2006

Ferrite-ferroelectric thin films with tunable electrical and magnetic properties

Ranko Heindl
University of South Florida

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Ferrite-Ferroelectric Thin Films With Tunable Electrical And Magnetic Properties

by

Ranko Heindl

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics
Department of Physics
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Keywords: BaFe$_{12}$O$_{19}$, Ba$_{0.5}$Sr$_{0.5}$TiO$_3$, PLD, sputtering, bilayers, multilayers, composites, coplanar waveguides, microwave characterization

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DEDICATION

To my parents Dunja & Vlatko,
my wife Karol,
and my wonderful grandma Enisa (1919 - 2005).
ACKNOWLEDGMENTS

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<thead>
<tr>
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<th>Description</th>
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<tbody>
<tr>
<td>ADS</td>
<td>Advanced Design System</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>AC</td>
<td>Alternating Current</td>
</tr>
<tr>
<td>Alumina</td>
<td>Polycrystalline Alumina (α-Al₂O₃)</td>
</tr>
<tr>
<td>A-Sapphire</td>
<td>Sapphire substrate with “A-plane orientation”</td>
</tr>
<tr>
<td>ATM</td>
<td>Atmosphere</td>
</tr>
<tr>
<td>Au</td>
<td>Gold</td>
</tr>
<tr>
<td>Ba</td>
<td>Barium</td>
</tr>
<tr>
<td>BaM</td>
<td>Barium-Iron-Oxide, Barium-(Hexa)-Ferrite, BaFe₁₂O₁₉</td>
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<tr>
<td>BST</td>
<td>Barium-Strontium-Titanate (Ba₀.₅Sr₀.₅TiO₃)</td>
</tr>
<tr>
<td>C, C₀</td>
<td>Capacitance</td>
</tr>
<tr>
<td>Co</td>
<td>Cobalt</td>
</tr>
<tr>
<td>CPW</td>
<td>Coplanar Waveguide</td>
</tr>
<tr>
<td>Cr</td>
<td>Chrome</td>
</tr>
<tr>
<td>C-Sapphire</td>
<td>Sapphire substrate with “C-plane orientation”</td>
</tr>
<tr>
<td>dB</td>
<td>Decibel</td>
</tr>
<tr>
<td>DC</td>
<td>Direct Current</td>
</tr>
<tr>
<td>DUT</td>
<td>Device Under Test</td>
</tr>
<tr>
<td>ε₀</td>
<td>Permittivity of Vacuum</td>
</tr>
<tr>
<td>εᵣ</td>
<td>Relative Dielectric Constant, Relative Permittivity</td>
</tr>
<tr>
<td>emu</td>
<td>Magnetic Moment Unit (Electromagnetic Unit)</td>
</tr>
<tr>
<td>eV</td>
<td>Electron-Volt</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>--------------</td>
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<tr>
<td>FMR</td>
<td>Ferrimagnetic (ferromagnetic) Resonance</td>
</tr>
<tr>
<td>FOM</td>
<td>Figure of Merit</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full-Width-Half-Maximum</td>
</tr>
<tr>
<td>G</td>
<td>Coplanar Waveguide Gap Between Signal and Ground Lines</td>
</tr>
<tr>
<td>G</td>
<td>Ground Connector</td>
</tr>
<tr>
<td>GSG</td>
<td>Ground-Signal-Ground</td>
</tr>
<tr>
<td>H</td>
<td>Magnetic Field</td>
</tr>
<tr>
<td>Ha</td>
<td>Anisotropy Field</td>
</tr>
<tr>
<td>Hc</td>
<td>Coercive Field (Coercivity)</td>
</tr>
<tr>
<td>IDC</td>
<td>Intedigitated (Interdigital) Capacitor</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>µ0</td>
<td>Permeability of Vacuum</td>
</tr>
<tr>
<td>µr</td>
<td>Relative Permeability</td>
</tr>
<tr>
<td>M, M-DC</td>
<td>DC-Magnetization</td>
</tr>
<tr>
<td>Mr</td>
<td>Remanent Magnetization</td>
</tr>
<tr>
<td>Ms</td>
<td>Saturation Magnetization</td>
</tr>
<tr>
<td>MgO</td>
<td>Magnesium-Oxide</td>
</tr>
<tr>
<td>M-H</td>
<td>Magnetization vs. Applied Magnetic Field</td>
</tr>
<tr>
<td>PLD</td>
<td>Pulsed Laser Deposition</td>
</tr>
<tr>
<td>PPMS</td>
<td>Physical Properties Measurement System</td>
</tr>
<tr>
<td>PPS</td>
<td>Pulses Per Second</td>
</tr>
<tr>
<td>RF</td>
<td>Radio-Frequency</td>
</tr>
<tr>
<td>RT</td>
<td>Room Temperature</td>
</tr>
<tr>
<td>SCCM</td>
<td>Standard Cubic Centimeters Per Minute</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>Si</td>
<td>Silicon Substrate</td>
</tr>
<tr>
<td>SOLT</td>
<td>Short-Open-Load-Thru</td>
</tr>
<tr>
<td>S-parameters</td>
<td>Scattering Parameters</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>Sr</td>
<td>Strontium</td>
</tr>
<tr>
<td>T</td>
<td>Tesla</td>
</tr>
<tr>
<td>tanδ</td>
<td>Loss Tangent</td>
</tr>
<tr>
<td>TEM</td>
<td>Transverse Electromagnetic</td>
</tr>
<tr>
<td>Ti</td>
<td>Titanium</td>
</tr>
<tr>
<td>TRL</td>
<td>Thru-Reflect-Line</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>VNA</td>
<td>Vector Network Analyzer</td>
</tr>
<tr>
<td>W</td>
<td>Coplanar Waveguide Central-Conductor-Width</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
<tr>
<td>$Z_0$</td>
<td>Characteristic Impedance</td>
</tr>
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</table>
Ferrite-Ferroelectric Thin Films With Tunable Electrical And Magnetic Properties

Ranko Heindl

ABSTRACT

A growing need for developing new multi-functional materials operating at microwave frequencies is demanding a better understanding of ferroelectric and ferrimagnetic materials and their combinations. Some of these materials exhibit tunable physical properties, giving an extra degree of freedom in the device design. New multifunctional ferroelectric and ferrimagnetic thin film structures are investigated in this dissertation research, in which dielectric and magnetic properties can separately be tuned over a certain frequency range. The materials of choice, \( \text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3 \) (BST) and \( \text{BaFe}_{12}\text{O}_{19} \) (BaM), both well studied and used in many microwave applications, were prepared using rf magnetron sputtering and pulsed laser ablation. Thin-film bilayers, multilayers and composite thin films were grown on various substrates, and their underlying microstructure and crystallographic properties were analyzed and optimized. After identifying the most successful growth conditions, dielectric and magnetic properties were measured. Unusual features in magnetic hysteresis loops in both sputtered and laser ablated films grown under different conditions were observed. Microcircuits were fabricated using optical lithography and microwave properties and tunability were tested in the range 1-65 GHz.
CHAPTER 1
INTRODUCTION

Over the past ten years, there has been a sustained effort to integrate existing ferri-
magnetic and ferroelectric materials in monolithic microwave integrated circuit (MMIC)
technology, in which ferrite and ferroelectric elements together with other active elements
are placed on a common semiconductor substrate [10, 115]. The benefits of such integration
can include some or all of the following: smaller device size, lower manufacturing costs,
better reliability, better performance, and lower parasitics. However, there are numerous
challenges such as thin film growth and processing, matching the film to the substrate,
controlling film stoichiometry, microstructure, stresses and defects. This work presents an
extensive research effort in development of ferrimagnetic-ferroelectric thin film structures
that exhibit tunable properties at microwave frequencies.

Ferrite materials in the form of high quality thin films have the potential to replace
bulky external magnets in current microwave devices [10]. They can provide unique circuit
functions that cannot be reproduced with any other materials. Ferrite materials have low
losses at microwave frequencies, high resistivity and strong magnetic coupling, making
them irreplaceable constituents in microwave device technology.

On the other hand, ferroelectrics have been known for over 30 years [43], yet only
since the improvements in microtechnology and thin-film deposition techniques in the early
1990’s have they created renewed interest in the scientific community [115]. In certain fer-
roelectric materials such as BaTiO$_3$, Ba$_x$Sr$_{1-x}$TiO$_3$, SrTiO$_3$ and Pb(Zr,Ti)O$_3$, complex
permittivity can be varied using an applied electric field [76, 99, 114, 115, 117, 128]. Ferro-
electric materials are important for the new generation of tunable phase shifters, varactors,
circulators, and antennas. The advantage of using ferroelectric thin films is high Q at mi-
crowave and millimeter wave frequencies, low dc power consumption, high rf power handling capabilities, and low manufacturing costs [76, 99, 114, 117, 128]. The problem with integrating tunable ferroelectrics into microwave devices is that the properties of fabricated thin films are much poorer than theoretically predicted [115]. The reason lies in the strong dependence of ferroelectric properties on the film quality (microstructure, composition, and orientation). Most of the studies to date have been done to address these issues and improve the tunability.

Figure 1.1. A diagram of non-licensed bands and their typical applications [71].

In 2001, the Federal Communications Commission (FCC) [4] allocated a continuous block between 57-64 GHz for non-licensed and commercial wireless applications (figure 1.1). The millimeter-wave part of the electromagnetic spectrum has been mostly unexploited for commercial wireless applications. At the frequencies around 60 GHz, the O$_2$ molecule highly absorbs the electromagnetic radiation, which enables more signals to be used in the same geographic area without interference, as well as increased security due to the rapid attenuation of the signal. Microwave devices need to be designed, utilizing materials that
operate at these frequencies. Both ferrites and ferroelectrics show excellent properties in this millimeter-wave portion of the electromagnetic spectrum. This is just one example of the possible commercial impact of these materials.

