FABRICATION AND FERROMAGNETIC RESONANCE STUDY
OF EPITAXIAL SPINEL FERRITE FILMS FOR
MICROWAVE DEVICE APPLICATIONS

by

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ABSTRACT

Single crystalline nickel ferrite and lithium ferrite thin films have attracted a lot of research attention recently, because of their unique physical properties for practical applications in next generation technologies, such as monolithic microwave integrated circuits (MMIC) and multiferroic heterostructures. The properties of these materials are closely related to the specific growth method and can be tailored by factors like surface morphology, microstructure and chemical composition. Different thin film growth techniques have been investigated in the past few decades for the fabrication of single crystalline thin films of both these spinel ferrites. However, the difficulty to attain high quality, homogeneous epitaxial films with limited surface and bulk defects and low microwave loss still remains a challenging task. Moreover, there have been very limited reports on the detailed ferromagnetic resonance (FMR) studies of these single crystalline nickel and lithium ferrite thin films, which is an essential aspect to understand the relaxation in magnetization precession (microwave damping) in these materials.

In this dissertation work, fabrication and study of structural, magnetic and FMR properties of single crystalline lithium ferrite (LiFe$_5$O$_8$) and nickel ferrite (NiFe$_2$O$_4$) films by direct liquid injection chemical vapor deposition (DLI-CVD) are studied in detail. The growth conditions, which play a crucial role in attaining the desired film morphology and stoichiometry, are optimized to achieve epitaxial, single crystalline lithium ferrite films having low ferromagnetic resonance linewidth coupled with excellent magnetic properties.
A detailed ferromagnetic resonance (FMR) study has been done to identify as well as quantify the magnetic relaxation mechanisms in the ‘as-grown’ nickel ferrite films. The broadband frequency, angle and temperature dependent measurements reveal the existence of two-magnon scattering as the active relaxation mechanism for the films.
DEDICATION

This dissertation is dedicated to my lovely parents, my brother Naresh and all my close friends.
## LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic force microscope</td>
</tr>
<tr>
<td>a.u.</td>
<td>Arbitrary units</td>
</tr>
<tr>
<td>at.%</td>
<td>Atomic percentage</td>
</tr>
<tr>
<td>acac</td>
<td>Acetylacetonate</td>
</tr>
<tr>
<td>DLI-CVD</td>
<td>Direct liquid injection chemical vapor deposition</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive spectrum</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>FMR</td>
<td>Ferromagnetic resonance</td>
</tr>
<tr>
<td>g/h</td>
<td>Gram/hour</td>
</tr>
<tr>
<td>ICP</td>
<td>Inductively coupled plasma</td>
</tr>
<tr>
<td>ip</td>
<td>In-plane</td>
</tr>
<tr>
<td>LFO</td>
<td>Lithium ferrite</td>
</tr>
<tr>
<td>LPE</td>
<td>Liquid phase epitaxy</td>
</tr>
<tr>
<td>MAO</td>
<td>Magnesium aluminium oxide</td>
</tr>
<tr>
<td>ME</td>
<td>Magneto-electric</td>
</tr>
<tr>
<td>min</td>
<td>Minute</td>
</tr>
<tr>
<td>NFO</td>
<td>Nickel ferrite</td>
</tr>
<tr>
<td>oop</td>
<td>Out-of-plane</td>
</tr>
<tr>
<td>PLD</td>
<td>Pulsed laser deposition</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>----------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>PZN-PT</td>
<td>Lead zinc niobate - lead titanate</td>
</tr>
<tr>
<td>PMN-PT</td>
<td>Lead magnesium niobate - lead titanate</td>
</tr>
<tr>
<td>SIMS</td>
<td>Secondary ion mass spectrometry</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>RMS</td>
<td>Root mean square</td>
</tr>
<tr>
<td>RF</td>
<td>Radio frequency</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscope</td>
</tr>
<tr>
<td>VSM</td>
<td>Vibrating sample magnetometer</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>YIG</td>
<td>Yttrium iron garnet</td>
</tr>
</tbody>
</table>
LIST OF SYMBOLS

a,c  Lattice parameters
θ   Angle
λ   Wavelength
ϕ   In-plane tilt angle in XRD
ω   Angular frequency or angle in transverse XRD
ΔH  FMR linewidth
ψ   Longitudinal tilting angle in XRD
M_{eff}  Effective magnetization
H_{4f}  Four fold anisotropy field
H_s   Saturation field
H_c   Coercive field
M_s   Saturation magnetization
M   Magnetization
γ'   Gyromagnetic ratio
H_{res}  Resonance field
H   Magnetic field
H_k   Anisotropy field
K_{1}  First order magnetocrystalline anisotropy coefficient
f   Frequency
\( \lambda_{100} \) Magnetostriction constant

d Lattice plane spacing

(hkl) Miller indices for a plane normal to the \([h k l]\) direction

E Electric field or Young’s modulus

e Electron charge

\( T_g \) Growth temperature

sccm Standard cubic centimeters per minute

ml millilitre

mg milligram

a,b,c Lattice constants, unit cell directions

t Thickness

k Wave vector

\( \omega_k \) Frequency of \( k \neq 0 \)

\( \sigma \) Induced stress

R Resistance

T Temperature

\( T_c \) Curie temperature

g Effective g factor

\( \mu_B \) Bohr magneton

x,y,z Cartesian coordinates

v Poisson’s ratio
ACKNOWLEDGMENTS

I take this opportunity to thank many faculty members, colleagues and friends who helped me with this research work. First, I would like to thank Dr. Patrick R. LeClair and Dr. Arunava Gupta, my research advisors, for their guidance, encouragement and discussion throughout this work and my academic progress. They encouraged me to work independently and gently guided me towards the right direction. I am grateful to Dr. Tim Mewes for his invaluable suggestions and motivation. The lengthy, interesting discussions I had with him were always very useful in getting additional insight into this project. The three months summer support given by him in 2010 is also highly appreciated. I thank Dr. J. W. Harrell who has been a wonderful mentor throughout my graduate school experience in UA. A special thanks to Dr. Claudia Mewes for all her support during my initial semesters and her suggestions in this research work. I thank Dr. Patrick Toale who is my committee member and all the professors in the Physics department with whom I have had the privilege of being associated as a graduate student and as a teaching assistant. Most importantly, I want to thank the Department of Physics and MINT centre for all the support.

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CHAPTER 1

OUTLINE

The presented work focuses on two magnetic systems with spinel structure: lithium ferrite and nickel ferrite. Both of them are of great importance in the current and future technological applications but suffer from consistent issues related to the fabrication of single crystalline films and understanding their fundamental physical properties. The introduction chapter 2 provides a brief overview of the studied materials, lithium ferrite and nickel ferrite, and the motivation that led to this dissertation work. The main experimental methods employed to investigate the above-mentioned spinel systems are briefly discussed in chapter 3. Chapter 4 includes a detailed study of the fabrication and properties of lithium ferrite films deposited on different substrates using chemical vapor deposition at varying growth conditions. The physical properties of a bulk single crystal of lithium ferrite are reported in chapter 5. A detailed study of nickel ferrite films is reported in chapter 6 primarily focusing on how the microstructure of the films can be greatly influenced by altering the deposition parameters, in particular the substrate temperature which further leads to a variation in the FMR properties. Chapter 7 reports the ferromagnetic resonance study of the magnetic relaxation mechanisms in non-stoichiometric nickel ferrite films.
2.1) Spinel ferrites

The ever increasing demand for ferrimagnets having low microwave loss for a wide range (1-100 GHz) frequency applications have been continually fuelling the research on fundamental understanding of relaxation mechanisms in these materials. [1-5] Spinel ferrites or ferrospinels (space group Fd-3m) are closed packed cubic ferromagnetic materials with general form \( XY_2O_4 \), where \( X \) represents divalent metal such as nickel, zinc, cobalt and \( Y \) represents the trivalent variety such as \( Fe^{3+} \). [1,6-7] Two types of crystallographic sites are present in a spinel structure due to the two different valence cations available. Table 2.1 shows the site occupancy in spinels.

<table>
<thead>
<tr>
<th>Site Type</th>
<th>Similar interstices (per unit cell)</th>
<th>Number occupied (per unit cell)</th>
<th>Normal spinel cation arrangement</th>
<th>Inverse spinel cation arrangement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahedral-A</td>
<td>64</td>
<td>8</td>
<td>( 8M^{2+} )</td>
<td>( 8 Fe^{3+} )</td>
</tr>
<tr>
<td>Octahedral -B</td>
<td>32</td>
<td>16</td>
<td>( 16 Fe^{3+} )</td>
<td>( 8 Fe^{3+} ; 8 M^{2+} )</td>
</tr>
</tbody>
</table>

Table 2.1: Site occupancy in Normal and Inverse spinels. [3]

One is the tetrahedral “A” site surrounded by four oxygen ions while the other is the octahedral
“B” site surrounded by six oxygen ions. The lattice constants of spinel ferrites are in the range of 8.3-8.5 Å, and are dependent on the metal–ion content. The cubic symmetry of the spinel crystal can be observed from the unit cell shown in Figure 2.1

Figure 2.1: a) Spinel unit cell structure. b) Octahedral interstice (B site: 32 per unit cell). c) Tetrahedral interstice (A site: 64 per unit cell).

(Reprinted from [1] with permission from Springer)

The magnetic moments of cations within each sublattice align parallel to each other and anti-parallel to the other sublattice. The magnetism in the spinel ferrite structure as well as in garnets and hexaferrites, arise from a superexchange mechanism. [8-11] Therefore, the net moment is given by the sum of individual moments on anti-aligned sub-lattices coupled ferrimagnetically.

A simplified representation at one A and two B sites around an oxygen atom for nickel ferrite is
shown in figure 2.2. The arrows represent the corresponding spins for nickel ferrite on these A and B-sites. Magnetic properties of spinel structures could be easily manipulated by introducing nonmagnetic cations (e.g. Zn, Cu and Li) or by inverting the distribution of cations under nonequilibrium growth conditions. [12-14] The room temperature properties of oxide spinel ferrites are shown in table 2.2.

![Figure 2.2: A simplified representation of A and B sites around an oxygen atom.](image)

Due to the cubic structure of the spinels the magnetocrystalline anisotropy energy is relatively small and the corresponding magnetic anisotropy fields are typically around 10 Oe. Since the ferromagnetic resonance (FMR) frequency is strongly dependent upon magnetic anisotropy fields, the FMR frequency of spinel ferrites without any applied field, i.e., the zero-field condition, typically falls near or below 1 GHz. [2] This limits the frequency of devices employing spinel ferrites to C-, S-, and X-bands, as the devices’ operational frequencies are largely determined by the ferrite’s ferromagnetic resonance (FMR) frequency. [2,3] The total loss in the microwave devices is determined by the magnetic damping associated with the ferromagnetic resonance.
Therefore, development of single crystal ferrite materials with narrow FMR linewidths, indicating low magnetic loss, has been one of the major goals. Following the description of Schloemann [15], Figure 2.3 shows the magnetic relaxation processes that affect the FMR damping in ferrites. [1] A group of spin waves excited by the electromagnetic signal can distribute its energy in two ways. The energy is either distributed within the magnetic system, i.e. system of electron spins responsible for the ferromagnetism that are coupled by exchange and dipolar interactions, or it can be dissipated through interaction with charge carriers, lattice vibrations, and strongly relaxing ions. The extrinsic losses may arise from the crystal imperfections (dependent on the growth method and conditions), random local anisotropy, porosity, grain boundaries, surface roughness, or valence exchange mechanism (Fe$^{3+}$, Fe$^{2+}$ hopping). [16] The relaxation processes mentioned above are usually represented by the FMR linewidth. Typical FMR linewidths are in the range of 1 Oe for single crystals and tens to hundreds of oersted in polycrystalline ferrites. Table 2.2 summarizes the properties of spinel ferrites. [15]

<table>
<thead>
<tr>
<th>Table 2.2: Room-temperature properties of oxide spinel ferrites</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>(a)</em></td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>MgFe₂O₄</td>
</tr>
<tr>
<td>Li₀.₅Fe₂.₅O₄</td>
</tr>
<tr>
<td>MnFe₂O₄</td>
</tr>
<tr>
<td>Fe₃O₄</td>
</tr>
<tr>
<td>CoFe₂O₄</td>
</tr>
<tr>
<td>NiFe₂O₄</td>
</tr>
<tr>
<td>γ-Fe₂O₃</td>
</tr>
</tbody>
</table>

*(a)* N, normal (2+ cation on A-sites) ; I, inverse (2+ cation in B-sites);
*(b)* Estimate; reverts to α-Fe₂O₃, above 800K.
Recently, much attention has been attracted to the growth of epitaxial single crystalline lithium ferrite and nickel ferrite films for magnetoelectric applications and monolithic microwave integrated circuits (MMIC). [17-19] The properties of both the ferrites are discussed in the following sections.

2.2) Lithium ferrite

Lithium ferrite (Li$_{0.5}$Fe$_{2.5}$O$_4$) has been known as an important material for microwave applications since 1930’s. Since it consists of a Fe$^{3+}$ as the only magnetic ion it has low microwave losses. [20-24] The structure of lithium ferrite is completely inverted and the valence states are represented by formula Fe$^{3+}$[Li$^+$ Fe$^{3+}$]O$^{2-}$. Since Fe$^{3+}$ has an electron configuration $6S$, the theoretical value of magnetic moment per formula unit for collinear magnetic structure is...
2.5 $\mu_B$. The distribution of lithium and iron ions in the octahedral sublattice (B-sites) can be either ordered or disordered. [25] The B-site occupancy is disordered at high temperatures (above 735–755°C) or in a quenched sample and the structure can be indexed according to the space group Fd-3m. In contrast, the lithium cations in the octahedral sites of a slowly cooled sample become ordered at low temperatures (below 735°C). In this ordered state, the rows of B-sites in [110] directions are occupied by regularly alternating sequence of lithium and iron atoms in ratio 1:3. This ordering implies that each iron atom in the octahedral site is surrounded by two lithium atoms and four octahedral iron atoms while all six nearest octahedral sites to each lithium ion are occupied by iron ions. The symmetry reduces to space group P4$_3$32 and the local symmetries of cationic sites are lowered, however, the crystal remains cubic. It has been studied that the magnetostriction of lithium ferrite is significantly affected by the cationic ordering. [26]

The interest in LFO has continued to grow over the years, since it has the properties (high Curie temperature, high saturation magnetization), which could make it superior to YIG in certain applications if low losses can be attained.

![Temperature dependence of FMR line width of Li-ferrite single crystal in ordered phase.](image)

(Reprinted from [27] with permission from JAP)
The intrinsic linewidth reported for bulk single LFO crystal is very small, the lowest reported for spinels. [27-29] Figure 2.4 and 2.5 show the temperature dependence of FMR linewidth of bulk Li-ferrite single crystal in ordered phase at different frequencies. It is linear in frequency and temperature and is on the order of 1 Oe at room temperature. The linear contribution represents the intrinsic linewidth and the temperature peak is indicative of impurity relaxation. The room temperature linewidth of bulk Li-single crystal in ordered phase ranges from 1.5 Oe to 6 Oe in different studies.

![Graph](image)

Fig. 2.5: Temperature dependence of FMR line width of bulk lithium ferrite single crystal in ordered phase at two frequencies. (Reprinted from [28] with permission from JAP)

Fabrication of high quality (structural, morphological, magnetic and microwave properties) single crystalline thick (1-10 micron range) films with losses substantially close to the theoretical intrinsic values is a difficult task. Over the years, a wide variety of thin film growth methods have been developed and investigated for lithium ferrite and its divalent cation substitutions.
Most of the reported lithium ferrite thin film depositions are based on physical vapor deposition (PVD) methods or liquid phase epitaxy (LPE). [30-35] LPE is a high temperature growth technique with film growth rates as high as tens of microns per hour. LFO films grown by LPE on (111) Mg(In,Ga)₂O₄ substrate gave a room temperature linewidth of around 12 Oe at 9 GHz in the perpendicular resonance orientation. [30] The FMR spectra is shown in figure 2.6. However, it suffers from poor surface morphology (hillock growth) and chemical inhomogeneities due to interdiffusion between substrate and thin film. Achieving precise thickness control is another drawback of the LPE method. Pulsed laser deposition has been extensively investigated to grow LFO films due to the relative ease of stoichiometry control.

