of Applied Physics*, vol. 115, p. 173905, 2014.
24. B. D. Cullity, *Elements of X-Ray Diffraction*, Addison-Wesley Publishing Company, Inc., 1967.
25. S. Speakerman, "Estimating Crystallite Size Using XRD," MIT Center for Materials Science and Engineering, Cambridge, 2008.
26. J. Goldstein, D. Newbury, D. Joy, C. Lyman, P. Echlin, E. Lifshin, L. Sawyer and J. Michael, *Scanning Electron Microscopy and X-ray Microanalysis*, New York: Springer Science, 2003.
27. K. Buschow and F. de Boer, *Physics of Magnetism and Magnetic Materials*, New York: Springer, 2003.
28. Agilent Technologies, "Agilent Solutions for Measuring Permittivity and Permeability with LCR Meters and Impedance Analyzers, Application Note 1369-1," Agilent Technologies, USA, 2008.
29. R. Dosoudil, "Determination of Permeability From Impedance Measurement Using Vector Network Analyzer," *Journal of Electrical Engineering*, vol. 63, no. 7s, pp. 97-101, 2012.
30. Agilent Technologies, "Advanced Impedance Measurement Capability of the RF-IV Method Compared to the Network Analysis Method," Agilent Technologies, USA, 2001.
31. B. Andrzejewski, W. Bednarski, M. Kazmierczak, K. Pogorzelec-Glaser, B. Hilczer, S. Jurga, M. Matczak, B. Leska, R. Pankiewicz and L. Kepinski, "Magnetization Enhancement in Magnetic Nanoparticles capped with Alginic Acid," Cornell University Library – arXiv.org, Ithaca, NY, 2013.
32. P. van der Zaag, P. van der Valk and M. T. Rekveldt, "A domain size effect in the magnetic hysteresis of NiZn ferrites," *Appl. Phys. Lett.*, vol. 69, no. 2927, 1996.

33. G. Herzer, *Nanocrystalline Soft Magnetic Alloys, Handbook of Magnetic Materials*, Vol. 10, Elsevier, 1997.
34. Y. Zhao, C. Ni, D. Krucznki, X. Zhang, and J.Q. Xiao, "Exchange coupled soft magnetic FeNi-SiO₂ nanocomposites", *J. Phys. Chem. B*, vol. 108, p. 3691, 2004.
35. R. M. Bozorth, *Ferromagnetism*, IEEE Press, New York, 1978.
36. Y. Zhang, and Y. Zhai, "Magnetic Induction Heating of Nano-Sized Ferrite Particles," in *Advances in Induction and Microwave Heating of Mineral and Organic Materials*, InTech, Open Access, pp. 483-500, 2011.
37. Agilent Technologies, "Application Note - Basics of Measuring the Dielectric Properties of Materials," Agilent Technologies, USA, 2005.
38. R. C. Johnson, *Antenna Engineering Handbook 3rd Ed.*, McGraw-Hill, New York, 1993.

Appendix

CHEMICAL REAGENTS USED IN STUDY

Reagent	Formula	Molar Mass (g·mol ⁻¹)	Supplier
Iron(II) Chloride Tetrahydrate	FeCl ₂ ·6H ₂ O	234.843	Sigma Aldrich
Iron (III) Chloride Tetrahydrate	FeCl ₃ ·6H ₂ O	270.296	Sigma Aldrich
Iron Oxide	Fe ₂ O ₃	159.688	Alfa-Aesar
Nickel (II) Acetate Tetrahydrate	Ni(OCOCH ₃) ₂ ·4H ₂ O	248.840	Sigma Aldrich
Nickel Oxide	NiO	74.693	Sigma Aldrich
Zinc (II) Acetate Dihydrate	Zn(CH ₃ COO) ₂ ·2H ₂ O	219.500	Sigma Aldrich
Zinc Oxide	ZnO	81.379	Sigma Aldrich
Sodium Hydroxide	NaOH	39.997	Alfa-Aesar
Ethylene Glycol	C ₂ H ₆ O ₂	62.070	Alfa-Aesar
Diethylene Glycol	C ₄ H ₁₀ O ₃	106.12	Alfa-Aesar