The goal of this thesis is to grow ferrite-ferroelectric multilayer and composite thin films incorporating ferrimagnetic material barium-ferrite ($\text{BaFe}_{12}\text{O}_{19}$, $\text{BaM}$) and ferroelectric material barium-strontium-titanate ($\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$, $\text{BST}$) on various substrates and study their growth conditions, underlying microstructure, electric, magnetic and high frequency properties, as well as electrical and magnetic tunability.

Characteristic impedance and phase velocity of a material are defined as: $Z_c \propto \sqrt{\mu/\epsilon}$ and $v_p \propto 1/\sqrt{\mu \cdot \epsilon}$, where, $\mu$ is its magnetic permeability, and $\epsilon$ is its electric permittivity [100]. In a nonlinear medium, applying an electric field will change its $\epsilon$. In a similar way, a ferrimagnetic material will change its $\mu$ in an applied magnetic field, although the potential for magnetic tuning $\delta \mu/\mu$ is smaller than the electric tuning $\delta \epsilon/\epsilon$ [10, 115]. Thus, in a microwave device containing both ferroelectric and ferrimagnetic materials, frequency and phase characteristics can be tuned in two ways: electrically and magnetically. For certain applications the characteristic impedance $Z_c$ and the phase velocity $v_p$ should remain independent of the tuning, while for other applications impedance tuning is desirable [61, 67, 115]. Both cases can be achieved with dual tuning. The main goal is to see if by using ferroelectric-ferrimagnetic thin films it is possible to create a dual tunable microwave material in which its impedance and phase velocity can be tuned electrically and magnetically. This research could provide further knowledge about growth and characteristics of ferroelectric and ferrimagnetic materials in thin film form, and is important for the development of future microwave devices. The $\text{BaM}/\text{BST}$ system has not been studied before, and moreover there is a lack of systematic research in this area, in terms of correlating the structure, magnetic, dielectric and frequency-dependent properties.
1.1 Literature Review

The field of magneto-dielectric materials has seen increase in publications in the recent years, and some of the results are promising for future technologies. Below is a short summary of the current research on tunable ferroelectric-ferromagnetic materials that would place this work in perspective of current state-of-the-art work in tunable microwave thin films:

- The most closely related paper to this research is "Electrically and magnetically tunable microwave device using (Ba,Sr)TiO$_3$/Y$_3$Fe$_{15}$O$_{12}$ multilayer" [67]. A BST thin film was deposited on a YIG substrate, followed by a Au/Ag coplanar waveguide on the top. A differential phase shift was measured as a function of frequency, electric and magnetic fields. It was reported that a 17°/cm differential phase shift was obtained at 10 GHz with 21 kV/cm of electric field and 160 Gauss of magnetic field, which is smaller than results reported in chapter 7. No further research has been done on this system.

- The paper "Magnetically and electrically tunable devices using ferromagnetic - ferroelectric ceramics" [65] reports on magnetic and electric hysteresis loops as well as electrical tunability of various bulk composite samples with different ratios of garnet ferrite and ferroelectric Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ (PZT). A higher electrical tunability for the composite material was obtained compared to the pure ferroelectric material.

- A study of a heterostructured device utilizing ferroelectric BST and ferromagnetic LSMO ((La,Sr)MnO$_3$) thin films was presented in the paper "High frequency tunable LC devices with ferroelectric-ferromagnetic thin film heterostructure" [132]. C-V (capitance-voltage) and L-V (inductance-voltage) tunability was measured at 1 MHz, and higher tunability was reported by tuning both L and C, compared to tuning only L or C, while monitoring the change of the characteristic impedance.
• In the paper "Integration of nonlinear dielectric barium strontium titanate with polycrystalline yttrium iron garnet" [61], biaxially oriented BST films were grown on polycrystalline YIG substrates with an MgO buffer layer to improve the BST crystallinity. Gold coplanar waveguides were deposited on top of the multilayered structure and capacitance and dielectric loss were measured at 100 kHz. Both (100) and (110) oriented BST films were reported, with tunability greater then 25% with an applied dc voltage of 40V, and decrease in dielectric loss with an increase of the dc bias voltage. However no data on magnetic tunability was reported.

• The paper "Preparation of all-oxide ferromagnetic-ferroelectric-superconducting heterostructures for advanced microwave applications" [53] presents an electrically and magnetically tunable $La_{0.70}Sr_{0.30}MnO_3$-Pb$(Zr_{0.52}Ti_{0.48})_3$O$_3$-YBCO multilayer. Ferroelectric and ferromagnetic properties were measured, but no data on high frequency properties or tunability was given.

• Stacked dielectric-ferromagnetic structures were described in the paper "Correlation between magnetic properties of layered ferromagnetic-dielectric material and tunable microwave device applications" [101], in which thick dielectric layers of Kapton were used to compensate for losses in metallic ferromagnetic CoNbZr thin films. Using applied dc magnetic field, the impedance of the layered structure was tuned. At the end, the structure was utilized into a tunable band stop filter and a magnetic switch.

• The paper "Addition Effect of Barium and Strontium Titanate on the Reflectivity of Ferri and Ferromagnetic Composites" [98] describes mixing of fine powders of $Co^{2+}$- and $Ti_{4+}$-doped barium hexaferrite (Co-TiBaM) and barium strontium titanate (BST). Transmission and reflection properties at microwave frequencies were investigated. Addition of the BST resulted in an increase in microwave absorption.

• Some theoretical and experimental work on electrically tunable ferrite-ferroelectric phase shifter was reported in the paper "Electrical Tuning of Dispersion Characteristics of Surface Electromagnetic-Spin Waves Propagating in Ferrite-Ferroelectric Lay-
“Erased Structures” [29]. Ferromagnetic yttrium-iron-garnet films grown on gadolinium-gallium-garnet substrates and ferroelectric Ba$_{0.65}$Sr$_{0.35}$TiO$_3$ thin films were used. Dispersion characteristics and phase shift of surface spin waves controlled by a dc voltage were measured and calculated. Significant improvements in electrical tunability was reported.

- Recently, two reports on electrically and magnetically tunable microwave resonators incorporating ferrimagnetic YIG and ferroelectric materials (BST and PZT) were published [36, 103]. The operating frequency was around 5 GHz. The ferroelectric material was fabricated in a metal-insulator-metal configuration and large voltages needed to be applied for electrical tuning (up to 1000V). The structures were not multilayer films, but thin bulk pieces bonded together. Both papers comment on advantages of using dual tunable devices.

This short review of the publications relevant to electrically and magnetically tunable materials shows an increase in interest over the past few years, and numerous research possibilities. However, the information available is fairly incomplete, limited to low frequencies (below 10 GHz) and lacks systematic research. In addition, many of the investigated samples are in bulk form or at least one component is bulk (substrate). In order to make it attractive for potential applications, the materials need to be deposited in thin film form on commonly used microwave substrates. The purpose of this research is to investigate the combinations of ferrite and ferroelectric thin films for microwave applications.
1.2 Dissertation Outline

Chapter two reviews the main properties of ferrimagnetic materials (ferrites) and ferroelectrics, as well as their properties at microwave frequencies. Chapter three gives an overview of all experimental techniques and measurement procedures used in this dissertation. Chapters four and five are summaries of author’s work on sputtered thin films, which resulted in his master’s thesis as well as four publications. Chapters six and seven are the main part of this dissertation. Chapter six describes the fabrication and results of crystallographic, microstructural and magnetic analysis of pulsed-laser deposited films, while chapter seven contains the results of microwave characterization of these films. Chapter eight gives the conclusion and further prospects of this work.
CHAPTER 2
REVIEW OF BASIC PROPERTIES OF FERRITES AND FERROELECTRICS

This chapter is intended to provide a review of basic physical properties of ferrites and ferroelectric materials and their behavior at high frequencies. Due to their favorable properties, both materials have very important technological applications.

2.1 Ferrites

Ferrites are a class of electrically insulating ferrimagnetic compounds of various mixtures of iron oxide $\text{Fe}_2\text{O}_3$. Examples include cubic (spinel) ferrites $\text{MO} \cdot \text{Fe}_2\text{O}_3$, garnets $3\text{M}_2\text{O}_3 \cdot 5\text{Fe}_2\text{O}_3$, and hexagonal ferrites (magnetoplumbites) $\text{MO} \cdot 6\text{Fe}_2\text{O}_3$. M can be a divalent ion such as Mn, Ni, Zn, Co, Mg in the case of cubic ferrites; in hexagonal ferrites M is usually Ba or Sr, and in garnets, M is yttrium or a rare earth element. Ferrimagnetic materials are similar to ferromagnetics, having a spontaneous magnetization below the Curie temperature. In ferrimagnets, two different sublattices have opposite but different magnetic moments, thus creating a non-zero net magnetic moment. Their low electrical conductivity makes them useful for applications where ferromagnetic materials (that are usually metallic) would be detrimental. At high frequencies, for example, eddy currents are not generated in insulating materials, and electromagnetic waves can propagate through and interact with the material. This propagation and interaction can be controlled using external magnetic field, making ferrites irreplaceable materials in many rf and microwave devices. Some typical magnetic properties of ferrites are illustrated in table 2.1. It can be seen that garnets and spinels are used in frequency range up to 12 GHz (X-band), while the hexaferrites are used usually up around 55 GHz. It can also be noticed that garnets
<table>
<thead>
<tr>
<th>Type (structure)</th>
<th>Ferrite composition</th>
<th>MO</th>
<th>Common ferrite materials</th>
<th>Typical magnetic properties: $4\pi M_r(G)$, $H_a(Oe)$, $\Delta H(Oe)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Garnet (cubic)</td>
<td>$5 \text{Fe}_2\text{O}_3$: $3 \text{M}_2\text{O}_3$</td>
<td>Rare earth metal oxide</td>
<td>Y$_3\text{Fe}<em>5\text{O}</em>{12}$</td>
<td>1750, 82, 0.5 (X-band)</td>
</tr>
<tr>
<td>Spinel (cubic)</td>
<td>$1 \text{Fe}_2\text{O}_3$: $1 \text{MO}$</td>
<td>Transition metal oxide</td>
<td>($\text{Ni, Zn})\text{Fe}_2\text{O}_4$, ($\text{Mn, Zn})\text{Fe}_2\text{O}_4$</td>
<td>3800, 300, 77 (X-band)</td>
</tr>
<tr>
<td>Magneto-plumbite (hexagonal)</td>
<td>$6 \text{Fe}_2\text{O}_3$: $1 \text{MO}$</td>
<td>Divalent metal oxide from group IIA - BaO, CaO, SrO</td>
<td>BaFe$<em>{12}$O$</em>{19}$, SrFe$<em>{12}$O$</em>{19}$</td>
<td>4700, 16500, 26 (55 GHz)</td>
</tr>
</tbody>
</table>

Table 2.1. Summary of ferrite crystal structure types [10].

have very small ferrimagnetic resonance linewidth ($\Delta H$) which is related to losses, and that hexagonal ferrites have very large anisotropy fields ($H_a$), useful for making self-biased magnetic devices.