![FMR spectra for LPE grown LFO film. Presence of inhomogeneity in the film is indicated by the complex FMR curve. (Reprinted from [30] with permission from Elsevier)](image)

PLD deposited LFO film has a reported in-plane linewidth of 335 Oe (figure 2.7(a)) which is the lowest achieved so far but the perpendicular spectra is highly distorted. [33,35] Moreover, there are major limitations like low growth rate and small deposition area in PLD. A range of
modifications is possible through zinc and other substitutions in lithium ferrite and has been investigated in detail. [36] Figure 2.7(b) shows a typical result for the derivative of the absorbed power versus static external field for the main resonance of a PLD grown lithium zinc ferrite film (700 nm thick) on MgO substrate in the perpendicular configuration. The vertical dashed lines delineate the negative to positive peak separation of 33 Oe that defines the derivative linewidth. For a Lorentzian line shape, the corresponding half power linewidth would be 57 Oe. The data indicates that the FMR mode response is not strictly symmetric and distorted on the low-field side. [34]

Fig.2.7: FMR spectra for PLD grown LFO films (a) FMR absorption derivative response vs. static applied field at 9.5 GHz in-plane (perpendicular distorted) (Reprinted from [32] with permission from JAP). (b) FMR absorption curve for LiZn-ferrites at 9.5 GHz in perpendicular configuration. (Reprinted from [34] with permission from JAP)
2.3) Nickel ferrite

Nickel ferrite (NiFe$_2$O$_4$), a well known insulating spinel ferrite, has a lattice constant of 8.340 Å, saturation magnetization of ~300 emu/cc (room temperature) and Neel temperature of 585°C. It has been studied for RF/microwave applications since the 1940s’, due to its high Neel temperature, low microwave loss and good temp stability of saturation magnetization. [37–41]

It possesses a spinel (Fd3m) structure ($a = 0.834$ nm) with the tetrahedral A sites occupied by half of the Fe$^{3+}$ cations, whereas the remaining Fe$^{3+}$ and Ni$^{2+}$ cations are distributed over the octahedral B sites. The magnetic structure of nickel ferrite is well understood as Neel configuration. [38] In detail, the antiferromagnetic superexchange interaction between nearest neighbor A and B sites (JAB) via oxygen is dominant and strong, which results in the antiparallel alignment of the local magnetic moment of A and B sites. The effect of cation distribution and addition of different divalent cations (Zn$^{2+}$, Cu$^{2+}$, Mn$^{2+}$) on its magnetic properties have also been widely investigated in the past. [41,42] Nickel ferrite shows high microwave losses due to the orbital state of Ni$^{2+}$, a relaxing ion. Microwave damping (relaxation behavior), which can be indicated by the linewidth of ferromagnetic resonance is an essential aspect to understand for fundamental and practical applications, such as in planar microwave devices and magnetic memory elements with high speed switching of magnetization. [7-10]
Fig. 2.8: Temperature dependence of FMR line width of bulk Ni-ferrite single crystal of two different compositions. (Reprinted from [48] with permission from APS)

The bulk single crystals of nickel ferrite (NiFe\textsubscript{2}O\textsubscript{4}) have been investigated both theoretically and experimentally by different groups since 1950’s. [43-46] It has been reported that the properties of nickel ferrite could be varied by bringing deviation in stoichiometry. [47-51] The relationship between linewidth behavior and ferrous ion content was first demonstrated by Yager et al. by studying the temperature dependence of linewidth and suggested that the two-magnon scattering as the dominating relaxation mechanism.[48] Figure 2.8 shows the temperature dependence of FMR line width of bulk Ni-ferrite single crystal of varying composition. In addition, there have been some reports on the temperature and frequency dependence of FMR linewidth in polycrystalline nickel ferrites. [55,56] However, detailed FMR studies on single crystalline
nickel ferrite thin films are quite limited. [52-53] A wide variety of thin film growth techniques have been developed and investigated in the past for single crystalline nickel ferrite films (and with divalent cation substitutions). The epitaxial growth of nickel ferrite films on MgO substrate by chemical transport and reactive sputtering has been achieved in the research by Schröder et al. [52] However, the FMR spectra obtained indicated the presence of defects in the films which resulted in a broad in-plane FMR linewidth (700~1700 Oe) and distorted out-of-plane FMR. Giannakopoulou et al. have studied microwave behavior of NFO by sol-gel method in 2002. [54] Chinnasamy et al. reported in 2007 the PLD growth of Ni-ferrite films on MgO (111) substrates. In this work, the thermal annealing (1000ºC) of nickel ferrite films has been reported to enhance the magnetic properties of the films and effectively decrease the out-of-plane FMR linewidth from 1500 to 330 Oe. [53] High quality epitaxial Nickel ferrite (NiFe₂O₄) films on (100)-oriented MgAl₂O₄ substrate by direct liquid injection chemical vapor deposition (DLI-CVD) have been recently studied. [57] The FMR linewidth of around 750 Oe and 160 Oe has been observed at a frequency of 10 GHz for the in-plane and out-of-plane orientations respectively, which is the lowest reported so far.[58] They conducted angle and frequency-dependent ferromagnetic resonance (FMR) experiments to determine the magnetic anisotropy and the magnetic relaxation. Nevertheless, the reported values are still higher than the reported bulk value of linewidth for NiFe₂O₄, which is around 40 to 80 Oe with microwave frequency in X-band. [48]
2.4) Multiferroic magnetoelectric effect in ferrite-ferroelectric composites

Multiferroic magnetoelectric (ME) materials have been an active area of research in the recent years due to their multifunctionality, which can be used in devices like signal processors including phase shifters, tunable resonators, and filters. [59-63] They exhibit an induced electric polarization by a magnetic field and vice versa, which is realized as magnetoelectric (ME) effect and is observable both in single-phase materials as well as composites.[64,65]

![Image of ME coupling in a ferrite-ferroelectric layered structure.](https://example.com/image1)

Fig.2.9: ME coupling in a ferrite-ferroelectric layered structure. (Reprinted from [19] with permission from APL)

However, the problem with the single phase materials is the low ME output which necessitates the study of an alternative materials which show enhanced ME properties. Multiferroic composite is one such promising alternative consisting of a ferri- or a ferromagnetic (FM) and ferroelectric materials. [66–70] Two types of ME effect are observed in composites, one is the...
direct ME effect and the other is the converse ME effect. In the direct ME effect, the application of a magnetic field produces a mechanical strain that results in an induced polarization. The converse ME effect involves the study of the magnetic response of the sample when it is subjected to an applied electric field $E$. [71] Recently, there have been several studies on different ferromagnetic-piezoelectric composites that exhibit strong ME effects of both types. Figure 2.9 shows the ME coupling in a ferrite-ferroelectric layered structure. The piezoelectric strain due to an electric field $E$ manifests as an internal magnetic field in the ferromagnetic phase that causes a frequency shift $df$ or a field shift $dH$ in the FMR or hybrid modes, with the strength of ME interaction ‘A’ defined by $A = df/dE$ (or $dH/dE$).

![Figure 2.9: ME coupling in a ferrite-ferroelectric layered structure.](image)

Figure 2.10: FMR spectra as a function of magnetic field in absence and presence of external electric field in DLI-CVD deposited in heteroepitaxial NiFe$_2$O$_4$/PZN-PT multiferroic composites. (Reprinted from [72] with permission from APL)
The electric-field tunable multiferroic composites can yield a better tuning of the magnetic response and provide an opportunity for various device applications. A significant electric field tuning of magnetic properties due to ME interactions (figure 2.10) has been recently reported in heteroepitaxial NiFe$_2$O$_4$/PZN-PT and NiFe$_2$O$_4$/PMN-PT multiferroic composites deposited by DLI-CVD. [72]

The main focus of this dissertation work, based on the aforementioned understanding of the properties of the two ferrospinels is to:

1.) Fabricate high quality single crystalline lithium ferrite and nickel ferrite films with low microwave loss (FMR linewidth ~100 Oe or less) using DLI-CVD by optimizing the growth and processing conditions.

2.) Explore the fundamental physical properties of the as-deposited ferrite films and the film growth modes.

3.) Study the complex magnetic relaxation mechanisms in the as-grown films by performing comprehensive frequency, angle and temperature dependent FMR measurements.

4.) Fabricate heteroepitaxial LiFe$_5$O$_8$/PZN-PT and LiFe$_5$O$_8$/PMN-PT multiferroic composites by DLI-CVD to study the ME effect.
CHAPTER 3
EXPERIMENTAL METHODS

3.1) Introduction
This chapter includes a description of the working principles for thin film growth method and characterization techniques used to study the structural, magnetic and microwave properties of the as-deposited spinel ferrite films. Direct liquid injection chemical vapor deposition was used to deposit the spinel ferrite films on the specific substrates at optimized experimental conditions. X-ray diffraction (XRD) was used to study the crystalline structure and the epitaxial growth. The film morphology was studied using the atomic force microscopy. Scanning electron microscope (SEM) was used for film imaging at high magnifications to obtain the thickness of the films, and also for the composition study with energy dispersive X-ray (EDX) analysis. Magnetic properties of the films were studied by vibrating sample magnetometer (VSM) and ferromagnetic resonance (FMR) technique was used to investigate the relaxation mechanism in the as-deposited films as well as the bulk materials. Some characteristic results obtained and analyzed from these instruments are also shown in this chapter.
3.2) Direct liquid injection chemical vapor deposition (DLI-CVD)

Chemical vapor deposition (CVD) is a thin film deposition technique in which one or more vapor phase chemical reactants react and nucleate on the thermal heated solid substrate surface. A typical CVD process includes chemical precursor source (gas, liquid or solid), gas transport line, thin film growth chamber where the substrate (wafer) is placed, and the exhaust system usually composed of various vacuum pumps and chemical trapping equipment.[73-75] The precursor selection is a major factor affecting the CVD growth quality of the thin films. The important properties to be considered for selection of a precursor include volatility, thermal stability and potential impurity formation in the grown films and the selection of a precursor depends on the specific type of CVD technique.

Direct liquid injection CVD (DLI-CVD), is a technique in which the precursor source is in the state of liquid solution and injected into the vaporization unit to generate vapors for the CVD reaction. A schematic diagram of a DLI-CVD system as described above is showed in figure 3.1. The DLI-CVD setup basically consists of a CVD system coupled with a liquid injection system and a vaporization unit. There are several advantages of using the DLI-CVD technique over the traditional vaporization techniques. In DLI-CVD, all the precursors are prepared as a single source by dissolving them into an appropriate solvent. These precursors can be vaporized simultaneously after being injected into the vaporizer, and therefore the molar ratio between the precursors would be the same as the corresponding mixing ratio in the solution. [76] This gives an easy control of element composition. Moreover, keeping the liquid source at room temperature leads to minimal problems of precursor degradation, which commonly happens at elevated temperatures in different growth techniques. The flow rate of the liquid can be also
controlled accurately by using liquid mass flow controllers thus making the mass flux of precursors entering the CVD chamber much more uniform and reproducible. This method has enabled the use of a variety of precursor chemicals in CVD thereby opening window for the deposition of materials that are very difficult to deposit by conventional vapor transportation. So far, DLI-CVD has been successfully used for the deposition of different oxides such as Ba(Sr,Ti)O$_3$, CoFe$_2$O$_4$, Pb(ZrTi)O$_3$, ZrO$_2$, La$_2$O$_3$ and NiFe$_2$O$_4$.[57,77-79]

![Schematic diagram of DLI-CVD set-up used for spinel ferrite film deposition.](image)

The vaporizer unit is designed to attain fast, smooth and gentle vaporization. The liquid precursor is broken into very small droplets (few microns size) using an ultrasonic nozzle and then these droplets are thermally heated. The carrier gas, used as a heating medium, minimizes
the thermal decomposition effect. A schematic diagram of a DLI vaporizer unit is shown in figure 3.2.

Figure 3.2. Schematic diagram of a DLI-CVD vaporizer unit.

The CVD reactor is a three-zone low-pressure quartz tube furnace. Epitaxial spinel ferrite films are deposited on different substrates in a horizontal quartz tube furnace. The tube reactor, with a diameter of 1.5 inch and length of 50 inch, is pumped down to the reaction pressure. Li(acac), Ni(acac)₂ and Fe(acac)₃ (acac: acetylacetonate), bought from Sigma-Aldrich, are used as metal organic precursors without any further purification. These precursors are dissolved in N,N-dimethylformamide (DMF), as the source for liquid injection. Ultrahigh purity He (20 psi) is used to pressurize the liquid flow from solution container to the vaporizer. Ultrahigh purity argon gas is used as the carrier gas, which served both as the vaporization medium and the delivery gas. At the vaporizer inlet, where the liquid and carrier gas flow intersect, is an atomizer, which breaks up the entering fluid into fine droplets (2~5µm) because of a large pressure drop. Ultrahigh purity oxygen was used as the oxidant. Atomically polished single crystals such as MgAl₂O₄ (100) and MgO (100) of dimensions 5 mm×5 mm×0.5 mm from CrysTecGmbh are
used as substrates. All the vaporizer parameters have to be tuned for optimal flow of the precursors into the CVD reactor without decomposition. Deviations from the optimized parameters, such as in the vaporizer temperature or liquid flow rate, results in a rough film surface and/or changes from the desired composition. This can be attributed to an inadequate vaporization process due to precursor(s) decomposition, condensation on tubing walls, or the presence of insufficiently vaporized droplets/clusters. The adjustable parameters are precursor concentration, precursor flow rate, vaporizer temperature, carrier gas flow rate, oxygen flow rate, reaction chamber pressure, and substrate temperature. The detail condition parameters for deposition of different spinel ferrite thin films on specific substrates will be described in the following chapters.

3.3) X-ray diffraction

X-ray diffraction (XRD) is a non-destructive and versatile technique, which is used to reveal the detailed information about the crystal structure and chemical composition of a material. X-rays have energy of 100 eV-100 keV in the electromagnetic radiation and since the wavelengths of X-rays are comparable to the atomic length scale, the structural properties of matter are studied using X-rays. We did the structural characterization of our epitaxial ferrite films with a Philips X’pert X-ray diffractometer, which has a line-focus beam configuration and rotatable sample detector and stage. An electron beam of very high energy coming out of a tungsten source is accelerated by applying a high voltage of \( \sim 45 \) kV and is hit on a copper target. The inner K shell electrons are ejected by the accelerated electrons, which lead to the electrons from the next higher energy level (L-shell) to jump to K shell. This results in release of energy in form of X-
rays, which are called Kα radiation. This Kα line is split into two lines as Kα1 and Kα2 because of hyperfine splitting (spin degenerate K-levels). The wavelength of these X-rays is characteristic of the target. These X-rays coming out of the source interact with the atoms of the material under investigation and undergo elastic scattering (change in direction of the electromagnetic wave motion without any energy loss).

For a periodic arrangement of atoms in the material and atomic distances comparable to the X-ray wavelength, constructive interference of the elastically scattered X-rays occurs from each atomic layer. A schematic diagram of X-ray diffraction from crystal lattice planes is shown in figure 3.3. The symmetry of the diffraction pattern corresponds to the symmetry of the atomic packing, which is the simplest way to determine the interatomic spacing that exists. Bragg’s law [80] gives the condition for the detector to give a peak corresponding to the radiation diffracted by the sample along θ direction:

\[ 2d \sin(\theta) = n\lambda \]

where, d is the atomic spacings and λ is the X-ray wavelength (=0.1541 nm for our Cu Kα source installed in Philips X’Pert machine).

![Figure 3.3: Schematic diagram of X-ray diffraction from crystal lattice planes.](image)

Plotting the angular positions and intensities of the resultant diffracted peaks gives a pattern
characteristic of the sample. Depending on the geometry of the diffractometer, atomic spacing in
different directions of a crystal can be calculated using Bragg’s law. This technique is known as
X-ray diffraction (XRD) was used to investigate substrate-induced strain in the films and to
determine the lattice constants as reported in chapters. The quality of the epitaxial film can be
checked by the rocking curve scan in XRD. In the rocking curve scan, the initial angular position
of the detector 2θ and the sample ω is aligned along a Bragg peak position found in the 2θ-ω
scan and the sample is rocked around the initial angle while the detector position 2θ is kept fixed.
An estimation of the portion of the crystal oriented at the specific crystallographic direction is
obtained from the broadening of the measured intensity peak in the intensity versus ω graph.
In the normal XRD (2θ-ω) scan, the crystal orientation of the lattice plane is measured in the film
plane direction.

Figure 3.4: Schematic of X-ray diffractometer for thin film crystal structure analysis.

Measuring diffraction at different angular directions of the specified film orientation can check
the preferred orientation of the film. Figure 3.4 shows the schematic of X-ray diffractometer for
thin film crystal structure analysis. To account for the symmetry of the crystal structure, phi scan is done in which the detector (2θ) and sample (ω) angular position is adjusted at the specific Bragg diffraction condition which is expected in the crystal structure at the specific angle other than the film plane direction. The in-plane tilting angle is represented by ϕ. The sample is tilted from the in-plane at the specific tilting angle ψ. Then, the film is rotated for the azimuthal angle to examine the specific diffraction peak (maximum intensity) and its repetition, which is used to confirm the crystal symmetry and also epitaxial growth on the substrate. [81]

3.4) Scanning electron microscopy

In a scanning electron microscope (SEM), a focused beam of high-energy electrons is used for imaging of a specimen, which is generated by applying high voltage in ultra-high vacuum between the specimen (anode) and the source of electron (cathode) and is focused on the specimen using magnetic lenses. The accelerated electrons can pass through the sample without interaction, undergo elastic scattering and can be inelastically scattered. The electron sample interactions reveal information about the samples regarding the morphology, chemical composition and the crystalline structure in the form of signals. The typical signals used for imaging include secondary electrons (SE), backscattered electrons (BSE), auger electrons and characteristic X-rays. A SE detector is placed closer to the specimen to detect low energy electrons. The elastic scattering between the incident electrons and the nuclei in the specimen results in BSE. The contrast in imaging is obtained from the numbers of secondary and backscattered electrons. Characteristic X-rays are generated when incident electrons knock off core level electrons, and electrons from next higher energy level fill the empty states.
This forms the basis of energy dispersive X-ray analysis (EDX) in which the signal from collected X-rays is proportional to the concentration of the elements present and therefore used to quantify the elements present. Figure 3.5 shows an example of SEM and EDX analysis performed on a nickel ferrite.

![SEM and EDX analysis](image)

Figure 3.5: (a) An example of a cross-sectional SEM image of a 700 nm thick nickel ferrite film. (b) EDX analysis performed on the same film gives the Fe:Ni ratio of 2.67.

### 3.5) Atomic force microscopy

Atomic force microscopy (AFM) is a scanning probe microscopy technique that generates a height mapping of the sample surface with a high degree of resolution.[82] The schematic is shown in figure 3.6. It uses a tip, mounted on the end of a cantilever spring, which is used to scan the sample surface. It has two modes of operation namely, contact mode and tapping mode. In contact mode, the tip is in mechanical contact with the surface and the force is measured by adjusting the vertical position of the tip while keeping the deflection constant. Tapping mode is commonly used to image soft samples that could be damaged due to the nano Newtons of force.
applied by AFM probe and prevents the tip from sticking to the sample surface. In tapping mode, the cantilever vibrates near its resonance frequency driven by an AC voltage as the sample is scanned. The amplitude of oscillation is used as a feedback signal. The tip doesn’t experience any deflection when it is far from the sample but when the tip approaches close to the sample surface, short range interactions like the vander Waals attractive force, Coulomb force etc., changes the amplitude of oscillation (usually becomes smaller). If the distance between the sample and the tip is further decreased, the tip experiences repulsion from the surface molecules and it is deflected in the other direction.

Figure 3.6: Schematic diagram of an atomic force microscope (AFM).
To detect these small deflections, a laser beam reflecting off from the back of the cantilever is used. The deflection of the tip is measured at a photodetector due to the alterations in oscillation amplitude and resonance frequency as the tip moves towards and away from the surface. The position of the reflected beam changes according to the deflection of the cantilever and these changes are converted into electrical signal by the photodetector. A feedback loop reacts to the change in position of the laser by adjusting the height of the sample in order to keep the force constant. This is done by controlling a piezoelectric actuator, which maintains the oscillation amplitude at a set level by moving the tip up and down as the cantilever scans over the sample. The important aspect is the adjustment of the feedback control to minimize the deflection of the tip to attain high accuracy in the topographic image. All AFM images taken during this work are in tapping mode.

3.6) Vibrating sample magnetometer

Vibrating sample magnetometer (VSM) works on the principle of electromagnetic induction to study the magnetic properties of thin films and bulk materials. Its basic structure is schematically shown in figure 3.7, which consists of an electromagnet, a vibration unit with a sample holder, a pair of pick-up coils, and a field sensor.
Figure 3.7: Schematic diagram of a vibrating sample magnetometer (VSM).

The test sample in uniform magnetic field can be treated as magnetic dipole. The magnetic fluxes from the sample, which vibrates in the direction perpendicular to the applied field, induces an electromotive force (emf) in the pick-up coil positioned nearby. This emf is proportional to the magnetic moment of the sample. After calibration with a standard sample, the output from the pick-up coil represents the magnetic moment of the sample, and the output from the field sensor gives the applied field value. The output of the instrument is therefore a M-H loop, or more accurately, a curve showing the field dependence of the magnetic moment of the test sample, from which many magnetic parameters can be obtained. We used VSM to determine magnetic hysteresis loops to measure the coercivity and saturation magnetization of the as-deposited thin film during this research work.
3.7) Ferromagnetic resonance

Ferromagnetic resonance (FMR) is a technique to measure magnetic properties by uniform excitation of the magnetization in a ferromagnetic sample.

![Diagram of FMR effect]

Figure 3.8: A schematic representation of the FMR effect.

It enables an effective study of the physical magnetic relaxation (damping) processes in magnetic samples. [83-85] The schematic representation of the FMR effect is shown in figure 3.8, where the magnetization M absorbs energy from the microwave magnetic field $h_{rf}$ and maintains a fixed angle of precession around the static magnetic field H. Macroscopically, the applied static magnetic field causes the total magnetic moment to precess around the direction of the local field $H_{\text{eff}}$, before relaxation processes damp this precession and the magnetization aligns with $H_{\text{eff}}$. Figure 3.9, shows a block diagram for an FMR linewidth measurement system. In a FMR setup, the sample is irradiated with a transverse RF field (microwaves of typically 1–55 GHz). When the microwave frequency coincides with the precessional frequency, the resonance condition is fulfilled and the microwave power is absorbed by the sample.
Figure 3.9: Schematic diagram of a ferromagnetic resonance (FMR) setup.

The dynamics of the magnetization $M$ is described by the Landau-Lifshitz-Gilbert equation [83]:

$$\frac{\partial \vec{M}}{\partial t} = \gamma (\vec{M} \times \vec{H}_{\text{eff}}) - \frac{\alpha}{M_s} (\vec{M} \times \frac{\partial \vec{M}}{\partial t})$$

The effective magnetic field $H_{\text{eff}}$ includes the external field, the RF microwave magnetic field component, the exchange field, the demagnetizing field (shape anisotropy) and the magnetocrystalline anisotropy field. $\alpha$ is the damping parameter, $\gamma$ represents the gyromagnetic ratio ($\gamma = g \mu_B / h$) and $M_s$ is the saturation magnetization.[86] From a microscopic point of view,
the magnetic field $H$ creates a Zeeman splitting of the energy levels. The microwave excites the magnetic dipole transitions between these split-levels. The FMR effect occurs in a peak response in the measurement of the power absorption $P_{\text{abs}}$ in the material as a function of the static magnetic field $H_{dc}$.

![Diagram](image)

Figure 3.10: A typical plot of $dP_{\text{abs}}/dH_{dc}$ as a function of $H_{dc}$.

The absorption derivative is measured usually. A typical plot of $dP_{\text{abs}}/dH_{dc}$ is shown in figure 3.10. The resonance signal resembles a Lorentzian lineshape. The linewidth $\Delta H$ is directly connected to the relaxation processes. The origin of the FMR linewidth is different in different materials. In ultrathin films, Gilbert damping is commonly used to describe the relaxation. But several other possible relaxation mechanisms like two-magnon scattering, spin-pumping effect, etc., are also known which can contribute to the linewidth.
Many of the relaxation processes show unique temperature or frequency dependencies. Some of the processes can be easily studied through a change in FMR configurations by changing the direction of the applied static field. For example, the two-magnon scattering effect can be simply suppressed by applying the static field normal to the film plane. The linewidth involves the contribution from two terms [83] and is expressed as:

$$\Delta H_{FMR} = \sum_{i=1,...,N} \Delta H_i + \Delta H_0$$

The first term denotes the contribution from a specific relaxation process ‘i’ and the second term gives the inhomogeneity-caused line broadening which arises from the simple superposition of several local FMR profiles for different regions of the sample.
4.1) Introduction

In this chapter, the study of the growth of pure lithium ferrite (LiFe$_5$O$_8$) thin films using DLI-CVD process is investigated. Lithium ferrite can be considered as derived from Fe$^{3+}$[Fe$^{2+}$Fe$^{3+}$]O$_4$ (magnetite) by substitution of about 0.5 iron atoms per formula unit in the octahedral sites (B-sites) with lithium. [20-25] Lithium ferrite has the highest Curie temperature amongst the ferrites ($T_c = 680^\circ$C), a high saturation magnetization of 2.5 Bohr magneton per formula unit, low dielectric losses due to the high electrical resistivity. The presence of only S state Fe$^{3+}$ ions results in a narrow ferromagnetic resonance linewidth (low microwave loss). These properties are the most important properties of lithium ferrite from the standpoint of microwave device applications, making it an ideal material.

Various growth techniques have been used to grow good quality epitaxial LFO films. Most of the reported LFO thin film deposition techniques are based on liquid phase epitaxy and physical vapor deposition methods [30-35]. The most recent method reported is using PLD, where a study of the effect of substrate chosen is discussed based on structural characterization [87]. As discussed in chapter 2, there have been very limited reports on the growth and study of high quality LFO thin films, specifically in terms of FMR properties, and to the best of our
knowledge, no reports has been found on growth of LFO films using the metal organic chemical vapor deposition technique. The focus of this chapter was on the fabrication of LFO thin films using the DLI-CVD technique to optimize processing conditions and achieves high quality films with the lowest FMR linewidth. This research on DLI-CVD of LFO films is novel, and can contribute significantly to the understanding of thin film growth mechanism of lithium ferrites.

4.2) Experimental details

The DLI-CVD setup used for the experiments has already been described in chapter 3. Anhydrous Li(acac) and Fe(acac)₃ (acac : acetylacetone) in a molar ratio of 1:5 were dissolved in N,N-dimethylformamide (DMF) to form a clear homogeneous precursor solution. DMF acts as a solvent and can simultaneously minimize intermolecular association by coordinating with the metal ions.[88,89] The solution was then introduced into a Brooks Instrument DLI 200 vaporizer system, vaporized by heated Argon gas, followed by reaction with oxygen (O₂) gas on heated substrates placed in a CVD reactor, resulting in the growth of LFO films on the substrate. The process conditions were optimized to attain high structural quality and low microwave loss films.

<table>
<thead>
<tr>
<th>Table 4.1: Processing conditions for DLICVD of LFO</th>
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<tbody>
<tr>
<td>Substrates</td>
</tr>
<tr>
<td>Deposition temperature (°C)</td>
</tr>
<tr>
<td>Vaporizer temperature (°C)</td>
</tr>
<tr>
<td>Argon flow rate (sccm)</td>
</tr>
<tr>
<td>Oxygen flow rate (sccm)</td>
</tr>
<tr>
<td>Solution flow rate (g/h)</td>
</tr>
<tr>
<td>Reaction pressure (torr)</td>
</tr>
<tr>
<td>Li(acac) (mol/l)</td>
</tr>
<tr>
<td>Fe(acac)₃ (mol/l)</td>
</tr>
<tr>
<td>DMF (ml)</td>
</tr>
<tr>
<td>Reaction time (min)</td>
</tr>
</tbody>
</table>
Table 4.1 summarizes all the experimental conditions used during the growth process of the LFO films. The most prominent growth parameter, which can significantly impact the FMR behavior of the spinel ferrite films, is the growth temperature. The film deposition was carried out at temperatures ranging from 400°C to 650°C for 100 min. After deposition, the films were slowly cooled to room temperature at the rate of 1.5°C per minute in the reactor under flowing O₂.

To achieve the expected quality of films, magnesium oxide (MgO), a non-magnetic crystal with the rocksalt structure, having both satisfactory match of the lattice parameter as well as favorable microwave properties was selected as the substrate. There is a lattice mismatch of 1.1% between bulk LFO (a\text{film}=8.330 Å) and rocksalt MgO (2a\text{MgO}=8.242 Å). [90-92] The LFO films on MgO were grown at different deposition temperatures to suitably investigate the optimum growth conditions and growth mode.

![Figure 4.1: Growth rate variation with the deposition temperature for LFO films on MgO. The line is a linear fit to the data.](image)

Figure 4.1: Growth rate variation with the deposition temperature for LFO films on MgO. The line is a linear fit to the data.
The film growth rate shows a clear trend with increasing temperature (figure 4.1). The growth rate increases with the growth temperature, with a maximum run-to-run growth rate variation of around 5% for films grown at a particular temperature. The growth rate is also extremely sensitive to the position of the substrate in the reactor. Moreover, there could be variations in the stoichiometry and the surface morphology of the grown films at different substrate positions. These deviations in thickness and stoichiometry can be related to the temperature and precursor concentration distribution in the hot-wall tube reactor. Due to thermal conductance, there is a gradual increase in the reaction zone temperature from the vaporizer outlet to the substrate position and the precursor concentration decreases because of thermal decomposition. The optimization of the substrate position was performed by looking at the color on the surrounding tube wall after each experimental run. It was observed that most of the deposition occurred in a range of around 4-5 inches away from the injector. The highest growth rate was obtained over this particular region of the reactor, which was probably a favorable combination of temperature and precursor concentration.

4.3) DLI-CVD growth temperature dependence of the LFO films

4.3.1) Structural characterization

The LFO films were deposited on MgO substrates at an optimized substrate position in the furnace for temperatures ranging from 400°C to 650°C. The deposition time was 100 minutes for each run. To determine the structural quality (crystal phase and epitaxy) of the resulting films grown at different temperatures, a detailed XRD analysis was done. Figure 2(a,b) shows the 2θ scans of the films showing diffraction peaks from the MgO substrate and the films grown at different temperatures. The LFO film grown at 400°C exhibits no film peak and hence was
deemed amorphous. This is probably due to the low crystallization rate of the film on the substrate at low deposition temperature. The LFO films between 450°C and 600°C clearly exhibited pure spinel phase without any additional peaks, as only (004) and (008) peaks from the lithium ferrite film were observed. The high intensity and appearance of a sharp Kα peak splitting of the (400) reflection peak for the film grown at 500°C indicated a high quality growth at this temperature. As we moved higher in the growth temperature, the deposition rate increased, which caused deterioration in the quality of films which was also reflected from the cracked surface of the films. This could be possible due to high density of defects at high deposition rates or also possibly due to migration of lithium at high temperatures, which is shown later in the SIMS results.

Figure 4.2: $2\theta$- $\theta$ plot around the (004) peak for LFO films grown at different temperatures, exhibiting a pure spinel phase with the (h00) planes parallel to the film surface.
As evident from Figure 4.2, the films are under strain and shifts towards the lower $2\theta$ side with increasing temperature. The bulk value for LFO is marked as dashed line in the figure. The presence of elastic strains in the film, due to the lattice mismatch between film and substrate, would induce a tetragonal distortion of the crystallographic structure and would affect the estimate of the true “relaxed” lattice parameter. The presence of strains in the film was investigated by measuring the lattice parameters of the as-deposited films. The in-plane orientation of the lithium ferrite films relative to the substrate was investigated using asymmetric reflections with different values of the misset angle. The misset angle $\psi$ is already defined in chapter 2. The moderate thickness of the film allowed us to observe both film and substrate peaks in the same scan. The calculated in-plane and out–of-plane lattice parameters using Cohen’s method [93,94] for all the films as reported in table 4.1. This demonstrated that there is stress induced by the substrate, which is not completely relaxed by mismatch dislocations at the interface between film and substrate.

Figure 4.3: Rocking curve of the (400) reflection of LFO film grown at 500°C on MgO substrate.
The mosaic spread of all the films grown at different temperatures was then estimated by measuring the width of the rocking curve of the (400) reflection. Figure 4.3 shows the $\omega$-scan of the (400) reflection of the sample grown at 500°C with a full width of half maximum value (FWHM) of 0.032°. This sample gives the best structural quality as compared to other LFO samples at different growth temperatures as shown in table 4.2.

![Image](image126x377_to_482x557)

<table>
<thead>
<tr>
<th>Growth Temperature (°C)</th>
<th>Thickness (nm)</th>
<th>Out-of-plane lattice constant (Å$^\circ$)</th>
<th>In-plane lattice constant (Å$^\circ$)</th>
<th>c/a</th>
<th>FWHM (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>250</td>
<td>8.277±0.001</td>
<td>8.438±0.003</td>
<td>0.981</td>
<td>0.08</td>
</tr>
<tr>
<td>500</td>
<td>450</td>
<td>8.281±0.001</td>
<td>8.424±0.001</td>
<td>0.983</td>
<td>0.032</td>
</tr>
<tr>
<td>550</td>
<td>580</td>
<td>8.296±0.003</td>
<td>8.428±0.001</td>
<td>0.984</td>
<td>0.141</td>
</tr>
<tr>
<td>600</td>
<td>750</td>
<td>8.316±0.001</td>
<td>8.395±0.002</td>
<td>0.991</td>
<td>0.16</td>
</tr>
</tbody>
</table>

Furthermore, carrying out a phi-scan at the (220) asymmetric reflection for the same sample grown at 500°C, the relative orientation between film and substrate was deduced. As expected, a perfect epitaxial relationship with no in-plane rotation between the film and the substrate (figure 4.4) is obtained.
Figure 4.4: Phi-scan at the (220) asymmetric reflection for the LFO sample grown at 500°C.

The phi-scan exhibited four sharp peaks, approximately of the same intensity, spaced at 90° apart from each other, which confirmed the cubic symmetry of the LFO film.

Surface morphology of the as-deposited films was characterized by field emission scanning electron microscopy (SEM) as well as atomic force microscopy (AFM). Films grown on MgO (100) at 500°C shows smoothest surface with RMS values around 1~2 nm, whereas, the samples grown at 450°C and 550°C are not as smooth having a surface roughness of around 14 nm and 6 nm respectively, as shown in figure 4.5.
Figure 4.5: AFM images of the surface of the LFO films grown at different temperatures.

The optical micrographs of the films indicated the presence of a tensile stress in the film. This stress may arise from a difference in thermal expansion coefficients. [95] Generally, when cracking occurs as part of the growth process, the cracks follow the crystallographic symmetry [96] and extend into the substrate. The presence of large tensile stress in the film is consistent with the known lattice parameters, 8.33 Å for the film and 8.424 Å for the MgO substrate. All
the films exhibit cracks, however they become less prominent at lower growth temperature. CVD-grown complex oxide films under tensile stress have been previously reported to exhibit surface cracking/crazing phenomenon. [97] Figure 4.6 shows the SEM cross-sectional view of a sample to obtain thickness of the film. A sharp interface is observed at the film-substrate interface for the sample deposited at 500°C and the film was smooth as expected.

![Figure 4.6: A cross-sectional SEM view of a 0.31 µm thick LFO film grown at 500°C on MgO exhibiting a smooth surface.](image)

Since lithium might be depleted in the films, particularly at higher growth temperatures, a direct measurement of the lithium content in the film by Secondary Ion Mass Spectrometry (SIMS) was attempted. In SIMS, the composition of the films is analyzed by sputtering the surface of the specimen with a focused primary ion beam and collecting and analyzing ejected secondary ions.
The significant lithium loss at higher growth temperatures is clearly evident from table 4.3. These results were further confirmed by ICP (Inductively Coupled Plasma) analysis. For reference, a bulk LFO single crystal (S1) was also measured for composition.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SIMS</th>
<th>ICP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Li-intensity / Fe-intensity</td>
<td>Li-intensity / Fe-intensity (normalized to single cry.)</td>
</tr>
<tr>
<td>perfect sample</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>LFO/MgO-450C</td>
<td>0.187</td>
<td>0.055</td>
</tr>
<tr>
<td>LFO/MgO-500C</td>
<td>0.66</td>
<td>0.125</td>
</tr>
<tr>
<td>LFO/MgO-550C</td>
<td>0.31</td>
<td>0.14</td>
</tr>
<tr>
<td>LFO/MgO-600C</td>
<td>0.032</td>
<td>0.007</td>
</tr>
<tr>
<td>LFO/MAO-500C</td>
<td>1.35</td>
<td>0.504</td>
</tr>
<tr>
<td>LiFe5O8 single crystal</td>
<td>2.63</td>
<td>0.92</td>
</tr>
</tbody>
</table>

Table 4.3: SIMS and ICP analysis for lithium ferrite films and bulk single crystal.