The non-linear relation between the applied magnetic field $H$ and magnetization $M$ results in magnetic hysteresis, and it can be observed in both ferromagnetic and ferrimagnetic materials. A typical magnetic hysteresis curve is shown in figure 2.1, and is usually referred to as M-H curve (magnetization $M$ vs. applied field $H$). The dotted line represents a “virgin” magnetization curve that occurs when an unmagnetized material is exposed to increasing magnetic field. Three important points in the hysteresis curve are marked - saturation magnetization (value of magnetization when sample is fully magnetized), remanent magnetization (value of magnetization after the sample is fully magnetized and the field is returned to zero), and coercive field or coercivity (value of magnetic field needed to bring the sample back to unmagnetized state). The magnetic structure in macroscopic samples is divided into magnetic domains in which all magnetic moments are oriented in the same direction. Since the orientation of the domains is in general random, a ferrimagnetic sample does not show any net magnetization without external magnetic field. During the magnetization process, the domains move, change size and rotate to minimize the overall energy. This process governs the value of the coercive field and the shape of the M-H curve. Crystal imperfections and impurities can hinder the movement of magnetic domain walls during magnetization (and demagnetization) process and thus increase the coercivity.
Depending on the values of saturation and remanent magnetization and coercivity, magnetic materials can be categorized in two groups - soft and hard magnets. Magnetically soft materials have small coercivity, and small area of the hysteresis loop. They are easy to magnetize and demagnetize, and are used in applications were magnetization has to be reversed many times a second with low dissipation, such as transformers, generators and motors. Commercially important materials like Permalloy have also large permeability and squareness ($M_r/M_s$) close to one. Hard magnetic materials, on the other hand, are more difficult to magnetize and demagnetize. They have large hysteresis and high coercivity. A classical example of a hard magnet is Alnico, an alloy of aluminum, nickel and cobalt.

Properties of ferrites at high frequencies are influenced by following effects [11]:

- Faraday rotation: rotation of the plane of polarization of a TEM wave as it propagates through a ferrite sample.
- Ferrimagnetic resonance: resonant absorption of electromagnetic radiation (more in section 2.1.2).
- Field displacement: displacement of electromagnetic field distribution transverse to the direction of propagation.
- Nonlinear effects: effects occurring at high power levels.
- Spin waves: short-wavelength waves of magnetization that propagate in the sample.

Ferrite materials have low losses at microwave frequencies, high resistivity and strong magnetic coupling, making them irreplaceable constituents in microwave device technology. In the form of high quality thin films, they have a potential to replace bulky external magnets in current microwave devices [10]. Common ferrite microwave devices include microwave phase shifters, isolators and circulators. These devices use reciprocal and non-reciprocal features of the ferrite materials, and provide unique circuit functions that cannot be reproduced with any other materials.
2.1.1 Magnetic Anisotropy

Magnetic anisotropy is an important factor influencing the magnetic properties of ferrite thin films. The magnetization of ferrimagnetic (and ferromagnetic) materials usually prefers a specific energetically favorable direction, called easy axis of magnetization. Less favorable direction is called a hard axis of magnetization. The main contributions to magnetic anisotropy (in the case of hexaferrite thin films) come from the crystal (magneto-crystalline) and shape anisotropies. The origin of the crystal anisotropy is the spin-orbit coupling and is related to the material’s crystallographic structure. The out-of-plane crystal anisotropy of a hexagonal crystal is much larger than the in-plane anisotropy (see figure 2.2). The source of the shape anisotropy is the demagnetization energy associated with the shape of the sample. In thin films, the easy axis lies usually in the film plane. The easy axis describes a direction of magnetization in which the total energy (sum of all anisotropy contributions) is minimized.

2.1.2 Ferrimagnetic Resonance

Ferrimagnetic (ferromagnetic) resonance (FMR) is the resonant absorption of electromagnetic radiation by the spin system of a ferrimagnetic (ferromagnetic) material. In a
standard FMR experiment, the sample under investigation is set in a dc magnetic field and irradiated by an electromagnetic field in the microwave range. FMR is mostly used for measurements of static and dynamic properties of magnetic materials such as effective and saturation magnetization, magnetic anisotropy, damping and electron g-factor.

Classical equation of motion of magnetization without damping, given by Landau and Lifshitz is:

\[ \frac{d\vec{M}}{dt} = -\gamma (\vec{M} \times \vec{H}_{\text{eff}}), \]  

(2.1)

where \( \vec{M} \): magnetization, \( \vec{H}_{\text{eff}}(H_{ex}, H_d, H_a, H_0) \): total effective field, \( \gamma \): gyromagnetic ratio, \( H_{ex} \): exchange field, \( H_d \): demagnetizing field, \( H_a \): anisotropy field, \( H_0 \): applied field.

Solution of the Landau-Lifshitz equation relates the resonant frequency \( \omega \) to the total effective magnetic field:

\[ \omega = \gamma \vec{H}_{\text{eff}}. \]  

(2.2)

From here we see that the resonance frequency of the ferrite depends on its magnetic anisotropy. For applications in GHz region, high anisotropy materials are required.
Figure 2.3 illustrates a typical relation of ferrimagnetic resonance to the applied field for anisotropic samples, when the magnetic field is applied parallel and perpendicular to the easy axis of magnetization of the sample. It can be seen that for the field parallel to the easy axis, there is a linear relation between the FMR frequency and the applied field. For the fields applied perpendicular to the easy axis, the relation is linear only at fields much larger than the anisotropy field. This will be observed in chapter 7.3.

2.1.3 Barium-Hexaferrite

The compound BaFe$_{12}$O$_{19}$ (Barium-ferrite, Barium-hexaferrite, Barium-M-hexaferrite, BaM, Ferroxdure, BaO$ \cdot 6$Fe$_2$O$_3$) is the most important of hexagonal ferrites, and is used in a variety of magnetic recording and high-frequency applications. It belongs to the M-type class of hexagonal ferites (hexaferrites). This type of hexagonal ferrites has a magnetoplumbite crystal structure, shown in figure 2.4, which consists of four interchanging spinel (S and S$^*$) and rhombohedral (R and R$^*$) blocks. The ferrimagnetic properties come entirely from the 24 Fe$^{3+}$ ions, each having a magnetic moment of 5$\mu_B$ ($\mu_B$: Bohr magnetron), and the total magnetic moment equals to 40$\mu_B$ [87].

The lattice parameters of the unit cell of BaM are \(a \approx 5.89\,\text{Å}\) and \(c \approx 23.19\,\text{Å}\) [123]. The most outstanding property of BaM is its large magnetic anisotropy (\(\approx 17\,\text{kOe}\) at room
tempreature [106]). The easy direction of magnetization is along the hexagonal c-axis, and
the hard direction is along the hexagonal a-axis, see also figure 2.2. This “built in” biasing
field is used for construction of many resonance isolators, phase shifters and circulators
[10]. The natural ferrimagnetic resonance frequency of BaFe$_{12}$O$_{19}$ is around 50 GHz, but
can be varied between 40 to 130 GHz by substitution of Co, Al, Ti or Zn for some of the
Ba atoms [87]. From the equation 2.2 it can be seen that the high values of FMR come
from the high magnetic anisotropy of BaM.

The relative permittivity of the BaM is around 15, while the values of the permeability
are ≈ 1 far below the ferrimagnetic resonance frequency [120], making it a good candidate
for lossless microwave applications.
2.2 Ferroelectrics

Ferroelectric materials belong to the important class of dielectric materials [23]. Their properties include high resistance to electric current and a nonlinear response of polarization to electric field. Below the Curie temperature, ferroelectric materials have long range dipole-dipole interactions manifested in spontaneous polarization and display hysteresis effects of polarization vs. electric field, just like ferri- and ferromagnetic materials, which is the origin of the prefix “ferro” (they do not contain any iron, though). Above the Curie temperature, spontaneous polarization disappears and the polarization response becomes linear - this state is called a paraelectric state. Ferroelectric materials also have domains in which the polarization is homogeneous. The permittivity of ferroelectric materials is a function of temperature, with real part having a sharp maximum at the Curie temperature. The permittivity also changes with applied electric field (electrical tunability). Figure 2.5 illustrates a typical behavior of a tunable ferroelectric material.

![Figure 2.5. A typical change of permittivity with applied voltage for a ferroelectric sample.](image)

2.2.1 Barium-Strontium-Titanate

Barium-strontium-titanate (BST) is the most widely used tunable ferroelectric, having the formula $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$. The compound with $x=0.5$ is in a paraelectric state, with Curie temperature well below the room temperature, reasonable tunability and low losses [126].
Curie temperature can be adjusted by changing the value of $x$ (BaTiO$_3$ is ferroelectric and SrTiO$_3$ is paraelectric at room temperature).

![Crystal structure of Barium-Strontium-Titanate](image)

**Figure 2.6.** Crystal structure of Barium-Strontium-Titanate.

The spontaneous polarization comes from the relative displacement of Ba(Sr) and Ti atoms to the O atoms. The crystal structure of BST is shown in figure 2.6, with lattice parameter around 4Å. At the Curie point, the lattice undergoes a phase transition from cubic (paraelectric) to tetragonal (ferroelectric).