To further confirm the epitaxial growth of the films, polarized Raman spectroscopy measurements were performed. The polarized Raman spectra were measured with XX, XY, X’X’, and X’Y’ scattering configurations using a 515 nm excitation source at room temperature. The first and second letters in the notations XX, XY, X’X’, and X’Y’ indicate the polarization of the incident and scattered light, respectively, along the cubic X||[100], Y||[010], X’||[110], or Y’||[-110] directions of the MgO substrate.
Figure 4.7: Polarized Raman spectroscopy results for films grown at different temperatures.

From symmetry considerations one expects large number of Raman allowed phonon modes, $6A_1 + 14E + 20F_2$, in the ordered phase (P4$_1$32), compared to only five $A_{1g} + E_g + 3F_2$ in the disordered-phase Fd3m. [98] The $A_1$ ($A_{1g}$) modes are allowed in the XX and X’X’ spectra, the E ($E_g$) modes—in XX and X’Y’, and $F_2$($F_{2g}$) modes—in the X’X’ and XY spectra, and hence the symmetry of Raman lines can unambiguously be identified from their polarization dependence.

The films are epitaxial with (100) directions parallel to the edges (figure 4.7). The ordered alpha phase is evident at low growth temperature of 500°C with some features of the beta-phase (e.g. the peak near 320 cm$^{-1}$ in the XX and X’Y’ spectra) also present. However, some shifts in peak positions and splitting are observed. At higher temperatures the spectra of LFO/MgO exhibit
only the Raman lines expected for the Fd3m phase, which indicates complete disorder of Li and Fe at the octahedral B-sites.

Figure 4.8: Comparison of the polarized Raman spectra of films grown using CVD (red) with that of an ordered single crystal of LFO (black).

We further compared the polarized Raman spectra of B-site ordered alpha-LFO single crystal (black) with the spectra of LFO/MgO film grown at 500°C by CVD (red). [98] The comparison, as shown in figure 4.8, clearly reflects that the spectra of LFO/MgO films at 500°C reproduces to a great extent that of the partially ordered single crystal. The spectra of the films exhibit similarities, but also differ significantly from the spectra of B-site ordered material. The comparison of the polarized Raman spectra CVD grown LFO/MgO, obtained from (001) surface with those of beta-LFO single crystal [(111) surface] is shown in figure 4.9, exhibiting both similarity and differences which indicates the possible coexistence of B-site ordered and
disordered domains. [98] The notations HH and HV correspond to parallel and crossed polarizations of incident and scattered light.

Figure 4.9: Comparison of the polarized Raman spectra of the CVD grown LFO film (black) with B-site disordered single crystal of LFO (red).

Transmission electron microscopy was used to analyze the as deposited LFO films on MgO (100) substrate. Electron diffraction patterns and bright field TEM images for the films deposited at different temperatures are shown in figure 4.10 and 4.12. Figure 4.11 shows the HRTEM image of the interface between lithium ferrite film and MgO substrate. TEM cross-sectional samples were prepared by conventional mechanical polishing and Ar ion milling. Imaging was performed in a FEI TITANR 80-300 kV microscope.
Figure 4.10 (a): Electron diffraction pattern of lithium ferrite film grown on MgO substrate at 500°C. (i) diffraction pattern from the substrate only, (ii) diffraction pattern from both the film and the substrate and (iii) diffraction pattern from the film only.

(b): Bright field TEM image of lithium ferrite film grown on MgO substrate at 500°C. The image is taken under two beam conditions with \( g = <400> \) and \(<220>\).

Figure 4.11: HRTEM image of the interface between lithium ferrite film and MgO substrate.
Figure 4.12 (a,b): Electron diffraction pattern and bright field TEM images of the LFO films grown on MgO substrate at 450°C and 550°C.

All the films samples appear to be homogenous, except for the one grown at 450°C. This sample seems to have a different layer in the surface region and is very rough as evident from the TEM image of presence of flower-like deposits, it seems to have a local ordering which is weak though. The LFO sample grown at 550°C is 'Li' deficient and shows no superlattice peaks.
However, it is clear that the film grown at 500°C (~ 450nm) shows a nice ordering in both “film+substrate” and “film only” image with consistent distance between the spots. This is shown in figure 4.10(b). For lattice planes with small as well as larger Miller indices, the spots from the film and the substrate overlap with each other. No separation of spots indicates the presence of strain in the as-deposited films, which is consistent with the XRD measurements, which indicate that the LFO films are not fully relaxed under these conditions. The diffraction pattern is taken along the zone axis <001> and spots from various lattice planes of spinel LFO film have been indexed in the patterns.

4.3.2) Magnetic characterization

The room temperature magnetic properties of the as-deposited films on MgO substrates were studied using a Vibrating Sample Magnetometer (VSM). Figure 4.13(a) shows the MH loops of samples deposited at temperatures ranging at 450°C, 500°C and 550°C. The saturation magnetization (M_s) values obtained are 261±15, 284±10 and 299±17 emu/cm^3 for films grown at 450°C, 500°C and 550°C, respectively. This compares favorably with the room temperature bulk value of M_s for LFO of 288 emu/cm^3. The variation of saturation magnetization and coercivity with growth temperature are plotted in figure 4.13(b). There is no significant change in saturation moment magnetization with increasing deposition temperature. However, the film coercivity decreases substantially with increasing deposition temperature. The possible factors contributing to the variation of coercivity can be stoichiometry deviation, cation ordering, strain and grain size. Among these, grain boundaries can act as pinning sites for magnetic domain walls. Small grain size and large wall density can result in large coercivity in the multi-domain regime. The
small coercivity values can be attributed to the high degree of texture, as indicated by the XRD results of the ω-scan.

Figure 4.13: (a) M-H curves of the LFO films at different growth temperatures; (b) Variation of saturation magnetization ($M_s$) and coercive field ($H_c$) with growth temperature.

The as-deposited lithium ferrite films on MgO (100) for different growth temperatures are further characterized for microwave properties by a coplanar waveguide (CPW) FMR system setup with a static magnetic field pointing along the [100] (in-plane) and [001] (out-of-plane) directions at microwave frequencies ranging from 7 GHz to 40 GHz. The dependence of the resonance frequency on resonance field for different crystal orientations for all growth temperatures can be described by formula for uniform FMR mode. [99] The FMR spectra obtained are clean, symmetric and undistorted for all three temperatures. Figure 4.14 illustrates the respective in-plane (ip) and out-of-plane (oop) FMR plots for the sample grown at 500°C. The corresponding FMR linewidth variation with frequency, representing the degree of
microwave loss, is shown in figure 4.15 (left) and 4.15 (right) for the ferrite films deposited on MgO at different temperatures.

![Graph showing frequency dependence of FMR resonance field]

Figure 4.14: Frequency dependence of FMR resonance field with external field pointing in the in-plane and out-of-plane orientations for the LFO film grown at 500°C.

It is evident by looking at the linewidth profiles of the films that the linewidth for the sample deposited at 500°C is the lowest, and also the best reported so far. The films deposited at 450°C show a higher microwave loss (larger FMR line width) as compared to the one deposited at 500°C. One important factor contributing to single crystal thin film FMR line width is the surface roughness. The poor crystallinity and surface roughness of the film grown at lower growth temperature leads to an increase in the FMR linewidth as compared to the sample grown at 500°C. This can be attributed to the limited surface diffusion behavior at low growth temperatures, which leads to a low structural quality and different ion distribution in the lattice.
structure. For higher growth temperature (550°C), the migration/loss of lithium (based on the SIMS results) could explain the significant increase in the linewidth compared to the sample grown at 500°C. Another possibility could be the crystalline defects generated by the Mg diffusion into lithium ferrite films at higher temperatures. A detailed FMR analysis for the films grown at 500°C, exhibiting the lowest microwave loss, will be discussed in the next section.

Figure 4.15: FMR linewidth profile for the LFO films grown at varying temperatures in the in-plane (left) and out-of-plane (right) orientations.

Electrical resistance of the lithium ferrite films grown at different temperatures was obtained by standard linear four-probe techniques. Electrical contacts were made with gold wire. Measurements were carried out in the temperature range between 200°C and 350°C and the temperature during the measurement was stabilized within one degree. As can be seen in figure 4.16, the RT plots indicate an increase in the high temperature resistance values with increasing growth temperature. The resistance values ranges from $10^9$ to $10^{12}$ at room temperature.
It is evident from all the structural, magnetic and FMR results, that the optimized growth temperature for the LFO films grown on MgO is 500°C. The study of the LFO films at this optimized temperature was further extended to thickness dependence as well as substrate dependence.

4.4) Thickness dependence of the LFO growth on MgO

From the growth temperature dependence study discussed in the previous section, it was concluded that there exists a very narrow window of growth temperature for LFO films deposition. Clearly, 500°C is the optimized temperature considering both the surface morphology as well as the FMR linewidth profile. We focused on the thickness dependence study of LFO films at 500°C where films ranging from 70 nm to 600 nm were grown. The other processing conditions were kept fixed, and only the deposition time was changed in each run to...
change the thickness. The position of the substrate was also kept fixed to avoid any variation in the film composition and the Li-content. Reproducibility was confirmed by repeating each run at least twice for a specific thickness. There is an expected linear increase in the thickness with the deposition rate as shown in table 4.4. The films were then carefully characterized in detail for structural, magnetic and microwave behavior.

The room temperature crystallographic data provide clear evidence of good epitaxial film quality and the presence of significant strain in all the LFO films of varying thicknesses grown on MgO substrates. This is shown in figure 4.17 where the dotted line indicates the bulk 2θ peak position of the LFO (400) reflection. The calculated lattice parameters using Cohen’s method [93-94] are shown in figure 4.18.

Figure 4.17: 2θ-0 plots around the (004) peak for LFO films of different thicknesses grown on MgO substrate.
Figure 4.18: Calculated lattice parameters (a: in-plane; c: out of plane; error margin ±0.003 Å for ‘a’ and ±0.001 Å for ‘c’) for LFO films grown on MgO at varying thickness. The red data indicates the lattice parameter of a LFO film grown on MgAl₂O₄ substrate.

Due to the fact that the films deposited at 500°C have the smallest FMR linewidth, a detailed angle and frequency dependence of the FMR behavior of films deposited at this temperature was carried out for all thicknesses. The primary magnetic properties for these films, which are of interest for microwave applications, are the FMR linewidth, gyromagnetic ratio, saturation magnetization, FMR resonance field positions, and the magnetocrystalline anisotropy. The frequency dependence of FMR resonance field with external field pointing at different crystal orientations is shown in figure 4.19 (a,b). The shift between lines is due to the change of
effective internal field, which can have contributions from the demagnetizing field, magnetocrystalline anisotropy, or strain-related effects.

Figure 4.19: FMR resonance field at different microwave frequencies and static field orientations. (a) in-plane; (b) out-of-plane

Figure 4.20: FMR linewidth at different microwave frequencies and static field orientations. (a) in-plane; (b) out-of-plane
The frequency dependence of FMR linewidth at different field orientations (figure 4.20) exhibits different trends. A surprising feature in the in-plane frequency-linewidth profile is obtained. Generally it is observed in most of the thin film linewidth profiles that linewidth ought to increase as frequency is increased. However, in these samples of LFO, the FMR in-plane linewidth decreases as the external field or frequency is increased. The linewidth is very large for the films at low frequencies but becomes significantly narrower for frequencies higher than 15 GHz. A similar decrease in linewidth has been reported in many different systems, and suggests an increase in damping at low frequencies. The in-plane measurements show larger FMR linewidth than the out-of-plane measurement, which indicates the presence of two-magnon scattering. The linewidth profile of the [001] direction, which is an out-of-plane measurement, should possess the least two-magnon scattering contribution to the linewidth. A linewidth peak at around ~14 GHz for the [001] direction for a 70 nm thick film has been observed. The peak moves towards the higher frequency side with the increasing thickness, but stabilizes at a frequency of around 24 GHz once a critical thickness stage of 300 nm is reached. This phenomenon could be attributed to the slow relaxing mechanism due to the existence of trace amount of contaminant ions. The effect of chemical impurities on FMR line width of ferrite materials has been widely investigated. [101,102]

A recent report on frequency-linewidth behavior in structured magnetic materials, both from experimental and theoretical points of view, suggests that this increase in linewidth at low frequencies does not necessarily indicate an increase in damping at low frequencies. The effective linewidths at extreme high field limit (5 kOe at 10 GHz) approach the intrinsic single crystal linewidths for both samples, indicating the absence of two-magnon processes at the extreme high field limit [103]. As the field is reduced, one approaches a range of fields where the
driven FMR mode is degenerate with moderate wave number (momentum) spin waves with wavelengths on the order of a micron. In this region, coupling to spin modes, i.e. two-magnon scattering, dominates the relaxation. [104,105] Another possibility of this increase in linewidth at lower frequencies could be due to the inhomogeneous linewidth broadening. The fields are not enough to saturate the sample completely for frequencies lower than 15 GHz. However, the presence of other relaxation mechanisms can also contribute to the shape of this profile and make the interpretation even more complicated. More insight into both in-plane and out-of-plane linewidth profiles of the LFO films is required to explain the characteristic effects observed. The smallest peak-to-peak FMR linewidth value, as shown in figure 4.20 (b), is $\Delta H_{\text{pp}} = 125$ Oe at 40 GHz.

Figure 4.21: FMR resonance field (left) and linewidth (right) at different microwave frequencies for two in-plane directions of [100] and [110].

Figure 4.21 shows the observed small difference between in-plane directions of [100] and [110], which comes from the intrinsic magnetocrystalline anisotropy of the (pseudo) cubic structure of
the as-deposited LFO films. There is a small, but not significant, change in the linewidth values for the [110] direction. The measured $M_s$ and $H_c$ values from VSM and the other fitted magnetic parameters obtained from the FMR experiments at varying frequencies for the [100] orientation are summarized in table 4.4.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>Reaction time (minute)</th>
<th>FWHM (nm)</th>
<th>RMS roughness (nm)</th>
<th>$H_c$ (Oe)</th>
<th>$M_{eff}$ (emu/cc)</th>
<th>$\gamma^\prime\prime$ (MHz/Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>14</td>
<td>0.032</td>
<td>0.24</td>
<td>252</td>
<td>-40</td>
<td>2.64</td>
</tr>
<tr>
<td>100</td>
<td>30</td>
<td>0.0387</td>
<td>0.45</td>
<td>188</td>
<td>-48</td>
<td>2.69</td>
</tr>
<tr>
<td>300</td>
<td>60</td>
<td>0.035</td>
<td>1.13</td>
<td>153</td>
<td>37.5</td>
<td>2.64</td>
</tr>
<tr>
<td>450</td>
<td>100</td>
<td>0.032</td>
<td>1.01</td>
<td>136</td>
<td>13</td>
<td>2.7</td>
</tr>
<tr>
<td>570</td>
<td>120</td>
<td>0.032</td>
<td>1.02</td>
<td>138</td>
<td>78</td>
<td>2.56</td>
</tr>
</tbody>
</table>

The $M_{eff}$ values clearly indicate the generation of the out-of-plane anisotropy for all the films. This was further confirmed by the VSM loops obtained for the films. Figure 4.22 shows the in-plane and perpendicular magnetic loops of the three as-deposited LFO films with 70 nm, 300 nm and 570 nm thicknesses respectively. Several effects may be responsible for the observed hysteretic behavior of both in-plane and out-of-plane $M$-$H$ loops. One possibility is that the film has regions with different anisotropies. For instance, separated areas of the film may have slightly different in-plane or out-of-plane orientation. Another possibility is that the strain is not homogenous through the film thickness – a larger strain near the substrate interface and more relaxed behavior near the surface would create a vertical distribution of anisotropy. In either case, for either the in-plane or out-of-plane measurement there would potentially always be regions of the film, which are not along the easy axis, leading to hysteretic behavior for either field orientation.
Figure 4.22: VSM loops obtained for the in-plane and perpendicular orientations of the three LFO films with 70 nm, 300 nm, and 570 nm thickness respectively.

Clearly, the stress is playing a significant role in all the LFO films grown on MgO. This apparent strain phenomenon will affect the internal magnetic field and thus change the resonance field. To analyze the affect of stress on the magnetic behavior of the LFO films, an approach incorporating the stress related terms in the basic FMR equations is used. [106] Resonance equations for
different crystallographic orientations of the applied dc magnetic field including a stress induced anisotropy field are:

\[
H \parallel \langle 001 \rangle : \left( \frac{\omega}{\gamma} \right)^2 = \left( H_{<001>} + \frac{2K_1}{M_s} \right) \left( H_{<001>} + \frac{2K_1}{M_s} + 4\pi M_{\text{eff}} \right)
\]

\[
H \parallel \langle 011 \rangle : \left( \frac{\omega}{\gamma} \right)^2 = \left( H_{<011>} - \frac{2K_1}{M_s} \right) \left( H_{<011>} + \frac{K_1}{M_s} + 4\pi M_{\text{eff}} \right)
\]

\[
H \parallel \langle 100 \rangle : \left( \frac{\omega}{\gamma} \right)^2 = H_{<100>} + \frac{2K_1}{M_s} - 4\pi M_{\text{eff}}
\]

where, \( M_{\text{eff}} = M_s + \frac{3\lambda_{100}\sigma}{4\pi M_s} \)

In these equations, \( \omega \) is the microwave frequency in rad/s, \( \gamma \) is the gyromagnetic ratio, \( H \) is the static magnetic field, \( K_1 \) is the first order magnetocrystalline anisotropy coefficient, \( M_s \) is the saturation magnetization, and \((3\lambda_{100}\sigma/M_s)\) is a term representing the strain effect. From these equations, it is clear when the magnetostrictive term is included in the resonance analysis, we get an additional stress-induced anisotropy field \((3\lambda_{100}\sigma/M_s)\). If there is small or negligible stress, these equations reduce to the basic FMR equations. It is important to note that the demagnetizing factors in the film plane are assumed to be zero and the strain in the film plane is assumed to be isotropic here.

The stress-induced anisotropy field and the cubic magnetocrystalline anisotropy field are calculated using the above equations for LFO/MgO film and LFO/MAO films grown at 500°C with a thickness of 300 nm.
The magnitudes of the first order cubic magnetocrystalline anisotropy field \( (2K_1/M_s) \) and stress induced anisotropy \( (3\lambda_{100} \sigma/Ms) \) field for LFO films on MgO and MAO substrates (300 nm thick).

Figure 4.23 shows a comparison of the magnitudes of the two calculated anisotropy fields at varying frequencies. The results shown in the figure clearly indicate that the stress induced anisotropy field dominates the magnetic anisotropy of the LFO films grown on MgO. The stress in the films is reflected by the stress induced anisotropy field in the magnetic data analysis and is also evident in the XRD
results where the cubic symmetry if the LFO unit cell is tetragonally distorted. The magnitude of the in-plane tensile stress can also be independently calculated from the XRD data. A quantitative analysis was done to estimate the stress using the in-plane and out-of-plane lattice constants obtained to directly compare the value of induced stress for all the films with the results obtained from FMR analysis. The calculation was based on the following equation [107]:

\[
\sigma = \left( \frac{a_\parallel - a_\perp}{a_{bulk}} \right) \frac{2E}{1 + \nu}
\]

where \( E (=13.23 \times 10^9 \text{N/m}^2) \) is Young’s modulus [133], \( \nu (=0.28) \) is the Poisson’s ratio [134], \( a_\parallel \) is the in-plane lattice constant measured using the asymmetric scans, \( a_\perp \) is the out-of-plane lattice measured using the symmetric 2θ-θ scan and \( a_{bulk} \) is the bulk lattice constant of LFO (8.330 Å). The calculated FMR and the XRD stress parameters, as shown in figure 4.24, are of the same order of magnitude and show similar thickness dependence. The smaller stress term for higher thickness coincides with this strain effect very well. There are various factors that can contribute to a large amount of stress in the LFO films. A stress model for heteroepitaxial magnetic oxide films based on the different thermal expansion rates between the substrate and the film during the cooling process is proposed by Besser et al. [97] The residual stress after cooling the sample to room temperature is related to the difference in the thermal expansion coefficients of the film and substrate and is not related to the bulk lattice parameters. A tensile stress on LFO can be created because LFO has a larger thermal expansion coefficient than that of MgO, which results in a faster contraction rate in LFO than in MgO during the cooling process.
Figure 4.24: A comparison of the induced stress based on FMR and XRD as a function of thickness for LFO films on MgO. Also, shown are the corresponding values for a LFO film (300 nm thick) on MAO.

4.5) LFO growth on MgAl$_2$O$_4$

The structural and magnetic properties of the epitaxial LFO films are affected by the choice of the substrate. Apart from MgO, which is the closest lattice match of LFO, the growth on MgAl$_2$O$_4$ (MAO) substrate, which is a spinel structure, was also investigated. Cihat et al. have reported the epitaxial growth of LFO on MAO as well on MgO by PLD technique and studied the effect of cation ordering on magnetization. The LFO films were deposited on MAO substrates at the optimised processing conditions (table 4.1) The standard 2θ-0 scan of the LFO
films with varying thickness grown on MAO substrate at 500°C is shown in figure 4.25 (a). The high intensity and appearance of a sharp Kα peak splitting of the (400) reflection peak for the film with thickness of 300 nm and 570 nm respectively indicating that the material is in single phase and has a very good epitaxial orientation. The full width at half maximum of the XRD rocking curve for a 300 nm thick film, shown in figure 4.25 (b), is 0.31° which gives a quantitative measure of the c-axis dispersion. As evident from figure 4.25 (a), the 300 nm film is under a strain with the (400) reflection peak is shifted towards the right side of the bulk LFO (400) peak position. There is an in-plane tensile stress present in this specific film, which is not expected as the lattice constant of MAO (8.083 Å) is smaller than LFO (8.330 Å). The calculated lattice parameter for this 300 nm thick LFO/MAO film are shown in figure 4.18.

Figure 4.25: (a) XRD 2θ-θ scan of the LFO films with varying thickness grown on MAO substrate at 500°C; (b) XRD rocking curve of a 300 nm thick LFO film, with FWHM value of 0.31°.
This unexpected in-plane tensile stress is strongly correlated with the density of the interface misfit dislocations, which are formed at the deposition temperature to relieve the stress caused by the lattice mismatch. [108] However, the thick LFO/MAO film is completely relaxed with no stress present. Figure 4.26 illustrates the AFM images of the surface of the films for 300 nm and 570 nm thick LFO films grown on MAO substrate respectively.

![AFM images of the surface of the LFO films for 300 nm and 570 nm thick LFO films grown on MAO substrate at an optimized growth temperature.](image)

Figure 4.26: AFM images of the surface of the LFO films for 300 nm and 570 nm thick LFO films grown on MAO substrate at an optimized growth temperature.

The presence of cracks and increase in the surface roughness (table 4.5) in the AFM image of the thickest film (570 nm) further confirms the stress relaxation. Thus, it can be concluded that the thermal expansion coefficient difference is not the cause for stress, but more likely the formation of misfit dislocations is more significant in the LFO films grown on MAO.
The room temperature saturation magnetization was measured by VSM. The data was obtained for the in-plane [100] and out-of-plane [001] applied field directions. Figure 4.27 shows the hysteresis loop data for the 300 nm thick LFO/MAO film, which is consistent with the known properties of the LFO material. The measured saturation magnetization value of the 300 nm thick film is 294 emu/cm³.

Figure 4.27: M-H curve for the 300nm thick LFO/MAO film. The field was applied perpendicular-to-plane (oop) and in-plane (ip).

The frequency dependence of FMR resonance field with external field pointing at different crystal orientations is shown in figure 4.29 (a). The relative magnitude of resonance field for the out-of-plane measurement indicates the presence of a large magnetic anisotropy with easy axis parallel to the thin film surface. The hard axis at the [001] direction, which is pointing out of the
film plane, is due to the demagnetization field resulting from the shape of the thin film sample. A small difference between in-plane directions of [100] and [110] has also been observed, stemming from the intrinsic magnetocrystalline anisotropy of cubic structure of lithium ferrite. The effective magnetization $M_{\text{eff}}$ is 173 emu/cm$^3$, which is lower than the saturation magnetization ($M_S$) value of 294 emu/cm$^3$ measured by vibrating sample magnetometry (VSM). The frequency dependence of FMR linewidth at different field orientations for the 300 nm thick LFO/MAO film is shown in figure 4.29(b).

Figure 4.28: A FMR absorption curve for LFO/MAO (300 nm thick), obtained at 35 GHz (in-plane).
Symmetric and non-distorted FMR curves for all orientations have been observed. An example absorption curve, obtained at 35 GHz (in-plane) for 300 nm thick LFO/MAO film is shown in figure 4.28, with a FMR linewidth of 146 Oe. The FMR linewidth profiles of the 300 nm thick LFO/MAO film are quite similar to the LFO/MgO films discussed in the previous section.

![Graph showing FMR curves for different orientations](image)

Figure 4.29: (a) FMR resonance field and (b) linewidth at different microwave frequencies and static field orientations.

But, there is a significant difference in the linewidth between the two in plane directions of [100] and [110]. The smallest peak-to-peak FMR linewidth value, as shown in figure 4.29 (b), varies from 40 Oe at 5 GHz to 70 Oe at 40 GHz in the out-of-plane orientation. A comparison of the in-plane FMR linewidth values for three different thicknesses was done and it is observed that a critical thickness of 300 nm gives the lowest line width in both in-plane and out-of-plane orientations. The in-plane linewidth for the 70 nm and 570 nm LFO films lie in the range of 250-270 Oe in the 5-40 GHz range. However, no out-of-plane FMR spectra were observed for both the films, which was not the case with the 300 nm LFO film on MAO. This seems to be
consistent with structural quality of the films and the strain relaxation mechanism discussed before. The calculated FMR and the XRD stress parameters for the LFO films (300 nm) grown on MAO substrate are shown in figure 4.24. The magnitudes of the two calculated anisotropy fields, stress induced anisotropy field and the magnetic anisotropy at varying frequencies are shown in the figure 4.23 indicating that stress induced anisotropy field is not as dominant as it was in the case of the LFO films grown on MgO.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>FWHM (nm)</th>
<th>RMS roughness (nm)</th>
<th>Hc (Oe)</th>
<th>Meff (emu/cc)</th>
<th>γ'' (MHz/Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>0.27</td>
<td>1.85</td>
<td>38</td>
<td>155</td>
<td>2.89</td>
</tr>
<tr>
<td>300</td>
<td>0.31</td>
<td>1.73</td>
<td>93</td>
<td>173</td>
<td>2.82</td>
</tr>
<tr>
<td>570</td>
<td>0.31</td>
<td>2.32</td>
<td>57</td>
<td>210</td>
<td>2.85</td>
</tr>
</tbody>
</table>

4.6) Bilayered heterostructures of magnetostrictive lithium ferrite and piezoelectric materials

LFO is a promising candidate for magnetoelectric (ME) heterostructures, which have been an active area of research in the recent years, due to its small coercivity, high resistivity, low eddy current losses and low anisotropy. The heteroepitaxial growth of LFO films on piezoelectric materials, such as lead zinc niobate - lead titanate (PZN-PT) and lead magnesium niobate - lead titanate (PMN-PT) using DLI-CVD. They have a perovskite structure with lattice constants of 4.023 Å and 4.06 Å (for ideal cubic phase). The corresponding lattice mismatch of lithium ferrite to these substrates is shown in table 4.6. These substrates have a high piezoelectric coefficient.
Therefore, the LFO films grown on these substrates are of great importance to understand the ME coupling in ferrite-piezoelectric heterostructures. [66-70] The heterostructures were characterized for composition, structure, morphology, magnetic and ferromagnetic resonance properties.

Figure 4.30: 2θ-θ plots around the (004) peak for LFO films grown on different substrates, exhibiting a pure spinel phase with the (h00) planes parallel to the film surface.

The LFO films used for structural and magnetic studies are grown under the same vaporization and CVD processing conditions on different substrates as mentioned in table 4.1. The deposition time for the experiment was 100 min. For direct comparison, the LFO films were deposited in the same experimental run on four different single crystal substrates, MAO, MgO, PMN-PT and PZN-PT, all with (100) orientation, which are of size 5 mm × 5 mm × 0.5 mm with atomically smooth surface. Large-angle 2θ-θ scans for LFO films on four different substrates are showed in
figure 4.30. Only (00l) peaks from both LFO film and different substrates are observed, with no evidence of any secondary phases. The lattice parameters values of film and substrates determined from X-ray 2θ-θ scans using Bragg’s law are shown in table 4.6.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Substrate lattice parameter (Å)</th>
<th>c (Å)</th>
<th>LFO-lattice mismatch (%)</th>
<th>FWHM</th>
<th>RMS roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFO/PZN-PT</td>
<td>4.063</td>
<td>8.332±0.001</td>
<td>-2.51</td>
<td>0.47</td>
<td>2.2-2.3</td>
</tr>
<tr>
<td>LFO/PMN-PT</td>
<td>4.024</td>
<td>8.323±0.002</td>
<td>3.5</td>
<td>0.53</td>
<td>1.9-2</td>
</tr>
<tr>
<td>LFO/MAO</td>
<td>8.083</td>
<td>8.334±0.001</td>
<td>-3</td>
<td>0.31</td>
<td>2.3-2.5</td>
</tr>
<tr>
<td>LFO/MgO</td>
<td>8.424</td>
<td>8.292±0.001</td>
<td>1.1</td>
<td>0.032</td>
<td>1.02</td>
</tr>
</tbody>
</table>

Figure 4.31: Rocking curve of the (400) reflection of LFO film grown at 500°C on different substrates.
The out-of-plane texture of NFO film on different substrates is examined by rocking curve analysis ($\omega$-scan) as shown in figure 4.31. The full width at half maximum (FWHM) values are $0.56^\circ$, $0.97^\circ$, $0.57^\circ$, and $0.89^\circ$ for LFO film on MAO, MgO, PMN-PT and PZN-PT substrate, respectively. The growth of LFO films on four different substrates under optimal DLI-CVD process conditions produces smooth surface topography. Surface roughness characterized by AFM (figure 4.32) shows rms roughness of 0.3 nm, 0.4 nm, 5 nm, and 7 nm for LFO films grown on MAO, MgO, PMN-PT and PZN-PT substrate, respectively. Considering the similar atomic flat substrate surface and film thickness, these differences of film surface roughness can be attributed to different thin film growth mode due to different substrate surface energies.

Figure 4.32: AFM images of the surface of the films grown on piezoelectric substrates.

The hysteresis loop data, shown in figure 4.33, obtained for the LFO films grown on PMN-PT substrate for in-plane and out-of-plane orientations is consistent with the known properties of LFO. The values of the saturation magnetization at room temperature are quite close to the bulk
value of 288 emu/cm$^3$ for LFO. However, the coercivity values obtained for the films grown on MAO and piezoelectric substrates are comparatively smaller than films grown on MgO substrates.

![MH curve](image)

Figure 4.33: MH curve obtained for the LFO films grown on the PMN-PT substrate.

Table 4.7 summarizes all the magnetic parameters obtained from the set of LFO films grown on different substrates. As evident from the difference between the $M_s$ and $M_{\text{eff}}$ values of the LFO films on piezoelectric substrates, there is a small out-of-plane anisotropy generated in these films too similar to that of LFO films on MAO but it is not as significant as it was in the case of LFO films grown on MgO.
### Table 4.7: Magnetic parameters dependence on substrate

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$H_c$ (Oe)</th>
<th>$M_{eff}$ (emu/cc)</th>
<th>$\gamma'$ (MHz/Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFO/PZN-PT</td>
<td>97</td>
<td>188</td>
<td>2.86</td>
</tr>
<tr>
<td>LFO/PMN-PT</td>
<td>60</td>
<td>210</td>
<td>2.85</td>
</tr>
<tr>
<td>LFO/MAO</td>
<td>53</td>
<td>164</td>
<td>2.83</td>
</tr>
<tr>
<td>LFO/MgO</td>
<td>142</td>
<td>78</td>
<td>2.56</td>
</tr>
</tbody>
</table>

![Image](image.png)

**Figure 4.34:** (a) FMR resonance field, and (b) linewidth at different microwave frequencies for in-plane orientation for the set of LFO films grown on different substrates.

The most interesting parameter to look for in these films is the FMR linewidth and if a strong and clean FMR signal can be achieved to study the ME effects in these heterostructures. In-plane FMR measurement (40 GHz) of LFO films deposited on these piezoelectric substrates show FMR line width in the range of 400 to 500 Oe. Figure 4.34 (a,b) shows the FMR resonance field
and linewidth at different microwave frequencies for in-plane direction for the set of LFO films grown on different substrates. The $\gamma'$ ratio extracted from the FMR data is quite close to the expected value of 2.8 MHz/Oe. The in–plane FMR peaks are fairly broad but symmetric for the films grown on PMN-PT and PZN-PT substrates while the out-of-plane FMR curves are greatly distorted.