Some of the main features of BST making it an attractive material for microwave applications include: large permittivity, high tunability, fast response to the electrical fields, high breakdown fields, low dielectric leakage currents, symmetric nonlinearity and simple fabrication [12, 76, 95, 99, 114, 115, 117].
2.3 Microwave Properties of Magnetic and Dielectric Oxides

Macroscopic behavior of ferrimagnetics and ferroelectrics can be described by their complex permeability ($\mu$) and permittivity ($\epsilon$). These quantities describe the interaction of the material with applied magnetic and electric fields, respectively. These interactions are manifested by energy storage (lossless part of energy that is exchanged by the field and the material) and energy dissipation (part of energy absorbed by the material). This leads to permeability and permittivity be complex quantities, and these can be also “tuned” in applied fields. Electrical tunability was described in the previous section.

For microwave applications, ferrites can be divided in two groups - ferrites that are magnetically tuned to ferrimagnetic resonance (FMR) and ferrites that are tuned away from the FMR [121]. The idea behind the magnetic tunability is that in ferrimagnetic materials, which are characterized by a hysteresis loop, the permeability is a function of applied magnetic field, and is in general a tensor quantity [100, 121]:

$$\vec{B} = [\mu] \vec{H},$$

where $\mu$ is a tensor. The $\mu(\vec{H})$ is defined as the derivative of magnetic flux density $\vec{B}$ with respect to applied magnetic field $\vec{H}$. Typical values of the initial permeability $\mu(\vec{H})/\mu_0$ range from 10 to $10^4$. For a lossless ferrite material in an applied magnetic field along the z-direction, the tensor permeability is given by [100]:

$$[\mu] = \begin{bmatrix} \mu & j\kappa & 0 \\ -j\kappa & \mu & 0 \\ 0 & 0 & \mu_0 \end{bmatrix},$$

where

$$\mu = \left(1 + \frac{\omega_0\omega_m}{\omega_0 - \omega_m} \right),$$

$$\kappa = \mu_0 \frac{\omega_m}{\omega_0^2 - \omega^2},$$
Figure 2.7. Example of magnetic tunability: $\mu$ spectrum of a 10-layer composite of 1.9 $\mu$m CoFe amorphous film on a 12 $\mu$m mylar substrate: left - bias $H=10$ Oe, right - bias $H=110$ Oe [124].

$$\omega_0 = \mu_0 \gamma H_0, \quad \omega_m = \mu_0 \gamma H_s,$$

and the gyromagnetic ratio $\gamma$ is around [31]:

$$\gamma = 2.8 \frac{GHz}{kOe}.$$

In order to account for losses, a damping factor $\alpha$ is introduced:

$$\omega \rightarrow \omega_0 + j\alpha \omega.$$

Applying this to the above expression for the permeability gives the complex permeability:

$$\mu = \mu' - j\mu''.$$

From this expression, it can be seen that the complex permeability will change depending on the applied magnetic field. This is referred to as magnetic tunability. An example of magnetic tunability is shown in figures 7.3, where the magnetic complex permeability of a ferrimagnetic material is changed by applying a small magnetic field. It can be seen that the values of $\mu'$ and $\mu''$ are changed in the low frequency region (away from the FMR), and also the position of the FMR frequency is changed, as they both depend on the applied magnetic field. These two phenomena can be used for tailoring tunable magnetic devices using ferrite materials.
The permittivity of a material, which describes material’s ability to transmit an electric field, is also a tensor quantity in general, and relates the electric displacement field $\vec{D}$ to the electric field $\vec{E}$:

$$\vec{D} = [\epsilon]\vec{E} = \epsilon_0 \vec{E} + \vec{P},$$

where $\epsilon_0$ is the permittivity of free space and $\vec{P}$ is electric polarization. The dielectric constant is defined as a relative permittivity $K=\epsilon_r=\epsilon/\epsilon_0$. The values of dielectric constant range from less than 10 for most dielectrics to several thousands for some ferroelectrics.

A schematic view of the frequency properties of magnetic and dielectric materials is shown in figure 2.8. The main polarization mechanisms in dielectric materials include ionic conduction, dipolar relaxation, atomic polarization, and electronic polarization. The permittivity is also influenced by the movements and resonances of ferroelectric domain walls. The permeability of magnetic materials is related to the movements and resonance of magnetic domain walls, and gyromagnetic resonance (ferro- and ferrimagnetic resonance).

### 2.4 Characteristics of Microwave Devices

When designing devices containing ferrimagnetic and ferroelectric materials, one has to consider both intrinsic as well as extrinsic factors influencing the device performance. Depending on the size of the device compared to the operating wavelength, they are divided into “electrically small” and “electrically large” devices [126]. The electrically small devices can be described with discrete circuit components (lumped-element model), while in the electrically large devices frequency dependence needs to be taken into account, and they are described by distributed networks of common circuit elements (inductors and capacitors). Most common example of electrically large device is a transmission line. The transmission line is characterized by its characteristic impedance $Z_c \propto \sqrt{\mu/\epsilon}$, which depends on the material’s permittivity and permeability, but also on its size and shape. Optimum value of characteristic impedance in most systems is 50Ω. Devices based on transmission lines
should be designed as to avoid changes in the values of the characteristic impedance, since that can cause impedance matching problems (part of the electromagnetic signal will be reflected at the places where the $Z_c$ changes). Presence of ferroelectric and ferrimagnetic materials in a transmission line can cause serious impedance matching problems, and care should be taken during the design.
CHAPTER 3
EXPERIMENTAL METHODS

This chapter describes the experimental set-ups and measurement techniques. Most of the work was performed at the USF (University of South Florida), but some work was done during research visits to the ORNL (Oak Ridge National Laboratory) and UCF-AMPAC (University of Central Florida - Advanced Materials Processing and Analysis Center) facilities. Thin films were fabricated using rf magnetron sputtering and laser ablation. The structural characterization was done using X-ray diffractometer, atomic force and scanning electron microscopes. Magnetic measurements were performed by the Physical Properties Measurement System. Special attention is given to microlithography and microwave characterization, which contain specially developed instrumentation and techniques presented in this work. FMR measurements were done through collaboration with Professor G. Srinivasan at Oakland University.

3.1 Thin Film Deposition

This work contains two methods of synthesizing thin films: rf sputter deposition and pulsed laser deposition. These techniques are part of the “Physical Vapor Deposition” (PVD) thin film preparation process, in which a target is bombarded and the removed material is deposited onto a substrate. Both sputtering and PLD have been used extensively to produce high quality ferrite and ferroelectric thin films.

3.1.1 RF Magnetron Sputtering

In an RF magnetron sputtering process, a high frequency plasma discharge is created by capacitively coupling a 13.6 MHz frequency to the cathode, as seen in figure 3.1 [125].
Using a small bias voltage between anode and cathode, the ionized gas atoms in the plasma are accelerated toward the target at the cathode and sputter off the deposits which travel toward the substrate located at the anode. Typical sputtering conditions for BaM and BST thin film deposition include argon gas or mixture of argon and oxygen gases, rf power densities of several W/cm², and substrate temperatures of several hundred °C. Postannealing of the as-deposited films is usually performed to improve film crystallinity. Sputtering has been successfully used to deposit BaM [18, 57, 58, 75, 93] and BST [13, 95, 116, 129] thin films.

![Image of sputtering process](image)

**Figure 3.1.** Sputtering deposition process - left figure shows a schematic of a rf sputtering system, right figure illustrates the sputtering process [125].

### 3.1.2 Pulsed Laser Deposition

Pulsed laser deposition (also referred to as pulsed laser ablation) is a deposition technique used to produce thin films with high stoichiometry. The process of laser deposition consists of bombarding the target with short, high-energy laser pulses, creating a plasma from the vaporized target surface - see figure 3.2. This plasma contains atoms, electrons, ions, molecules, clusters and particulates eroded from the target, which get deposited on the substrate placed parallel to the expansion direction of the plasma. The substrate is usually heated to several hundred °C to promote the nucleation and growth of the film.
The laser target interaction is a complex process involving evaporation, ablation, plasma formation and exfoliation [25]. One of the main advantages of PLD is that the plasma arriving at the substrate is highly energetic, providing sufficient ion mobility for growth of epitaxial films. Another advantage is that PLD can be performed both in high vacuum as well as in the presence of a background gas, e.g. oxygen. A disadvantage of PLD is that small droplets (particulates) of the target material are often deposited on the substrates, which is referred to as “splashing” [25, 125]. Also, the area of deposition is relatively small compared to sputtering and other deposition techniques. This is associated with the highly directional nature of the plume. Highest quality BaM [25, 84, 85, 105, 107] and BST [19, 20, 25, 54, 62] thin films have been reported using this deposition technique.

Figure 3.2. Pulsed-laser deposition process: (a) typical experimental set-up, (b) schematic of the evolution of the plasma plume [125].

3.2 Structural Characterization

Structural investigation is an important step in thin film characterization. It helps in understanding what deposition conditions provide optimum film quality as well as in relating microstructural properties to other thin film properties such as magnetization, polarization, conductivity, high-frequency response, etc, which are relevant for technological
applications. The techniques used in this study include X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM).

3.2.1 X-Ray Diffraction

X-ray diffraction can provide information about thin film crystallinity, chemical makeup, phase identification and planar orientation. In thin films, certain crystallographic directions are usually preferred leading to anisotropic properties of crystal orientation. This phenomenon is called texture or preferred orientation [16]. In such films, certain Bragg reflections in $\theta/2\theta$ diffraction scans are more pronounced than the others. The techniques used here to study thin film texture include determination of Bragg peaks by $\theta/2\theta$-diffraction, rocking curves ($\omega$-scans), azimuthal scans ($\phi$-scans) and pole figure measurements of selected Bragg peaks.