In summary, lithium ferrite (LFO) films were grown on different substrates for a range of deposition temperatures using DLI-CVD. The growth conditions were optimized to achieve epitaxial, single crystalline films with low ferromagnetic resonance linewidths. The FMR profiles were measured at varying frequencies (5-40 GHz) with the static field perpendicular and parallel to the film plane. The linewidths range from 41 Oe to 119 Oe for the 300 nm thick films grown on MAO and MgO substrates at a substrate temperature of 500°C. This is the lowest reported so far for pure lithium ferrite (without any substituents). The stress induced anisotropy field for films is studied for varying thickness of the LFO films grown on MgO. For ME effects study, the ferrite-ferroelectric heterostructures are grown. The linewidth for the LFO film grown on PMT-PT substrate is in the range of 400-450 Oe, which is comparatively higher than the values obtained for MgO and MAO substrates. However, more optimization can be done to get the linewidth values lower in the range of 100-200 Oe with sharp and smooth FMR curves which is required for the study of the ME effect.
CHAPTER 5
STUDY OF STRUCTURAL AND FERROMAGNETIC RESONANCE PROPERTIES OF
LITHIUM FERRITE SINGLE CRYSTAL

5.1) Introduction
Lithium ferrite, a ferromagnetic spinel Li_{0.5}Fe_{2.5}O_{4} or LiFe_{5}O_{8} (LFO), has been an important
candidate for microwave devices such as gyrators, circulators, isolators and phase shifters
because of its low loss rate at high microwave frequencies coupled with excellent magnetic
properties. [15,21-23] The exact origin of the loss rate in ferrites is not precisely known, but has
been attributed to mechanisms like two-magnon scattering, valence exchange, fast and slow
relaxing impurities and eddy current dissipation. [5] One key to understand the origin of these
losses lies in the studying the frequency dependence of their FMR linewidths. The measurement
of the intrinsic linewidth is very difficult as there are too many extrinsic effects that influence the
measurement. These hidden contributions coming from crystal imperfections (dependent on
growth method and conditions), surface roughness, volume defects, magnetostatic excitations,
size, and excitation of high-order spin waves, etc. can result in an overestimation of the
experimental value of the linewidth we obtain from FMR. Measurements to date in LFO provide
no definite conclusion as to the linewidth frequency dependence. [109-111] The narrowest
intrinsic linewidth measurements in the single-crystal materials reported are of the order of 1.35
Oe at a frequency of 5.1 GHz at room temperature. [109] A recent theoretical study for ordered
magnetic materials presents an approach to understand the relaxation mechanisms for these materials taking into consideration the elastic, magnetic and electrical properties and compare it with the experimental results obtained. [112] The present work was performed in order to study the structural, magnetic and ferromagnetic resonance properties of the LFO single crystal, and quantitatively measure the room temperature FMR linewidth in the LFO samples. We report the measurements on the frequency dependence of the ferromagnetic resonance in well-characterized lithium ferrite single crystal at room temperature for both B-site ordered ($\alpha$) and B-site disordered ($\beta$) phases. The measurements were done using a fully automated broadband ferromagnetic resonance set-up to obtain clean FMR profiles in the frequency range of 9-40 GHz. The FMR linewidth increases linearly with the frequency at a rate of 0.86 Oe/GHz. The FMR linewidth values at 9.5 GHz for $\alpha$ and $\beta$ phases are 3.5 Oe and 7 Oe respectively.

5.2) Experimental

In this study, the single crystal lithium ferrite material was prepared by conventional flux-melt growth technique. We studied a LiFe$_5$O$_8$ (LFO) crystal in two phases. The first one is as-grown LFO crystal named as S1 and the second one is the ordered LFO crystal S2 obtained by post annealing of S1 in oxygen for two hours at 600°C followed by a very slow cooling at the rate of 0.5°C/minute. The determination of the crystal phase of the as-grown LFO-S1 and the annealed LFO-S2 was carried out by a standard x-ray diffraction setup (Bruker D8 Discover XRD with GADDS) with a cobalt radiation ($\lambda$=1.7903 Å). Polarized Raman spectra were measured under the microscope using T64000 and LabRAM HR Raman spectrometers. The spectra were obtained from (100) or (111) crystal surfaces in backscattering configuration with 515 nm (2.41 eV) excitation. The notations HH and HV, used for scattering from the (111) surface, correspond
to parallel and crossed polarizations of incident and scattered light. Transmission electron microscope (TEM) cross sectional sample was prepared by mechanical polishing followed by Ar ion milling at 3.0 kV to prepare electron transparent thin area. Magnetic properties of the crystal were determined by vibrating sample magnetometry (Quantum design PPMS DynaCool) at temperatures $5 \text{ K} \leq T \leq 400 \text{ K}$ and in magnetic fields of up to 5 T. The sample was air milled and polished to the shape of a sphere of 0.5 mm in diameter for FMR characterization to avoid complicated FMR spectra from the irregular shaped crystal because the sample shape and edges have significant effects on the FMR absorption profiles and linewidth measurements.

5.3) Structural characterization

LFO possess an inverse spinel structure with a specific 1:3 ordering of Li$^{1+}$ and Fe$^{3+}$ at the octahedral B-sites. [25] The X-ray diffraction trace of the crystal (figure 5.1) indicated a disordered state of the crystal with missing superlattice lines. The lattice parameter fitted from the lines was obtained to be $8.331\pm0.001 \text{ Å}$ for LFO-S1, which is very close to the bulk value listed in JCPDS. To study the effect of ordering on the room-temperature linewidth uncomplicated by other effects, the LFO-S1 spherical crystal was annealed at different temperatures in presence of oxygen. X-ray diffraction showed that this treatment for 2 hours at 600°C changed the disordered state of the S1 crystal to the highly ordered state, but higher temperatures introduced disorder. [98] S2 gave the superlattice XRD reflections (210,211) corresponding to the ordered phase in XRD pattern.
Figure 5.1: Powdered XRD for S1 sample (disordered) of the LFO single crystal. Inset shows the simulated XRD patterns of ordered (SO) and disordered (SD) phases for comparison. The normal reflections of LFO are indexed for disordered phase and the additional reflections due to ordering are indexed for the ordered phase.

Figure 5.2: Polarized Raman spectra for S1 (disordered) and S2 ordered states of the crystal.
The cationic ordering was further confirmed by Raman Spectroscopy data as shown in figure 5.2. The Polarized Raman spectra also confirmed the conversion of the crystal S1 from the disordered beta phase to the ordered alpha phase, consistent with a reported Raman study on LFO crystals. [98] TEM images show some local ordering in the crystal. Figure 5.3(a) shows TEM bright field image with \( g = <400> \) diffracting vector. No strain contrast associated with either line or planar defects are observed. Diffraction pattern (figure 5.3(b)) shows single crystalline pattern with superlattice (SL) spots. The intensity of SL spots is weak. Only \(<100>\) and \(<110>\) and its odd multiples SL spots are present. \( \frac{1}{2}<400>\) SL spots are absent. This means that the periodicity of octahedral planes ordering is \(<100>\) or the lattice parameter of the unit cell. Figure 5.3(c) is the HRTEM image from the film.

Figure 5.3: TEM images for S1 sample (disordered) of the LFO single crystal.
5.4) VSM and FMR results

Figure 5.4 shows the hysteresis loops of the sample magnetic moment versus the applied static magnetic field at 5 K and 300 K. The saturation magnetization obtained from the MH-loops was 320 emu/cm³ and 290 emu/cm³, both in agreement with the theoretical $M_s$ value for LFO. The M-T curve shown in figure 4(b) shows the variation of the magnetization with temperature ranging from 5 K to 400 K. The saturation value was obtained for the annealed crystal at room temperature, which was similar to the previous value of 290 emu/cm³. This is expected for LFO since the distribution of Fe³⁺ does not change between the tetrahedral and octahedral sites. [20]

![Figure 5.4: (a) M-H plot for S1 sample at 5 K and 300 K (b) M-T plot for S1.](image)

FMR on the spherical sample is usually complicated by a large number of magnetostatic mode absorption lines, which make interpretation and accurate linewidth determination difficult. In contrast, the present spherical samples show clean and simple FMR profiles. The higher order modes are weak and well separated from the main FMR lines.
Figure 5.5: An air milled spherical crystal of LFO (S1) with a diameter less than 0.5 mm.

Figure 5.6: A FMR absorption curve for LFO-S2, obtained at 30 GHz with a linewidth of 26 Oe.

The most important parameter of interest is the FMR linewidth. An example absorption curve, obtained at 30 GHz, is as shown in figure 5.6, with a FMR linewidth of 26 Oe. As evident, the FMR profile is quite clean, with little distortion or additional structure. Figure 5.7 shows the measured FMR resonance field as a function of frequency ranging from 9-40 GHz in steps of 1 GHz for both beta and alpha phases of LFO crystal respectively.
The dynamics of the magnetization $\mathbf{M}$ is described by the phenomenological Landau-Lifshitz Gilbert equation. [83] For a spherical ferrite crystal, the uniform FMR mode of resonance field $H_{\text{res}}$ is given by:

$$ f = \gamma' (H_{\text{res}} + H_a) $$

where, $f$ is the resonance frequency, $\gamma' = \gamma/2\pi$ is gyromagnetic ratio and $H_a$ is the anisotropy field, $M_s$ is the saturation magnetization. [1]

![Figure 5.7: Frequency dependence of FMR resonance field for samples S1 and S2.](image)

The value obtained from the fitted data for $\gamma'$ is 2.77 GHz/kOe, which is in good agreement with theoretical value of 2.8 GHz/kOe. The linewidth dependence of the frequency is given by equation:

$$ \Delta H(\omega) = \Delta H_0 + \frac{2}{\sqrt{3}} \frac{\alpha}{\gamma} \omega $$
From the equation, it is very clear that the theoretical Landau-Lifshitz linewidth increases linearly with frequency.

Figure 5.8: FMR linewidth dependence on frequency for samples S1 and S2. Inset shows the fitted plot for sample S1, giving a value of 0.002 for the damping parameter.

A plot of the measured FMR linewidth vs. frequency is shown in Figure 5.8. The FMR linewidth linearly increases with frequency at 0.86 Oe/GHz. The error margin in the linewidth measurement is around 7%. The damping parameter obtained from the fit is 0.002 for sample S1. It is clear that the linewidth does not vary significantly with the cationic ordering on the B-sites.
Our fitted value corresponds to a g-value of 1.98 (DO) and 1.99 (ordered), which are consistent with the literature values, ranging from 1.98 to 2.05 for lithium ferrite crystal. These results support the operational assumption in this analysis of uniform mode FMR.

In summary, the FMR linewidth dependence on frequency for the single crystal lithium ferrite crystals was measured in the 9-40 GHz range at room temperature. The LFO crystal was well characterized by other techniques to look closely at the structural and magnetic properties. The measured FMR profiles consisted of a single large mode, which was clean with little distortion. The FMR resonance position has a linear dependence on applied field and fitted well with the dependence predicted from uniform mode theory. The FMR linewidth versus frequency measurements indicated that the linewidth scales linearly with frequency in the 9-40 GHz range. This is in accordance with the Landau Lifshitz damping model. It is clear that there is not a significant variation in the linewidth with the cationic ordering of the crystal. However, more theoretical and experimental studies are required to further identify and explain the physical relaxation mechanisms responsible for the extrinsic contribution to the linewidth.
CHAPTER 6
EFFECT OF GROWTH TEMPERATURE AND COMPOSITION ON THE PROPERTIES OF EPITAXIAL NICKEL FERRITE FILMS

6.1) DLI-CVD growth of Ni$_x$Fe$_{3-x}$O$_4$ films

Nickel ferrite has a lattice constant of 8.340 Å, saturation magnetization of ~300 emu/cm$^3$ (room temperature) and Neel temperature of 858 K which makes it one of the important members of the spinel ferrites. The microwave damping behavior is one of the most essential properties of NFO for their practical application in planar microwave devices and magnetic memory elements with high speed switching of magnetization. This is indicated by the linewidth of the ferromagnetic resonance (FMR). [53,113-115] The FMR properties of the bulk single crystal of nickel ferrite (NiFe$_2$O$_4$) have been theoretically and experimentally investigated by different groups since 1950s. [47,48] However, there have been very limited detailed FMR studies on the single crystalline nickel ferrite thin films.[53,58]

In this chapter, the focus is to study the effect of the growth conditions on the structural and magnetic properties and, more interestingly, on the FMR linewidth behavior of the deposited nickel ferrite (NFO) films grown on MgAl$_2$O$_4$ substrates using direct liquid injection chemical vapor deposition (DLI-CVD). A systematic study of the growth of NFO films on various substrates and at different growth temperatures has already been done. [46] However, further optimization of the growth conditions was done, which resulted in an overall improvement in the
quality of the films. A comprehensive FMR measurements and analysis was performed to understand the basic relaxation mechanism of the as-deposited films. DLI-CVD technique was used for the growth of epitaxial nickel ferrite films on MgAl₂O₄ substrates under optimized vaporization conditions and oxygen flow rate. [46] The experimental setup has already been discussed in the previous chapter 3.

Ni(acac)₂ and Fe(acac)₃ were used as the precursors in a molar ratio of 1:2 which were injected into a vaporization system after dissolving them in the solvent. The optimized processing conditions used for nickel ferrite growth are listed in table 1. To study the growth temperature dependence on the FMR properties, the films were deposited at three different deposition temperatures 500°C, 600°C (optimized and reported), and 700°C. These films were then characterized for the structural, morphological and magnetic properties.

<table>
<thead>
<tr>
<th>Processing conditions for DLICVD of NFO</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>MgAl₂O₄</td>
</tr>
<tr>
<td>Deposition temperature</td>
<td>500°C-700°C</td>
</tr>
<tr>
<td>Vaporizer temperature</td>
<td>175°C</td>
</tr>
<tr>
<td>Liquid flow rate</td>
<td>6 g/hour</td>
</tr>
<tr>
<td>Argon flow rate</td>
<td>300 sccm</td>
</tr>
<tr>
<td>Oxygen flow rate</td>
<td>120 sccm</td>
</tr>
<tr>
<td>Reaction pressure</td>
<td>2 torr</td>
</tr>
</tbody>
</table>

Table 6.1: DLI-CVD processing conditions of NFO.

6.2) Structural and magnetic characterization

The crystalline structure of the as-deposited films has been analyzed using an X-ray diffractometer (Philips X’pert Pro, Cu Kα source). As shown in figure 6.1, all the films deposited
between 500°C to 700°C exhibited a pure spinel phase with the (h00) planes parallel to the film surface. The films in consideration here are relatively thick (ranging from 500 nm to 1000 nm), so they are expected to be completely relaxed, despite the 3% lattice mismatch with the substrate. The calculated lattice parameters are pretty close to that of the bulk (0.834 nm) value of nickel ferrite. The structural parameters for different growth temperatures are summarized in table 6.2.

![XRD plots](image)

**Figure 6.1:** (a) XRD plots of the NFO films deposited on MAO (100) at 500°C, 600°C and 700°C; (b) Phi-scan of (220) planes confirms the epitaxial growth; (c) Rocking curve of NFO (400) peak with a FWHM value of 0.36° grown at 600°C.
Rocking curve ($\omega$-scan) analysis of NiFe$_2$O$_4$ (400) diffraction is used to characterize the degree of film texture as shown in the figure 6.1. The full width at half maximum (FWHM) decreases from 0.40° to 0.26° with increasing growth temperature (FWHM value of MgAl$_2$O$_4$ substrate is ~ 0.02°). A similar decrease in FWHM has been observed in PLD grown NiFe$_2$O$_4$ films on MgAl$_2$O$_4$ substrates. [92] Phi-scan results of both the NiFe$_2$O$_4$ films on MgAl$_2$O$_4$ substrate deposited at different temperatures are shown in figure 6.1. The four 90° spaced diffraction peaks confirms cube-on-cube epitaxial growth and clearly illustrate the four-fold symmetry of the spinel structure.

<table>
<thead>
<tr>
<th>Deposition temperature (°C)</th>
<th>Growth rate (μm/hour)</th>
<th>c (Å)</th>
<th>a (Å)</th>
<th>FWHM (degree)</th>
</tr>
</thead>
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<tr>
<td>500</td>
<td>0.68</td>
<td>8.332</td>
<td>8.326</td>
<td>0.4</td>
</tr>
<tr>
<td>600</td>
<td>0.67</td>
<td>8.333</td>
<td>8.325</td>
<td>0.36</td>
</tr>
<tr>
<td>700</td>
<td>0.66</td>
<td>8.338</td>
<td>8.321</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Table 6.2: Structural parameters of stoichiometric NFO films grown at different temperatures.

The film surface roughness has been characterized by atomic force microscopy (AFM) and cross-sectional scanning electron microscopy (SEM). The surface roughness shows a decreasing trend with increasing growth temperature as shown in figure 6.2. It is evident that at 600°C and 700°C, films grown on both MgAl$_2$O$_4$ exhibit an atomically smooth surface in comparison to film grown at 500°C. This is illustrated from figure 6.3, which shows the cross-sectional SEM views of thick NiFe$_2$O$_4$ films on MgAl$_2$O$_4$ substrate deposited at varying temperatures. EDX analysis indicates chemically pure NiFe$_2$O$_4$ films without any detectable contamination with Fe:Ni ratio ranging from 2.18-2.20 for different growth temperatures.
Figure 6.2: AFM images of the NFO samples grown at 500°C, 600°C and 700°C with rms surface roughness of 6.9 nm, 1.5 nm and 1.2 nm respectively.

Figure 6.3: Cross-sectional SEM views of the 1.1 µm thick NFO films deposited on MgO (100) at different temperatures. EDX analysis give a Fe: Ni ratio of 2.18-2.20 for all the films.
The room temperature magnetic properties of the as-deposited nearly stoichiometric NFO films on MgAl$_2$O$_4$ substrate were measured using VSM. The hysteresis loops of samples deposited at 500°C, 600°C and 700°C observed for the film grown at different temperatures are shown in figure 6.4.

![VSM hysteresis loops for NFO films deposited at 500°C, 600°C and 700°C.](image)

Figure 6.4: VSM hysteresis loops for NFO films deposited at 500°C, 600°C and 700°C.

The plots on the right show the dependence of the saturation magnetization ($M_s$) and coercivity ($H_c$) on the deposition temperature.