XRD data was collected using Philips X’Pert (at USF Nanomaterials and Nanomanufacturing Research Center - NNRC) and Bruker AXS (at USF Physics Department) diffractometers equipped with thin-film diffractometer and pole-figure goniometer - figure 3.3(a). Some measurement parameters are shown in table 3.1. Qualitative analysis was done using X’Pert HighScore software as well as by comparison with the published crystallographic database [1, 2, 3].

<table>
<thead>
<tr>
<th>XRD Diffraction Parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode Material</td>
<td>Copper</td>
</tr>
<tr>
<td>Monochromator</td>
<td>PW3123/10 for Cu</td>
</tr>
<tr>
<td>Incident Slit</td>
<td>Soller 0.04 rad</td>
</tr>
<tr>
<td>Divergence Slit</td>
<td>Fixed, $1/2\theta$</td>
</tr>
<tr>
<td>Incident Mask</td>
<td>Fixed, 5 and 10 mm</td>
</tr>
<tr>
<td>Generator Settings</td>
<td>45 kV, 40 mA</td>
</tr>
<tr>
<td>Scan Type</td>
<td>$\theta/2\theta$, $\omega$-tilt and $\theta$-tilt followed by $\phi$-azimuthal rotation</td>
</tr>
</tbody>
</table>

Table 3.1. X-Ray diffraction parameters for $\theta/2\theta$ and pole-figure scans.

The basic principle of determining the crystal structure using X-rays is given by the Bragg’s law - see figure 3.3 (b and c). A beam of parallel X-rays impinges the crystal surface at an angle $\theta$, and is reflected from the parallel planes of atoms formed by the
crystal lattice of the material. Two consecutive reflected beams have a phase difference because they travel a different path. Constructive interference of the reflected rays occurs only when their path difference is equal to a multiple of the wavelength [69]:

\[2d \cdot \sin \theta = n \cdot \lambda, n = 1, 2, ...\]  \hspace{1cm} (3.1)

In a conventional \(\theta/2\theta\) scan (also called a powder diffraction method), the sample under investigation is bombarded by an X-ray beam directed to the sample surface at the constant angle \(\theta\), while on the other side a detector measures the intensity of the scattered radiation at the same angle [16]. During the scan, the angle of incidence and the angle of detection are continuously varied but kept equal to each other. A characteristic diffraction pattern emerges and is usually plotted as a function of \(I(2\theta)\) type. The measured pattern is then compared with a known database of reference patterns.

Thin films deposited on single crystal substrates are usually textured polycrystalline or an epitaxial single crystal. Textured polycrystalline films often grow in a preferred orientation as shown in figure 3.4 and very rarely have random crystallite morphologies.
The degree of texture can be probed by several x-ray diffraction techniques mentioned earlier. The conventional $\theta/2\theta$ diffractogram shows only the Bragg reflections of the lattice planes that are parallel or nearly parallel to the surface of the thin film - figure 3.3 (b). In order to determine the orientation distribution, the intensity of the Bragg reflections of all crystallites is measured for various values of azimuth angle $\phi$ and tilt angle $\psi$, see figure 3.3(a). The intensity $I(\phi, \psi)$ is usually plotted in a circular plane, and such plot is called an intensity pole figure. Typical pole figures for different types of crystallite orientation are shown in figure 3.4. If the crystallite orientations were perfectly random, the pole would be uniformly distributed on a pole figure. In a textured material, the poles group together in certain places. The stronger the texture, the tighter the grouping of the poles, as illustrated in figure 3.4 (b and c).

Rocking curve analysis ($\omega$-scan) is used to quantitatively measure planar orientation or mosaicness of thin films. It is mostly useful for highly oriented or epitaxial films. This measurement is performed by fixing the detector on the $2\theta_0$ position of the Bragg peak under investigation, and then tilting (“rocking”) by angle $\omega$ in the vicinity of the Bragg angle $\theta_0$. The full width at half maximum (FWHM) obtained from the rocking curve reveals the degree of film orientation. A narrow peak is indication of a greater textural

Figure 3.4. Schematic illustration of preferred orientation of polycrystalline thin films (arrows show a chosen hkl direction): (a) random orientation, (b) weak orientation, (c) strong orientation.
coherence of the crystallites. Figure 3.5 illustrates the dependence of the rocking curves on the orientation of thin film lattice planes. For a perfect single crystal, the peak is a δ function. Two perfect crystals give two δ-peaks. The rocking curve of a highly oriented polycrystalline thin film would show a finite peak width.

Azimuthal- or φ-scan is a high-accuracy “slice” of the pole figure, used to provide quantitative data for thin film texture and epitaxy. It is performed by tilting the angle ψ to a desired value and varying the azimuth angle φ. The FWHM of the measured peaks in the φ-scan also serves as a measure of the quality of the thin films.

### 3.2.2 Scanning Electron Microscopy

Scanning electron microscopy is used to image a sample surface with a high resolution, by detecting secondary electrons emitted from the surface when excited by the primary electron beam. The electron beam with energies ranging from a few hundred eV to tens of keV is emitted from a tungsten or lanthanum hexaboride (LaB₆) cathode, focused and rastered across the sample by means of condenser and deflecting coils. As illustrated in
figure 3.6, several processes occur and can be detected when the electron beam hits the sample surface: elastic and inelastic backscattering, emission of x-rays, Auger electrons and secondary electrons [8, 125].

The topology of the sample surface (hills and valleys) determines the resolution of the SEM. The steep surfaces and edges emit more secondary electrons than a flat surface. This produces a difference in the brightness on the projection screen creating a three-dimensional appearance of the surface. The advantage of the SEM is its ability to image large sample area and also bulk samples, while one of the main disadvantages is relatively low spatial resolution when compared to other imaging techniques such as transmission electron microscopy and atomic force microscopy.

3.2.3 Atomic Force Microscopy

Atomic force microscopy (AFM) is a very high resolution scanning probe technique, used for imaging at the nanoscale. A typical atomic force microscope consists of a microscale cantilever with a fine tip positioned close to the sample. The distance to the sample surface is controlled by piezoelectric elements.

During the scan, the probing tip is brought close to the sample surface, and is being affected by van der Waals forces between the tip and the surface. The deflection of the cantilever is picked up by a laser spot reflected from the top of the cantilever - see figure 3.7.
The height of the deflection is then plotted as a function of the lateral position, revealing the topography of the surface [7, 125]. AFM is capable of imaging surfaces with atomic resolution.

Atomic force images of samples in chapter 6 were performed in collaboration with Professor G. Matthews and his graduate student A. Heim at their laboratory.

### 3.3 Magnetic Characterization with PPMS

Physical Properties Measurement System (PPMS) from Quantum Design was used to perform magnetization measurements on all samples. The PPMS consists of a liquid Helium dewar with a 7 T longitudinal superconducting magnet and a temperature controller in the range 1.9 to 400 K - see figure 3.8(a). The orientation of the sample with respect to the magnetic field inside the PPMS can be varied. In this study, the sample surface is positioned either parallel or perpendicular to the applied magnetic field.

Figure 3.8(b) shows an idealized magnetization versus applied magnetic field (M-H) curve of a thin film having easy magnetization axis parallel to the film plane. When the sample is positioned with its surface parallel to the applied field the sample is easily
magnetized to saturation. When the sample lies with its surface perpendicular to the magnetic field, much larger field is necessary to fully magnetize the sample.

3.4 Microwave Characterization of Thin Films

The final stage of the thin film characterization involves the study of high frequency response in the presence of electrical and magnetic fields. For this purpose a specially designed experimental set-up was assembled in a magnetic field environment generated by an electromagnet, and customized circuits were designed and fabricated using microlithography. The data was taken using a vector network analyzer after careful calibrations. Ferrimagnetic resonance measurements were done through a collaboration with Oakland University, the experimental set-up is briefly described. This section is presented in greater detail, as unlike the other analytical instruments that were commercial, the microwave measurements were set-up entirely during the course of this research.

3.4.1 Experimental Set-Up

A specially designed experimental stage was used for measurements of high-frequency response and the electric and magnetic tunability of thin films - see figure 3.9. The set-up consists of a custom built microwave probe station inside a water-cooled electromagnet (0
- ±9000 Gauss). The electromagnet was powered by a Kepco power supply ATE (1000 W), and the magnetic field was measured by a Lakeshore Gaussmeter model 410. The probe station is equipped with a microscope with CCD camera and LCD display, used for viewing and magnifying the microcircuits. Keithley power supply in combination with bias-tees was used for the electric field biasing. The microcircuits were probed by ground-signal-ground microprobes from GGB Company with 150 μm pitch separation. The probes were connected to the network analyzer via non-magnetic semi-rigid coaxial cables. Scattering parameters of the microwave circuits were measured by Anritsu 37397C vector network analyzer operating in the frequency range from 40 MHz to 65 GHz (this will be explained in more detail in the section 3.4.4.).

Some of the electrical tuning experiments were also performed at the USF Center for Wireless and Microwave Information Systems (WAMI), equipped with a probe station and VNA, but without the magnetic field.

The fundamental concept behind the experiment is that the high frequency response in the material is measured using the network analyzer, while the sample is in the magnetic field and/or under a bias dc electric field. The preparation for the microwave experiment includes deposition of microcircuits (coplanar waveguides and interdigitated capacitors) on the thin film, calibration and probing the circuits with the microprobes.
Figure 3.9. Experimental set-up for high frequency measurements of thin film properties.
3.4.2 Micro-Circuit Design

In order to measure frequency dependent dielectric and magnetic properties, coplanar waveguides (CPW’s) are fabricated on the top of the samples under investigation. A coplanar waveguide is a type of guided planar transmission line used in microwave integrated circuits, in which all conductors (ground and signal) lie on the top surface of the substrate - see figure 3.10. The three parallel conductors build a Ground-Signal-Ground (GSG) configuration (see also figure 3.13(a)), in which the outer two conductors carry the “ground” signal and the middle conductor carries the actual high-frequency signal. The fundamental mode of propagation is quasi-TEM (transverse electromagnetic) mode, only at very high frequencies it becomes non-TEM due to a longitudinal component of magnetic field [45]. The electric and magnetic field distribution is nearly symmetrical above and inside the substrate. The main advantage of a CPW is that all three conductors are on the same side of the substrate, which is an easier geometry to fabricate, and that the impedance does not depend on the thickness of the substrate, but only on the dielectric constant and the width of the gap and the central conductor.

Figure 3.10. Electromagnetic fields distribution in a coplanar waveguide. The solid line represents electric field and the dashed line represents magnetic field [23].

Three different substrates were used in this study: sapphire with A- and C- plane orientation, and (100)-oriented MgO. The properties of these substrates are listed in table 3.2.

In order for the circuits to be probed with the 150 \( \mu \)m pitch probes, special “tapers” were designed that have larger gap and central conductor size - see figure 3.13(a).
<table>
<thead>
<tr>
<th></th>
<th>C-sapphire</th>
<th>A-sapphire</th>
<th>(100)-MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dielectric constant</td>
<td>11.58</td>
<td>9.4</td>
<td>9.8</td>
</tr>
<tr>
<td>Loss tangent ($\times 10^{-5}$)</td>
<td>5</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Substrate thickness (microns)</td>
<td>500</td>
<td>500</td>
<td>1000</td>
</tr>
</tbody>
</table>

Table 3.2. Substrates parameters

The dimensions of CPWs and tapers were calculated using a freely distributed transmission line calculator “TXLine Version 1.1” from the company Applied Wave Research, Inc. - figure 3.11 [6]. The analysis of coplanar waveguides was done according to the reference [52], and the reported accuracy is within 5%.

Figure 3.11. Transmission Line Calculator program.

Four different gap sizes were chosen - 5, 10, 15 and 20 µm. All work was done with the circuits with 5 µm gap size, but it was desirable to design optional gap sizes in case that either fabrication or measurement of 5 µm gap did not produce desirable results. Dependence of the circuit performance on the gap size will be also discussed in chapter 7. For different substrates and different gap sizes, the central conductor width was adjusted to bring the characteristic impedance as close to 50Ω as possible. Conductivity of gold conductors was $\sigma = 4.1 \times 10^7 S/m$ for all circuits. The length of the lines was adjusted
for different frequencies, so that the electrical length value is around 90°. For the TRL calibration, the optimum electrical length of a delay line at particular frequency is chosen to be 90° or quarter wavelength, but it is acceptable for all frequencies that have the electrical length between 20° and 160°. Different lengths of delay lines were designed, giving a possibility of a TRL (Thru-Reflect-Line) calibration in the frequency range from 1 to 80 GHz. More details regarding the design of the CPWs will be addressed in section 3.4.4.1 when discussing the calibration procedures. The dimensions of all CPWs and tapers for the three substrates are given in tables 3.3 and 3.4. After the circuit dimensions were calculated using the Transmission Line Calculator, the complete mask was drawn in AutoCAD as seen in figures 3.14(a, b). In order to account for small feature sizes (5 µm CPW gap), a special chrome-on-glass mask was fabricated by Advance Reproductions Corporation. The pattern from a chrome mask was then transferred to an iron oxide mask for easier handling of the mask and in order to keep the original mask protected.

<table>
<thead>
<tr>
<th>Gap (microns)</th>
<th>C-sapphire</th>
<th>A-sapphire</th>
<th>(100)-MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Center line width (microns)</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Length (microns)</td>
<td>200</td>
<td>200</td>
<td>200</td>
</tr>
</tbody>
</table>

Table 3.3. Tapers dimensions for different substrates

In addition to the CPW, coplanar waveguide interdigitated capacitors (IDC) were also fabricated, in order to study the change of capacitance with applied electric field. Interdigitated (interdigital) capacitor is a multifinger periodic structure that uses the capacitance that occurs across a gap in thin film conductors [88]. The design and dimensions of the IDCs are shown in figure 3.13(b). The capacitance is varied by changing the number and dimensions of the fingers or by changing the dielectric properties of the thin film below, which is exactly the intention of this experiment. Approximate analytical methods exist to extract the capacitance of the thin film from measured S-parameters.

Two types of masks were designed, one with CPWs and IDCs - figure 3.14(a), and one with “bent” CPWs, as shown in 3.14(b). The CPWs consist of 'Thru', 'Reflect' and 'Delay
Line' structures, which will be explained later. The 'Taper-to-Taper' structure is used to deembed the effect of tapers from the measurement. The 'bent' lines are specially designed for measurements in applied magnetic field. Figure 3.12 illustrates the relative orientation of the ac and dc magnetic fields in the experiment (see also figure 3.10 for magnetic field distribution in CPW structure). For the “bent” CPWs the applied dc magnetic field is perpendicular to the propagating ac magnetic field. This set-up is essential for microwave measurements of magnetic samples, as in the FMR experiment, the perturbing ac field is perpendicular to the large dc field.

![Figure 3.12. Relative orientation of ac and dc magnetic field vectors in the high-frequency measurement experiment. Left: “straight” CPWs, right: “bent” CPWs.](image-url)
<table>
<thead>
<tr>
<th>Material</th>
<th>Shape</th>
<th>Width (µm)</th>
<th>Gap (µm):</th>
<th>Lines (µm):</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-sapphire</td>
<td>straight line</td>
<td>G=5µm</td>
<td>8000, 7000, 3000, 615, 400</td>
<td></td>
</tr>
<tr>
<td>C-sapphire</td>
<td>bent line</td>
<td>G=10µm</td>
<td>8000, 7000, 3000, 615, 400</td>
<td></td>
</tr>
<tr>
<td>C-sapphire</td>
<td>straight line</td>
<td>G=15µm</td>
<td>8000, 7000, 3000, 615, 400</td>
<td></td>
</tr>
<tr>
<td>C-sapphire</td>
<td>bent line</td>
<td>G=20µm</td>
<td>8000, 7000, 3000, 615, 400</td>
<td></td>
</tr>
<tr>
<td>C-sapphire</td>
<td>straight line</td>
<td>G=5µm</td>
<td>8000, 7000, 3000, 615, 400</td>
<td></td>
</tr>
<tr>
<td>A-sapphire</td>
<td>straight line</td>
<td>G=10µm</td>
<td>8000, 7000, 3000, 615, 400</td>
<td></td>
</tr>
<tr>
<td>A-sapphire</td>
<td>bent line</td>
<td>G=15µm</td>
<td>8000, 7000, 3000, 615, 400</td>
<td></td>
</tr>
<tr>
<td>A-sapphire</td>
<td>straight line</td>
<td>G=20µm</td>
<td>8000, 7000, 3000, 615, 400</td>
<td></td>
</tr>
<tr>
<td>A-sapphire</td>
<td>bent line</td>
<td>G=10µm</td>
<td>8000, 7000, 3000, 615, 400</td>
<td></td>
</tr>
<tr>
<td>A-sapphire</td>
<td>bent line</td>
<td>G=5µm</td>
<td>8000, 7000, 3000, 615, 400</td>
<td></td>
</tr>
<tr>
<td>A-sapphire</td>
<td>bent line</td>
<td>G=20µm</td>
<td>8000, 7000, 3000, 615, 400</td>
<td></td>
</tr>
<tr>
<td>A-sapphire</td>
<td>straight line</td>
<td>G=20µm</td>
<td>8000, 7000, 3000, 615, 400</td>
<td></td>
</tr>
<tr>
<td>A-sapphire</td>
<td>bent line</td>
<td>G=10µm</td>
<td>8000, 7000, 3000, 615, 400</td>
<td></td>
</tr>
<tr>
<td>A-sapphire</td>
<td>bent line</td>
<td>G=15µm</td>
<td>8000, 7000, 3000, 615, 400</td>
<td></td>
</tr>
<tr>
<td>100-MgO</td>
<td>straight line</td>
<td>G=5µm</td>
<td>8000, 7000, 3000, 615, 400</td>
<td></td>
</tr>
<tr>
<td>100-MgO</td>
<td>straight line</td>
<td>G=10µm</td>
<td>8000, 7000, 3000, 615, 400</td>
<td></td>
</tr>
<tr>
<td>100-MgO</td>
<td>straight line</td>
<td>G=20µm</td>
<td>8000, 7000, 3000, 615, 400</td>
<td></td>
</tr>
<tr>
<td>100-MgO</td>
<td>bent line</td>
<td>G=20µm</td>
<td>8000, 7000, 3000, 615, 400</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.4. Mask design parameters: G - gap between central and ground conductor, W - width of the central conductor, “Lines” - delay lines for TRL calibration.
Figure 3.13. CPW mask design details: (a) CPW line, (b) IDC.
Figure 3.14. CPW mask design: (a) mask with CPW lines and interdigitated capacitors, (b) mask with “bent” CPW lines.
3.4.3 Micro-Circuit Fabrication

Microcircuit fabrication was performed inside a class 1000 cleanroom at USF-NNRC. The masks were fabricated using the Negative Photoresist NR1-3000PY and developed in Resist Developer RD6. The resist was removed by Resist Remover RR4, all from Futurrex, Inc. The recommended procedure outlined on company’s web-site [5] had to be modified for sapphire and MgO substrates. These substrates are very small (1cm × 1cm), and are poor heat conductors. The baking time had to be increased 3.5 times that of silicon wafers. The development time was kept at 25 sec. The microlithography procedure is illustrated in figure 3.15, and step-by-step fabrication process is described below.