The saturation magnetization increases steadily with increasing deposition temperature to approach the bulk value (300 emu/cm$^3$), which can be attributed to the increased degree of texture with an increase in the deposition temperature, as indicated by the results of the ω scan. However, the film coercivity in figure 6.4 doesn’t show a clear trend, the lowest being for the optimized growth temperature of 600°C. Factors such as stoichiometry deviation, cation
ordering, strain and grain size can play an important role in the variation of coercivity. For instance, the grain boundaries can act as pinning sites for magnetic domain walls. Small grain size and large wall density can result in large coercivity in the multi-domain regime. [116-117]

6.3) Ferromagnetic resonance

The linewidth of FMR resonance curve represents the degree of microwave loss, which is an important concern for practical microwave device applications. Ferromagnetic resonance measurements were done at a frequency range of 5-40 GHz at different crystal orientations w.r.t. the static magnetic field. Similar FMR studies have been reported on CVD grown nickel ferrite films [58] at an optimized temperature of 600°C. However, the task was to further improve the experimental conditions to get lower linewidths (close to the bulk) by having less impurities and inhomogeneities. A better optimization of the growth conditions gave better in-plane linewidth values than the reported values so far. Moreover, it is observed that change in the stoichiometry drastically affects the in-plane linewidth profile behavior of the as-deposited films. The nickel ferrite films deposited on MgAl₂O₄ at different growth temperatures were characterized in both in-plane and out-of-plane orientations in a broadband frequency range. The frequency dependence of FMR resonance field and linewidth with external field pointing at different crystal orientations for all three samples is shown in figure 6.5.
Figure 6.5: Frequency dependence of resonance field and linewidth for two different orientations of the nearly stoichiometric nickel ferrite samples grown at three different temperatures.
It is evident from the data that the FMR line width of film deposited at 600°C is the lowest. Smooth and undistorted single resonance FMR curves are obtained at this specific temperature. Films deposited at 500°C show distorted and broad FMR curves and have a higher linewidth profile for both in-plane and out-of-plane directions. This is due to the limited diffusion behavior at low growth temperatures, which results in low single crystal quality (indicated from structural characterization) and different ion distribution in nickel ferrite lattice structure. However, it is noteworthy that the increased single crystal quality at higher temperatures is compromised by the decreased FMR performance. The possible reason is interface diffusion of Mg element from the substrate to the film at higher temperatures. Effect of chemical impurities on FMR linewidth of ferrite materials has been widely investigated. [101-102] The linewidth profiles in figure 6.5 for all three samples show a shift of the resonance field from a lower value in the in-plane orientation to a much higher position for the out-of-plane measurement. This indicates the presence of a large magnetic anisotropy with easy axis parallel to the thin film surface. The in-plane measurements [100] and [110], show larger FMR linewidth than the out-of-plane [001], measurement, which can be attributed to the presence of the two-magnon scattering effect and will be discussed in detail in the next chapter. The peak-to-peak FMR linewidth obtained for the nearly stoichiometric NFO films at the optimized growth temperature is 653 Oe (in-plane) and 130 Oe (out-of-plane) at 10 GHz, the best obtained so far. The smallest peak-to-peak FMR linewidth value is quite around 90 Oe at 6 GHz much lower than reported value 135 Oe in a previous study. [58]

The FMR center field position $H_{\text{res}}$ as a function of the in-plane resonance field angle phi relative to [100] orientation is measured at two different frequencies (10 GHz and 40 GHz). The angle dependence of $H_{\text{res}}$ for the samples obtained at 600°C and 700°C shows the expected clear four-
fold symmetry, consistent with the cubic structure of nickel ferrite as observed in the XRD phi scan. Figure 6.6 shows the $H_{\text{res}}$ and linewidth variation with the in-plane angle for the sample deposited at 700°C.

The in-plane cubic magnetic anisotropy field can be extracted by fitting the raw data of $H_{\text{res}}$ versus in-plane angle graph with the following function:

$$H_{\text{res}} = -H_{\text{ua}} \cos(\theta - \alpha) + H_{\text{u}} \sin^2(\theta - \beta) + H_{4f} \cos^2(\theta - \gamma) \sin^2(\theta - \gamma)$$

where, $H_{\text{u}}$ is the uniaxial anisotropy field and $H_{4f}$ represents the four-fold in plane anisotropy field. An example fit is shown in figure 6.7.

The extracted parameters from the fits are listed in table 6.3. A small difference between in-plane directions of [100] and [110] comes from the intrinsic magnetocrystalline anisotropy of the cubic structure of nickel ferrite.
Figure 6.7: Resonance field as a function of the in-plane resonance field angle $\phi$ relative to [100] orientation at 40 GHz for a ferrite sample. The raw data (dotted) is fitted (solid curve) to extract the in-plane cubic anisotropy field.

However, for the sample deposited at 500°C, an interesting behavior in the FMR center field position $H_{\text{res}}$ as a function of the in-plane resonance field angle is observed. As shown in figure 6.8, the angle dependence of $H_{\text{res}}$ measured at 9.5 GHz is close to the four-fold profile, although not exact. But, this symmetry evolves into an unexpected eight-fold symmetry when measured at a higher frequency of 45 GHz. This is in contrast to the expected four fold cubic symmetry observed for this sample in the XRD phi-scan. The linewidth, however, continues to follow the four-fold symmetry profile at all frequencies. To get more insight into this behavior, three additional in-plane angle dependent measurements were performed on this particular sample at higher angle resolution and intermediate frequencies and the raw FMR data at different in-plane
angle was carefully examined for two-resonance behavior. Interestingly, all the intermediate frequencies again gave a clear eight-fold profile for the resonance field. Figure 6.9 shows the linewidth profile as well as the raw data at different in-plane angles for the measurement at 45 GHz.

Figure 6.8: $H_{\text{res}}$ as a function of the in-plane resonance field angle at 9.5, 20, 30, 40 and 45 GHz.
Figure 6.9: (Top) Raw data for the FMR signal at different in-plane angles for the measurement at 45 GHz; (Bottom) Linewidth variation with the in-plane angle at 45 GHz for the sample grown at 500°C.

Not many studies have reported an eight-fold symmetry in FMR measurements, although there are a few on the systems involving coupling across an interlayer that show a behavior like this. [118-119] More detailed FMR measurements and other magnetic measurements are required to explain this unexpected symmetry for the ferrite sample.
6.4) Effect of change in stoichiometry on the FMR properties

As mentioned before it is important to optimise the vaporizer parameters as well as the flow of precursors into the CVD reactor without any decomposition. The deviations can result in rough film surface and changes in stoichiometry. We fabricated and studied the properties of two different non-stoichiometric compositions, at the optimised growth temperature of 600°C. EDX analysis gave the Fe:Ni ratio of 2.67 and 3.66 for the two as-deposited films. The variation of the lattice parameter ‘c’ is plotted versus the in-plane linewidth obtained for different compositions at 10 GHz in figure 6.10.

![Graph showing the in-plane linewidth dependence on the lattice parameter of the NFO films of different compositions at 10 GHz. Fe:Ni ratio is 3.66 for red data points and 2.67 for the blue data points.](image)

Figure 6.10: In-plane linewidth dependence on the lattice parameter of the NFO films of different compositions at 10 GHz. Fe:Ni ratio is 3.66 for red data points and 2.67 for the blue data points.
It is evident that a slight variation in the lattice constant of the stoichiometric NFO films does vary the linewidth by almost 100 Oe. One possible reason for this change in linewidth could be a small surface roughness variation for each sample grown in separate runs at same experimental conditions. Figure 6.11 gives the frequency dependence of linewidth for all three compositions in both in-plane and out-of-plane orientations.

Figure 6.11: Frequency dependence of linewidth for varying compositions of NFO films for two orientations, in-plane (top) and out-of-plane (bottom).
In all the NFO films, a big difference in both the resonance field and the FMR line between the in plane and out-of-plane orientation can be attributed to the decreased two-magnon scattering effect for the out-of-plane measurement. [120] Clearly, the FMR linewidth values vary significantly in the in-plane direction for non-stoichiometric films and has the lowest values for the NFO film with Fe:Ni ratio of 2.66. The linewidth at 9.5 GHz is almost reduced by 200 Oe for this non-stoichiometric composition ($\Delta H = 450$ Oe) as compared to the stoichiometric NFO films ($\Delta H = 650$ Oe) of the same thickness at the same frequency.

Figure 6.12: Composition dependence of the linewidth of the NFO films.

Figure 6.12 compares the room temperature linewidth values of three varying composition NFO films at three different frequencies. This could be related to the distribution of the Fe$^{2+}$/ Fe$^{3+}$ ratio
on the octahedral sites and the eddy current loss associated with each sample. However, for the out-of-plane direction we see an increase in linewidth with the Fe content and follow the expected trend similar to the bulk sphere shaped single crystals. [48] FMR measurements in NFO with different Ni/Fe composition have been obtained in spherically shaped samples and the relaxation effect is explained with a thermodynamic model. The bulk samples are reported to show an increase in linewidth observed for larger iron content NFO sample. All the important magnetic parameters for the films of varying compositions are summarized in table 6.3.

<table>
<thead>
<tr>
<th>$T_g$ (°C)</th>
<th>Fe:Ni ratio</th>
<th>$M_s$ (emu/cc)</th>
<th>$H_c$ (Oe)</th>
<th>$M_{eff}$ (emu/cc)</th>
<th>g-factor</th>
<th>$H_{af}$ (Oe)</th>
</tr>
</thead>
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<tr>
<td>500</td>
<td>2.2</td>
<td>222</td>
<td>151</td>
<td>188</td>
<td>2.175</td>
<td>NA</td>
</tr>
<tr>
<td>600</td>
<td>2.2</td>
<td>256</td>
<td>136</td>
<td>218</td>
<td>2.168</td>
<td>-286</td>
</tr>
<tr>
<td>700</td>
<td>2.2</td>
<td>279</td>
<td>185</td>
<td>140</td>
<td>2.132</td>
<td>-664</td>
</tr>
<tr>
<td>600</td>
<td>2.66</td>
<td>300</td>
<td>105</td>
<td>267</td>
<td>2.261</td>
<td>-630</td>
</tr>
<tr>
<td>600</td>
<td>3.67</td>
<td>237</td>
<td>124</td>
<td>203</td>
<td>2.089</td>
<td>-612</td>
</tr>
</tbody>
</table>

Table 6.3: Structural and magnetic parameters of the NFO films with different Ni:Fe ratio grown on MAO substrates.

Temperature dependent FMR study on bulk single crystal of nickel ferrite has proven the nonstoichiometry generated relaxation behavior. [48] In single crystals of ferrites, the linewidth of the ferromagnetic resonance increases with the ferrous ion concentration and the temperature variation of linewidth gives a maximum appearing at 160 K.

However, for crystals containing no ferrous ions the line width depends upon the orientation of the crystal and increases towards low temperatures. The damping parameter $\alpha$ is of the order of magnitude 0.008 for spinels containing no ferrous ions and increases to a value approximately 10
times higher in the spinels of higher ferrous content. The presence of redundant ferrous ions (Fe$^{2+}$) leads to a valence-exchange effect in which the hopping of electrons between Fe$^{2+}$ and Fe$^{3+}$ sites constitutes as a main channel of relaxation. [121-122] A detailed low temperature measurement study for all three samples was done to understand the relaxation mechanism contributing to the extrinsic linewidths of the samples.

![Graph showing temperature dependence of linewidth of different compositions of NFO films.]

Figure 6.13: Temperature dependence of linewidth of the different compositions of NFO films.

The observed FMR line broadening of the thin films has been mainly attributed to two-magnon scattering effect, which is surface and bulk defects (inhomogeneities) related. The details will be discussed for the optimised films in the next chapter. Figure 6.13 shows a direct comparison of
the in-plane linewidth at three frequencies for all three compositions at room temperature and at 10 K. The temperature variation of the in-plane linewidth for three compositions from 10 K to 300 K at 9 GHz.

In summary, the epitaxial growth of nickel ferrite films on MgAl$_2$O$_4$ (100) substrates by the DLI-CVD technique was studied at different growth temperatures and Fe/Ni compositions. Improving thin film quality by optimizing thin film processing conditions and understanding the relationship between the FMR linewidth and thin film defects (inhomogeneities) are the two important aspects to attain high quality NFO films with low microwave loss. A lowest FMR linewidth of 80 Oe has been achieved at 10 GHz, which confirms the good crystalline quality of DLI-CVD nickel ferrite films. The angle and frequency dependent study of the FMR linewidth suggests the presence of two-magnon scattering as a magnetization damping mechanism which is primarily related to crystalline defects and inhomogeneities, including dislocations, anti-phase boundaries, and different cation ordering.
CHAPTER 7

STUDY OF MAGNETIC RELAXATION IN NON-STIOCHIOMETRIC NICKEL FERRITE FILMS

Detailed FMR studies on single crystalline nickel ferrite thin films are quite limited in the literature, which is an essential aspect to understand the relaxation in magnetization precession (microwave damping) in this material for fundamental and practical applications, such as in planar microwave devices and magnetic memory elements with high speed switching of magnetization. As discussed in the previous chapter, the properties of nickel ferrite are closely related to specific growth method and process conditions. They can be tailored by factors like surface morphology, microstructure and chemical composition etc., for potential applications in next generation tunable microwave devices (e.g. electric field tunable filters and phase shifters) and monolithic microwave integrated circuits (MMIC). [17-19]

In this chapter, the high quality epitaxial non-stoichiometric nickel ferrite films (NFO) on MgAl$_2$O$_4$ substrate exhibiting a symmetric, single-peak and narrow FMR spectra grown by direct liquid injection chemical vapor deposition (DLI-CVD) is reported. A comprehensive FMR measurements and study was performed to identify and quantify the relaxation mechanism in the as-grown non-stoichiometric NFO films. The films are deposited at an optimized growth temperature of 600°C and are characterized for crystal structure, surface morphology, chemical
composition, and static magnetic properties. The crystalline structure of the as-deposited films has been analyzed using an X-ray diffractometer.

7.1) Structural characterization

Large-angle θ-2θ scans show only diffraction peaks corresponding to Ni$_{0.8}$Fe$_{2.2}$O$_4$ films and the substrates. No evidence of any secondary phase is found from X-ray measurements. Figure 7.1 shows θ -2θ plot around the (004) peak for Ni$_{0.8}$Fe$_{2.2}$O$_4$ films of varying thicknesses, exhibiting a pure spinel phase with the (h00) planes parallel to the film surface and having out-of-plane lattice parameters close to that of the bulk which indicates complete strain relaxation.

![X-ray diffraction pattern of NFO film grown on (100) oriented MgAl$_2$O$_4$ substrate at 600°C, showing that the films exhibit pure spinel phase.](image)

The film reflection intensity and rocking curve (ω-scan) analysis of Ni$_{0.8}$Fe$_{2.2}$O$_4$ (400) diffraction is used to characterize the degree of film texture (figure 7.2(a)). The measured full width at half
maximum (FWHM) is 0.26° (FWHM value of the MgAl₂O₄ substrate is ~ 0.028°). The in-plane texture of the films was examined by from phi-scans of the Ni₀.₈Fe₂.₂O₄ (220) planes. Figure 7.2 (b) shows the phi-scan results of both the Ni₀.₈Fe₂.₂O₄ film and MgAl₂O₄ substrate. The four 90°-spaced diffraction peaks clearly illustrate the four-fold symmetry of the spinel structure. The coincidence of these four peaks with the (220) peaks from the MgAl₂O₄ substrate confirms cube-on-cube epitaxial growth.

Figure 7.2: (a) Rocking curve of NFO (400) reflection with narrow FWHM=0.26°, indicating high structural quality of the film and (b) Phi scan of NFO (220) reflection confirming the epitaxial growth.
The film surface roughness has been characterized by cross-sectional SEM and atomic force microscopy (AFM). Figure 7.3(a), shows a cross-sectional SEM view of a 0.84 µm thin $\text{Ni}_{0.8}\text{Fe}_{2.2}\text{O}_4$ film grown on $\text{MgAl}_2\text{O}_4$ exhibiting an atomically smooth surface. The inset is EDX analysis indicating non-stoichiometric chemically pure $\text{Ni}_{0.8}\text{Fe}_{2.2}\text{O}_4$ films without any detectable contamination. Figure 7.3(b) is a 5 µm x 5 µm AFM image of the surface of the same sample, with a rms roughness of ~ 0.3 nm. In the experiments, smooth (rms < 0.5 nm) and dense (without voids or detectable grain structure) films are formed.

Figure 7.3: (a) Cross-section SEM view of the same film giving a thickness of 840 nm for the NFO film. The inset shows the EDX spectra confirming the non-stoichiometric NFO film with Fe:Ni ratio of 2.67 ; (b) A 5 µm x 5 µm AFM image of the surface of the same sample, with a rms roughness of ~ 0.3 nm.
The epitaxial film growth has been further confirmed using polarized Raman spectroscopy measurements. The comparison of the polarized Raman spectra of Ni$_{0.8}$Fe$_{2.2}$O$_4$ films with those of a bulk NiFe$_2$O$_4$ single crystal and stoichiometric film provides evidence that the films are epitaxial and of single-crystal quality. [46] Indeed, except for negligible differences in the peak positions and relative intensities, the corresponding spectra of the films and the crystal are practically identical. In figure 7.4, the first and second letters in the notations XX, XY, X’X’, and X’Y’ indicate the polarization of the incident and scattered light respectively, along the pseudo-cubic X||[100], Y||[010], X’||[110], or Y’||[-110] directions.

Figure 7.4: Polarized Raman spectra for the non-stoichiometric NFO film.
7.2) Temperature dependent VSM and FMR study

The magnetic properties of the as-deposited film on the MgAl₂O₄ substrate were investigated using a VSM. Figure 7.5(a,b) illustrates the in-plane and out-of-plane hysteresis loops of the non-stoichiometric NFO sample at 10 K and 300 K respectively. The room temperature saturation magnetization of the film is 329 emu/cm³.

Figure 7.5: M-H curves at 10 K and 300 K for the in-plane and out-of-plane orientations of the NFO film grown on MAO.

The magnetic relaxation mechanism in the as-deposited non-stoichiometric nickel ferrite films was investigated by the ferromagnetic resonance (FMR) technique. The measurements were done using a fully automated broadband variable temperature ferromagnetic resonance set-up in the frequency range of 2–50 GHz. The FMR signal could be measured while the static field is applied along any desired direction in the film plane or out of the film plane. The dependence of
the resonance frequency on resonance field for different crystal orientations is shown in figure 7.6 (a). The corresponding FMR linewidth variation with frequency, representing the degree of microwave loss, for the ferrite films deposited is represented in figure 7.6(b). A low in-plane FMR linewidth of 450 Oe was observed at 9.5 GHz in the optimized CVD deposited 840 nm non-stoichiometric NFO film, which is significantly less than the so far lowest reported value of 752 Oe for nearly stoichiometric NFO films. [58]

Figure 7.6: Frequency dependence of FMR resonance field and linewidth of the NFO film grown on MAO.

Detailed FMR characterization of Ni$_{0.8}$Fe$_{2.2}$O$_4$ thin film indicates that changes in the effective magnetic damping as a function of temperature, frequency and external magnetic field direction are caused by variations in the two-magnon scattering relaxation rate. The decrease in the linewidth values from parallel configuration (external field in the plane of the film) to the perpendicular configuration (external field normal to the plane of the film) can be seen in figure
7.6(b) for the non-stoichiometric NFO thin film, which is consistent with the two-magnon relaxation hypothesis.

Two-magnon scattering is an extensively used mechanism to explain the extrinsic damping. According to the two-magnon scattering theory [120,123,124], any inhomogeneity in magnetic properties could couple the homogeneous magnon or FMR mode magnon (with $k=0$) to another magnon with $k \neq 0$. This way, the FMR mode is relaxed to the magnon with $k \neq 0$ in the scattering process caused by the magnetic inhomogeneity. The initial and final magnons should be degenerate in energy while the linear momentum is not conserved. However, in the out-of-plane geometry, when the static external is normal to the plane of the film due to the changes in dispersion relation band, the degeneracy is removed. Therefore, the two-magnon scattering relaxation mechanism is absent, which leads to narrower linewidth in the out of plane geometry. [120,124]

![Diagram](image)

Figure 7.7: Paths for degradation of uniform motion: (1) Direct relaxation to the lattice; (2) Decay into non-uniform motions (spin waves); (3) which in turn decay to the lattice. [125]
However, it is important to notice that in both configurations a significant contribution to the linewidth originates from the large scale inhomogeneities causing the inhomogeneous linewidth broadening [126,127] that appear as an offset at zero frequency. The origin of magnetic inhomogeneity that scatters the FMR mode to the $k \neq 0$ magnon could originate from the variations in surface magnetic anisotropy [128] or exchange bias field [129], due to the surface roughness at the ultra thin film interfaces. However in the thin ferrite films, the two-magnon scattering potential most likely arises from the variations in the dipole-dipole interaction caused by bulk defects. [113,120,126-129]

Figure 7.8: (a) FMR signal at different temperatures for a fixed frequency of 9 GHz. (b) FMR frequency dependence of resonance field at different temperatures. The inset shows the change in the position of $H_{\text{res}}$ with temperature at 9 GHz.

The frequency dependent measurements were done in both in-plane and out-of-plane orientations in a temperature range of 10 K-300 K. Figure 7.8(a) shows the clean, undistorted FMR spectra obtained at 9 GHz at different temperatures. Figure 7.8(b) is the FMR frequency dependence of
resonance field at varying temperatures. The inset indicates the increase in the $H_{res}$ value with increase in the temperature at 9 GHz, due to the decrease in the internal field. The temperature dependence $M_{eff}$ ($M_{eff} = 4\pi N_c M_s - H_u$) data obtained from the FMR measurements is shown in figure 7.9. The $M_{eff}$ significantly increases at lower temperatures accompanied by a decrease in the $g$-value with a slower rate.

![Figure 7.9: Temperature dependence of $M_{eff}$ (blue) and $M_s$ (red) obtained from FMR and VSM.](image)

Comparing the room temperature $M_{eff}$ with the $M_s$ value measured by VSM, it can be concluded that there is no significant perpendicular magnetic anisotropy field ($H_u$), thereby indicating a small growth related anisotropy. This implies that the temperature dependence of $M_{eff}$ comes solely from the increase in $M_s$ at lower temperatures.
Figure 7.10: Increase of in-plane linewidth as temperature decreases caused by larger contribution from two-magnon scattering due to the increase of $M_s$ at lower temperatures.

It has been recently shown [58] that the misfit dislocations, which act as scattering defects, lead to two-magnon relaxation in nearly stoichiometric NFO thick films. Therefore, an increase in two-magnon contribution to the FMR linewidth at lower temperatures is expected. This can be seen in figure 7.10, which shows the variable temperature FMR linewidth data in a broadband frequency domain in the parallel configuration indicating an increase in the linewidth as the temperature is decreased for a specific frequency.
Figure 7.11: The out-of-plane FMR linewidth values are in the same order at different temperatures, consistent with the absence of two-magnon mechanism in the out-of-plane geometry.

However, as shown in figure 7.10, the splitting between linewidth values at different temperatures and the increase of linewidth at low frequencies is not observed in the perpendicular configuration (figure 7.11), consistent with the two-magnon scattering origin.
Figure 7.12: (Top) In plane four-fold magnetic anisotropy shown by the in plane angle dependency of $H_{\text{res}}$ at 40 GHz; (Bottom) Four-fold symmetry in FMR linewidth at 40 GHz, in-plane angle of zero is equivalent to the [100] crystallographic direction.
In-plane angle dependent FMR measurements reveal a fourfold magnetic anisotropy, figure 7.12 (top), for a fixed frequency of 40 GHz. More interestingly, the linewidth also exhibits a similar four-fold behavior, as shown in figure 7.12 (bottom). This can be related to the anisotropy in two-magnon scattering potential, which using a similar reasoning as proposed by Heinrich and Woltersdorf [130], originates from the symmetry in the distribution of misfit dislocations. In this model, the magnitude of the two-magnon relaxation obeys the fourfold symmetry of the misfit dislocations and the misfit dislocations themselves form along low index crystallographic planes. Misfit dislocations were observed in a previous study on nearly stoichiometric NFO films too. [58] However currently, no data regarding the in-plane orientation of the misfit dislocations is available for this material.

So far, no theoretical model predicting the complicated frequency dependence of the in-plane linewidth shown in figure 7.10 is known. However, the linewidth increase observed at low frequencies could be related to the inhomogeneous broadening caused by domain growth, which is consistent with $H_s$ values measured by VSM as shown in figure 7.13. The VSM measurements imply that $H_s$ increase at lower temperatures, which can explain the onset of the inhomogeneous broadening at higher frequencies as temperature decreases. Also, one well-known temperature dependent relaxation mechanism that could generate peaks in the linewidth is the slow relaxer, which previously had been used to explain magnetic relaxation for single crystal ferrites. [102] However, no such peak is seen in other geometries like the perpendicular configuration as shown in figure 7.11, therefore, the slow relaxer in these non-stoichiometric NFO films does not contribute significantly to the linewidth. Similar results have been obtained for the stoichiometric NFO films. [58]
Figure 7.13: Temperature dependence of saturation magnetization $H_s$ derived from VSM.

In order to understand the reason behind the lower in-plane linewidth in the Ni$_{0.8}$Fe$_{2.2}$O$_4$ thin film compared to the stoichiometric film, the variable temperature conductivity measurements of the both films, 840 nm thick and deposited under identical CVD deposition parameters, were done. The results show a higher conductivity for the stoichiometric film as compared to non-stoichiometric film in the full temperature range. Although the absolute value of conductivity is still very low one would claim that the eddy current relaxation mechanism is responsible for higher loss in the stoichiometric film. However, eddy current loss is supposed to scale with the square of the film thickness. [131,132] Therefore, in order to validate the role of eddy current relaxation, 1250 nm and 375 nm non-stoichiometric films are made using the same deposition parameters used for depositing the 840 nm non-stoichiometric film. However, no evidence for
strong thickness dependence of magnetic relaxation is observed (figure 7.14) which shows the frequency dependent linewidth profile for the three samples.

Figure 7.14: Frequency dependence of the resonance field and linewidth for three different thicknesses of the NFO films grown on MAO.

As a result the possibility of eddy current loss as the mechanism responsible for generating the difference in the FMR linewidth between non-stoichiometric and stoichiometric films is ruled out, and thus the change in linewidth is more likely due to the difference in the distribution of microstructural defects between the two films. In other words, the variation of conductivity is too small to cause any significant magnetic relaxation through eddy current loss channel.

On the other hand, due to the large contributions from the extrinsic parameters like two-magnon relaxation and inhomogeneous linewidth broadening to the FMR linewidth, discussion of the effect of intrinsic damping on the stoichiometry is not relevant in this regime. Similar
temperature and angle dependent FMR study was also performed for the two other compositions of nickel ferrite as discussed briefly in the last section of chapter 6.

Figure 7.15: Qualitative analysis of temperature variation of anisotropy for 800 nm thick NFO film on MAO substrate with Fe:Ni ratio of ~3.67. (a) Calculated difference $\Delta H_{\text{res}}$ between the resonance fields of the two in-plane directions [100] and [110] (easy axis) at different frequency. Inset shows the frequency dependence of the resonance field in the two in-plane directions at 10 K. (b) Temperature dependence of average value of $\Delta H_{\text{res}}$.

For the non-stoichiometric films with higher Fe:Ni ratio of ~ 3.7 and also for the nearly stoichiometric films, the linewidth variation with temperature confirms the existence of two-magnon scattering as the prominent relaxation mechanism, similar to what has been discussed and explained in this chapter. Moreover, for qualitative analysis of the anisotropy dependence on
temperature, two different in-plane angle directions were measured. A comparison of the
temperature variation of the resonance field at 10 K is shown in inset of figure 7.15(a). For each
frequency, the difference $\Delta H_{\text{res}}$ between the resonance fields of the two in-plane directions [100]
and [110] (easy axis) is calculated which basically should give an estimate of the anisotropy
field. This analysis is further extended to all temperatures, as shown in figure 7.15(b) and the
average value of $\Delta H_{\text{res}}$ for a particular temperature is calculated. As evident from the figure
7.15(b), the anisotropy shows no significant variation and is almost independent of the
temperature. Hence, this qualitative analysis rules out the possibility of any drastic contribution
originating from anisotropy change to increase in the linewidth at lower temperatures.

In summary, the optimization of the DLI-CVD deposition parameters and modifying the
stoichiometry can lead to the fabrication of low loss nickel ferrite thin films. A very low FMR
linewidth of 450 Oe has been observed at a nominal frequency of 9.5 GHz in the in-plane
geometry, which is significantly less than the lowest reported value of 752 Oe for nearly
stoichiometric NFO films. Studying the broadband FMR linewidth as a function of out-of-plane
angle, in-plane angle and temperature reveals the existence of two-magnon scattering as the
prominent relaxation mechanism. The results show a novel behavior of FMR linewidth regarding
the anisotropic in-plane symmetry and frequency dependence. The frequency and temperature
dependent behavior of two-magnon relaxer as well as its in-plane asymmetry likely implies a
certain symmetry and periodicity in the distribution of micro-structural defects.
8.1) Lithium ferrite

8.1.1) DLI-CVD of epitaxial lithium ferrite films with low microwave loss

DLI-CVD growth of lithium ferrite was investigated by using Li(acac) and Fe(acac)₃ as the metal organic precursors dissolved in DMF and vaporized under optimum conditions for flow of the injected precursors and oxygen. MgAl₂O₄ (100) and MgO (100) substrates with cubic normal spinel \((a = 0.808 \text{ nm})\) and fcc \((2a = 0.842 \text{ nm})\) structure, respectively, were used for systematic study of film growth due to their close lattice match with nickel ferrite (lattice mismatch of 3% and 1%, respectively). The films were first prepared for a wide range of deposition parameters, 400°C-650°C, to address the mismatch problem between the film and the MgO substrate. It was observed that under optimized vaporization conditions, the growth temperature plays a crucial role in attaining the desired film morphology and stoichiometry, because of changes in the surface diffusion behavior. A detailed investigation of structural and magnetic properties of films deposited on MgO (100), reveals a growth temperature of 500°C to be the optimised growth temperature. The films grown at this temperature on MgO (100) substrates have low surface roughness and exhibit excellent single crystal quality, verified from X-ray diffraction and magnetic properties. X-ray diffraction pattern indicated an epitaxial growth of the films with pure spinel phase with local normal axis deviations below 0.04° and the AFM data show smooth
surfaces. The film growth rate was observed to be in the range of 0.45-0.50 µm/hr and can be further increased by increasing the liquid flow rate and the precursors concentration. The saturation magnetization value of the films obtained from VSM, were in the same range as the comparable values for bulk Li-ferrite materials. The FMR measurements were performed at varying frequencies (5-40 GHz) with the static field perpendicular and parallel to the film plane. Symmetric and non-distorted FMR curves for all orientations have been observed. The linewidths range from 41 Oe to 119 Oe for the 300 nm thick films grown on MAO and MgO substrates at a substrate temperature of 500°C. These are the lowest values reported so far for pure lithium ferrite but are still above the <10 Oe linewidths observed for single crystals.

Different LFO compositions can be systematically studied with controlled stoichiometric growth and further can be correlated with FMR linewidth profiles. This can be done by appropriately increasing the precursor concentrations in the solvent and optimizing the growth conditions accordingly. Also, more magnetic characterization and analysis is required to explain the dominant stress induced anisotropy field for different thicknesses of LFO films grown on MgO substrates. An improved theoretical understanding of the system and additional temperature dependent FMR measurements are required to explain the FMR linewidth profile in different crystallographic orientations. The correlation of the strain and cationic distribution in the films with the characteristic peak shift observed in the loop linewidth profile is another important aspect to focus on. Mossbauer spectroscopy can give useful information in this regard. In-plane angle measurements can give an insight into the anisotropy fields and the symmetry of the structure. Effect of annealing on films can be tried to achieve complete ordered/disordered states and further characterize the films to explore the ordering affect on the structural, magnetic and microwave behavior of the films. Deposition on piezoelectric substrates like PMN-PT and
PZN-PT is still challenging due to the greater lattice mismatch and requires more optimization in the CVD processing conditions. This can be helpful in attaining low FMR linewidths, which is important for the fundamental research in ferrite-ferroelectric layered heterostructures.

8.1.2) Bulk lithium ferrite single crystal

The FMR linewidth dependence on frequency for the single crystal lithium ferrite crystals was measured in the 9-40 GHz range at room temperature. The measured FMR profiles consisted of a single large mode, which was clean with little distortion. The FMR resonance position has a linear dependence on applied field and fitted well with the dependence predicted from uniform mode theory. The FMR linewidth versus frequency measurements indicated that the linewidth scales linearly with frequency in the 9-40 GHz range. This is in accordance with the Landau Lifshitz damping model. It is very clear that there is no significant variation in the linewidth with the cationic ordering of the LFO crystal. However, temperature dependence of the FMR linewidth can be helpful to clearly identify the differences between ordered and disordered crystals as they have been reported to be more visible at low temperatures in previous studies.

8.2) Nickel ferrite

Study of Nickel ferrite films was mainly focused on two important aspects:
1.) Improving thin film quality by optimizing thin film processing conditions: We observed that the optimization of the DLI-CVD deposition parameters and modifying the stoichiometry can lead to the fabrication of high quality epitaxial and smooth NFO films with minimum magnetic loss coupled with excellent magnetic properties at higher growth rates. The elimination of imperfections and impurities by optimizing the growth conditions is the key to achieve films
with purely intrinsic losses and low linewidth. A very low FMR linewidth of 450 Oe has been observed at a nominal frequency of 9.5 GHz in the in-plane geometry for the off-stoichiometric films, which is significantly less than the lowest reported value of 752 Oe for nearly stoichiometric NFO films. For stoichiometric films, the lowest FMR linewidths reported so far, ranging from 80-140 Oe in the perpendicular orientation have been achieved, which confirms the good crystalline quality of DLI-CVD nickel ferrite films. The damping parameter is of the order of magnitude 0.007 for the as-deposited films, which is close to the reported values for the bulk spinels containing no ferrous ions. Hence the target to fabricate the single crystalline NFO films with linewidth close to the bulk value (40-80) Oe is successfully achieved.

2.) Understanding the relationship between the FMR linewidth and thin film defects: There are limited reports on the detailed FMR analysis of the NFO single crystalline films, mostly restricted to few frequencies just reporting the linewidth value and not the overall linewidth profile of the grown films. Systematic FMR measurements have been performed on the nickel ferrite films for the first time to understand the relaxation mechanisms contributing to the linewidth profile at varying frequencies and temperatures. This included a detailed study of broadband FMR linewidth as a function of out-of-plane angle, in-plane angle and temperature for optimised Ni$_{0.8}$Fe$_{2.2}$O$_4$ films, revealing the presence of two-magnon scattering as a magnetization damping mechanism, which is primarily related to crystalline defects and inhomogeneities, including dislocations, anti phase boundaries, and different cation ordering. The results also show a novel behavior of FMR linewidth regarding the anisotropic in-plane symmetry and frequency dependence. The frequency and temperature dependent behavior of two-magnon
relaxer as well as its in-plane asymmetry likely implies a certain symmetry and periodicity in the distribution of micro-structural defects.

However, further investigations are required to interpret the composition dependent in-plane linewidth behavior in the nickel ferrite films. For films with low resistivity or high thickness, eddy current loss mechanism can play an important role. Therefore, a theoretical study of effective damping incorporating the intrinsic and eddy current loss is required. It would be interesting to see if there is any relation of the angle dependence of eddy current contribution to the relaxation mechanism in FMR. Mossbauer spectroscopy can be helpful to study the Fe$^{2+}$/Fe$^{3+}$ ratio on the octahedral sites, which will give more insight into the stoichiometry deviation effect on the in-plane FMR linewidth. Moreover, it would be also important to understand the magnetic anisotropy constants change for the different Ni/Fe compositions to correlate it with the linewidth profiles of the films.
REFERENCES