Microcircuit fabrication procedure:

- Clean the substrates with acetone and methanol and dry in nitrogen.
- Spin-coat the photoresist onto the substrate at 3000 rmp for 30 seconds with 3 seconds ramping time.
- Bake on a hotplate at 155°C for 165 seconds.
- Expose to UV light for 60 seconds.
- Postbake on a hotplate at 110°C for 165 seconds.
- Develop in RD6 for 25 seconds.
- Gently rinse in distilled water and dry with N₂.
- Place the sample in the RF-Plasma Etch for about 45 seconds at 75 W. This is necessary to remove any remaining photoresist that was not removed by the RD6 developer.
- Deposit the Cr/Au metal using thermal evaporator (the details are given below).
- Lift-off the photoresist in the resist remover RR4 by heating at 115°C for 25 min or as long as necessary to remove all photoresist from the substrate.
- If necessary, ultrasonicate in acetone for 30 seconds and repeat the previous step, until all photoresist is removed.
• Finally, clean the samples in acetone, rinse with methanol and dry with N$_2$.

• Another RF-Plasma-Etch may be needed to remove any residues on the substrate surface.

![Figure 3.15. Microlithography procedure with negative photoresist.](image)

The Cr/Au metal was deposited in a thermal evaporator. Prior to deposition, the chamber was evacuated down to low µtorrs. First, a thin chrome layer ($\approx 15nm$) was deposited to promote the adhesion of gold. Then the gold layer was deposited to a thickness of about 1µm, which was confirmed with a profilometer. Immediately after metal deposition, the photoresist was removed.

The microlithography process was very problematic. One of the main issues was the small size of the sample. After the spin-coating of the photoresist on the substrate, the edges of the resist were always slightly higher than the middle, which on a small substrate can have a very pronounced effect - see figure 3.16(a). This resulted in uneven development of the resist and created various defects in the fabricated circuits - see figure 3.16(b). The solution was to reduce the development time, but this made some of the resist to remain
Figura 3.16. Problemas con la fabricación: (a) una ilustración exagerada del perfil de altura de la capa de fotoreastro espinado, (b) defectos en la máscara de resistido después del desarrollo.

undeveloped and stay on the places from which it should have been removed. That caused some of the samples to become “contaminated” by photoreastso lying underneath the metal layer. A partial solution was to expose the substrates with mask to rf-plasma etch before and after metalization. This step removed some of the unwanted resist from underneath and between the metal layers.

3.4.4 Network Analyzer Measurements

Network analyzer is an instrument that analyzes the reflection and transmission of electromagnetic signals in electrical networks. Network analyzers are used at high frequencies (MHz and GHz), and can be either scalar (measure amplitude properties only) or vector...
network analyzers (measure both magnitude and phase properties). As illustrated in figure 3.17(a), a network analyzer consists of a source, signal separation devices, and detectors. It can independently measure the two incoming waves $a_1$ and $a_2$, and the two reverse traveling waves $b_1$ and $b_2$. These input and output waves for a two-port network are shown in figure 3.17(b). The relationship between these parameters can be described by scattering- or S-parameters:

$$\begin{pmatrix} b_1 \\ b_2 \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} \quad (3.2)$$

The components of the scattering matrix are called:

$S_{11}$: input reflection coefficient

$S_{21}$: forward transmission coefficient (gain)

$S_{12}$: reverse transmission coefficient (isolation)

$S_{22}$: output reflection coefficient

Figure 3.17. Network analyzer measurements: (a) a block diagram of a network analyzer [23], (b) a two port network.

### 3.4.4.1 Probe Calibration

Before making measurements of the S-parameters, an accurate two-port calibration was performed in order to eliminate systematic errors associated with the VNA, cables, and
probes. For on-wafer measurements, calibration standards are needed to correct for the losses in the probes. Two common methods of calibration were used in this study: SOLT and TRL.

Short-Open-Load-Thru (SOLT) calibration is the most commonly used calibration, and it has been used for the most part in this study. Four known standards are needed (short, open, load and thru), which are found on a commercially available ceramic calibration substrate from GGB Company. For this calibration, the 'reference plane' is located at the probe tips, meaning that error contributions from the VNA up to this point are calibrated out.

![Figure 3.18. SOLT calibration.](image)

Thru-Reflect-Line (TRL) calibration is an alternative, so-called “self-calibration” method, developed by researchers at the U.S. National Institute of Standards and Technology (NIST). The advantage of the TRL calibration is that calibration standards can easily be fabricated on any substrate under investigation - see figures 3.13 and 3.14. The 'reference plane' in this case is placed at the 'center of the Thru', see figure 3.13(a). The 'Line' sections were designed to be close to 1/4 wavelength (90°) for different frequencies, ranging from 1 to 80 GHz. The shorter 'Lines' correspond to higher frequencies. One of the disadvantages of TRL calibration is large length of lines at low frequencies.

Another problem with the TRL calibration in this study was that DUT as well as the calibration standards depend on the changes in the characteristic impedance of the underlying BaM-BST thin films. This problem could be resolved by calibrating at different voltages and magnetic fields before each measurement, but such procedure is quite tedious.
TRL calibration was attempted a few times, but in the end SOLT calibration was used for measurements in chapter 7.

3.4.5 Ferrimagnetic Resonance Measurements

Ferrimagnetic resonance (FMR) is a spectroscopic technique used for probing spin waves and spin dynamics of a ferrimagnetic material. The FMR effect comes from the precessional motion of the magnetic moment of electrons when exposed to an external magnetic field.

Conventional FMR experiments are usually performed inside a resonant cavity placed in an external magnetic field. The cavity resonates at a specific frequency determined by its dimensions. The sample under investigation is placed at specific regions where the magnetic field lines are maximum, figure 3.19. As the magnetic field is changed, absorption of the microwaves inside the cavity is measured. When the precession frequency of magnetic moments is the same as the resonant cavity frequency, a maximum absorption is observed.

![Figure 3.19. Schematic of a resonant cavity.](image)

3.5 Summary

This chapter gave an outline of the experimental methods and procedures used in this work. High quality thin films were prepared using rf magnetron sputtering and pulsed laser deposition. Structural characterization was studied using X-ray diffraction, scanning
electron and atomic force microscopy. Measurements of microwave properties required fabrication of coplanar waveguides using microlithography, and assembly of a home-made microwave probe station in a magnetic field. Scattering parameters were measured using a vector network analyzer. In addition, ferrimagnetic resonance measurements were performed through collaboration using a microwave resonant cavity. Following chapters elaborate on the results obtained from these experiments.
CHAPTER 4
BAM-BST COMPOSITE THIN FILMS

This chapter contains a brief summary of the author’s work for his master’s thesis [47] and the publications that followed [48, 49]. Much of this dissertation is based on the results and experiences of this work. The film preparation, Cobalt-implantation and some structural characterization were done in Dr. N. J. Dudney’s laboratory at the Oak Ridge National Laboratory, during a summer internship in 2001. Magnetic characterization was done at the University of South Florida.

4.1 Composite Thin Films

Composite thin films of BST/BaM were synthesized using RF magnetron sputtering and their magnetic response was studied using PPMS. Different volumetric proportions of BST and BaM phases were sputtered from stoichiometric ceramic target materials (BaM and BST) on to alumina substrates, and the total film thickness was about 2 \( \mu \text{m} \). During the simultaneous sputtering from two targets, the substrate holder was rotated in order to obtain uniform film deposition. The deposition conditions outlined below followed several recipes available in the literature [75, 95] and were varied methodically until high-quality films were obtained confirmed by x-ray diffraction scans.

<table>
<thead>
<tr>
<th>Gas and pressure</th>
<th>Argon, 10 mTorr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposition rate</td>
<td>Varying from 2-5 A/min</td>
</tr>
<tr>
<td>Annealing</td>
<td>10 h at 1000(^{\circ})C in O(_2)</td>
</tr>
<tr>
<td>Thickness</td>
<td>2(\mu\text{m})</td>
</tr>
</tbody>
</table>

Table 4.1. Deposition parameters of thin composite films sputtered at ORNL.

\(^1\)The contents of this chapter have been published in JAP 2003 [48] and ICF-Proceedings 2005 [49].
The films were deposited at ambient temperature and post-annealed in flowing oxygen. Film thickness was determined by a profilometer and the crystal structure and composition by XRD and SEM. Following volumetric compositions were made and their properties compared: pure BaM, pure BST, 25% BaM - 75% BST, 50% BaM - 50% BST, 75% BaM - 25% BST. The figures below (4.1 and 4.2) show the measured properties of the 50%-50% BaM/BST composite.

Figure 4.1. XRD of 50% - 50% BaM/BST sputtered composite thin film on alumina.

Figure 4.2. SEM of 50% - 50% BaM/BST sputtered composite thin film on alumina.
The XRD scan shows a polycrystalline film with all the peaks accounted for by BST and BaM phases and their orientation is appropriately labeled using powder diffraction database [1, 2, 3]. The peaks without labels are attributed to the alumina substrate. The sharpness of the peaks and the absence of other impurity phases indicate that these two phases coexist without mutual degradation. This is an important result which demonstrates the formation of BST/BaM composites in thin-film form. The SEM scan shows a coarse crystallite structure of the film surface. Using local chemical analysis with an energy dispersive spectroscopy capable SEM, it was confirmed that the brighter crystallites are Fe rich, indicating that these are the hexaferrite crystallites that are embedded in a more continuous surrounding BST matrix [47]. Formation of elongated crystallites and network structure as seen in the SEM image is typical and has been observed in other hexaferrite films [93]. The figure 4.3 shows the M-H hysteresis loop for the 50% BaM/BST composite measured at 300K using PPMS, after the diamagnetic background had been subtracted to obtain the intrinsic magnetic parameters of the ferrite alone (due to presence of alumina substrate and BST, the raw magnetization curve shows large negative slope, typical of a diamagnetic material). At room temperature, a coercivity ($H_c$) of nearly 6 kOe is obtained.
with a somewhat modest saturation magnetization ($M_s \approx 80 \text{ emu/cm}^3$). The most striking feature seen in the M-H data is the presence of a distinct double transition evident from the shape of the loop, which is only observed in the BST/BaM composite films and not in the pure BaM films grown under identical deposition conditions. So, it appears to exclusively be a property in composites and suggests a strong possibility of influence of BST on the shape and orientation of hexaferrite crystallites and overall magnetic properties. The double transition was also observed in composites of other ratios (75% and 25%) of BaM to BST, and comes from the presence of two types of BaM crystallites with different shapes and orientations. A more detailed explanation is given in chapters 6.4 and 6.5 where it will be shown that PLD deposited composite thin films from a single composite target also show a similar behavior.

4.2 Cobalt-Implantation of Composite Thin Films

From the above mentioned composite films, two sets were grown under identical conditions. One of them was subjected to high energy Co ion implantation using the ion-beam facility at the ORNL. Surface bombardment with high-energy ions and implantation has been known to alter the crystallite structure and possibly break down the average crystallite size from the micron to nanometer length scale. It has also been reported that the ion tracks create local stresses and thus change the local magnetic properties [26]. The table below lists the key parameters used during the Co ion implantation process.

<table>
<thead>
<tr>
<th>59Co$^+$</th>
<th>Energy of the beam</th>
<th>Beam Flux</th>
<th>Thin film heated by the beam</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beam 1</td>
<td>450 keV</td>
<td>$8 \cdot 10^{16}/\text{cm}^2$</td>
<td>90$^\circ$ C</td>
</tr>
</tbody>
</table>

Table 4.2. Cobalt-implantation process parameters.

A comparative analysis of the microstructure and magnetic properties in bare and ion-implanted BST/BaM composite films is presented below. The microstructure variation in Co ion-implanted composite films, in comparison with samples without any surface
modification, is shown in Fig. 1. These are typical SEM images for one particular case with the ferrite component being 25%.

Figure 4.4. SEM of 25% - 75% BaM/BST sputtered composite thin film on alumina: (a) pure composite film, (b) Co-implanted composite thin film.

The trend seen in these images is also present in samples with different ratios of the BaM to BST. The bright regions correspond to the BaM crystallites and this fact was confirmed by doing local energy dispersive spectroscopy (EDS) on individual crystallites to ascertain the chemical phase [47]. From a comparison of the two SEM images, a significant reduction in the size of the ferrite crystallites is evident in the Co-implanted film with the size range anywhere between 40 and 150 nm. As will be seen in the later part of the discussion, this modification in the microstructure has significant impact on the magnetic properties. The expectation was that with Co-ions, the radiation damage combined with possible magnetic contributions from Co itself could be used to tune the magnetic response in the hexaferrite samples. However, it should be noted that the fluence of Co ions in the beam flux is pretty low and unlikely to play any significant role in altering the local magnetization. Rather, it is expected that any change in magnetic response would primarily be a result of the modification of the BaM crystallite structure caused by the ion implantation. Radiation damage in permanent magnetic materials has been studied in the past and it is generally understood that this will reduce the overall magnetization [59]. The mechanism is due to the altered local microstructure. Local heating by the intense ion beams above the Curie
temperature results in stabilizing regions with opposite magnetic orientations resulting in an overall demagnetization effect. While the reduction in saturation magnetization can be reconciled, it would be of interest to see how this ion-beam modification would affect the coercivity and the shape of hysteresis loops.

Figure 4.5. M-H loops of Co-implanted BaM/BST sputtered composite thin films on alumina: (a) 75% BST - 25% BaM, (b) 50% BST - 50% BaM, (c) 25% BST - 75% BaM.

The figure 4.5 shows the M-H hysteresis loops for different composites at 300K and 5K. A diamagnetic background was seen in all composites and this was corrected in the data shown here. All the curves show sizable coercivity consistent with a hard magnetic
BaM phase. A distinct feature is a sharp double-transition in the M-H data seen in the composite films that was discussed earlier. The coercivity ($H_c$), saturation magnetization ($M_s$), and the remanent magnetization ($M_r$) decrease as the BST content increases. The decrease in $H_c$ with addition of BST was also reported recently in bulk composite samples of Z-type hexaferrite ($\text{Ba}_3\text{(Co}_{0.4}\text{Zn}_{0.6})_2\text{Fe}_{23.4}\text{O}_{41}$) and attributed to the decrease in effective magnetocrystalline anisotropy [56]. For all the composites, with increase in temperature the saturation magnetization decreases but the coercivity increases. This is opposite to what one would normally expect and can be understood by taking into account the competition between the shape and magnetocrystalline anisotropy in the system [74].

The M-H curves and the double-transition feature in Co-implanted films are qualitatively similar in shape to that in bare composites but quantitative differences can be noted. There is a “pinching off” near zero fields, leading to a decrease in the coercivity in the ion-implanted composite films. However, the 75% BST sample does not show this trend and instead has a larger coercivity for the Co-implanted case. This reflects the significant role that BST matrix plays in mediating the magnetic interactions between ferrite crystallites. The remanent field also is significantly reduced because of the shape of the loop. The decrease in $M_s$ with irradiation is also observed in bubble garnet films [34] and is attributed to the decrease of the ferrimagnetically ordered volume due to the formation of nuclear tracks. These magnetic parameters for all the samples studied are tabulated in table 4.3.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Before Co-Implantation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$H_c$ (Tesla)</td>
</tr>
<tr>
<td>25% BST - 75% BaM</td>
<td>0.58</td>
</tr>
<tr>
<td>50% BST - 50% BaM</td>
<td>0.16</td>
</tr>
<tr>
<td>75% BST - 25% BaM</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Table 4.3. Magnetic parameters of the Cobalt-implanted composite thin films.
The changes in magnetic properties are clearly due to the influence of the strong coupling between the microstructural modifications with the magnetism. The decrease in coercivity is expected just from the consideration of the smaller crystallites size seen from the SEM images of the Co-implanted samples. In nanostructured materials, it is well known that as the crystallite size is reduced, there is initially an increase in the coercivity followed by a rapid decrease as the size is reduced further [46]. There are also additional stress-induced changes in local permeability that one should consider in ion-implanted materials. This has been observed by other groups [26]. These observations clearly show that the coercivity and remanence can perhaps be controllably varied even with the overall M-H shape still preserved. This could have important implications for recording media where materials with high anisotropy (like hexaferrites) are needed but lower fields are desirable from a practical point of view.

4.3 Summary

Structural and magnetic properties of sputtered ferrite-ferroelectric composite thin films were investigated. A set of films was also subjected to high energy Cobalt-ion implantation. Hysteresis loops exhibited a double transition that is observed only in the composite films and not in pure hexaferrite films grown under identical deposition conditions. The unusual feature in the M-H data is ascribed to the existence of BaM crystallites with different shapes and orientations influenced by the surrounding BST matrix. The most striking feature in the Co-implanted films was the reduction of the ferrite crystallite size seen in the SEM scans. That had a direct influence on the reduction of the coercivity and saturation magnetization of the samples as seen in the M-H loops.
CHAPTER 5
SPUTTERED BAM-BST THIN FILM MULTILAYERS¹

After the success of the sputtered composite thin films, the research on BaM-BST system continued, and multilayered thin films of BaM and BST were grown using RF magnetron sputtering during another internship at ORNL in 2003, as well as during several research visits to Professor K. Coffey’s laboratory at the UCF-AMPAC facilities in 2004 and 2005. This chapter is a summary of the work on sputtered BaM/BST multilayers which resulted in two publications [41, 109].

5.1 Thin Film Multilayers Sputtered at ORNL

The work on the sputtered thin film multilayers was done together with N. Frey and Dr. S. Sanyadanam, only partial results that are relevant to this dissertation are presented here. More detailed discussion can be found in the referred publications.

Multilayers of BST and BaM were deposited on alumina and silicon substrates using RF magnetron sputtering in the presence of high purity (99.999%) Ar gas. The as-grown films were amorphous and were subsequently annealed at 1000°C in flowing O₂ for 10h to obtain crystalline single phases. Films on silicon substrates displayed poor adhesion and flaked off during annealing. It was found that heating the substrate could surmount this problem while sputtering, resulting in good adhesion and a high-quality film. The thickness of the entire films consisting of a stack of four alternating layers of BST and BaM was optimized to be around 1.5 µm. The table 5.1 summarizes the growth conditions for each layer. The base pressure in each case was less than 6.8*10⁻⁶ Torr. Technical difficulties limited the substrate heating to 350°C during the sputtering. However, this temperature

¹The contents of this chapter have been published in JAP 2005 [109] and MRB 2005 [41].
was not sufficient to get the proper crystalline phases and annealing was necessary. Multilayers were deposited on polycrystalline alumina and (100) oriented Si substrates.

<table>
<thead>
<tr>
<th>Base Pressure= 6.8 × 10^{−6} \text{Torr}</th>
<th>First Layer</th>
<th>Second Layer</th>
<th>Third Layer</th>
<th>Fourth Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposition temperature 350°C</td>
<td>(BST)</td>
<td>(BaM)</td>
<td>(BST)</td>
<td>(BaM)</td>
</tr>
<tr>
<td>Argon pressure (mTorr)</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Argon flow (sccm)</td>
<td>57.0</td>
<td>56.7</td>
<td>56.6</td>
<td>56.4</td>
</tr>
<tr>
<td>Power (W)</td>
<td>71</td>
<td>70</td>
<td>71</td>
<td>70</td>
</tr>
<tr>
<td>DC Bias (V)</td>
<td>146</td>
<td>242</td>
<td>148</td>
<td>245</td>
</tr>
<tr>
<td>Deposition rate (/min)</td>
<td>60.0</td>
<td>39.2</td>
<td>71.6</td>
<td>46.4</td>
</tr>
</tbody>
</table>

Table 5.1. Multilayer sputtering parameters.

Figure 5.1 shows the representative X-ray diffraction pattern of the multilayer alumina/BST/BaM/BST/BaM. The spectrum indicates the presence of the desired composite multiphase consisting of reflections from BST and BaM and also those of the alumina substrate. No traces of impurity were found, however possibility of inter-diffusion at the interfaces of the multilayer structure cannot be ruled out. Multilayers grown on Si(100) displayed poor crystallographic texture. Traces of impurity phases were found (not shown here) indicating the interaction of Sr with the Si substrates forming Sr_{3}Si_{3}O_{9}. It is believed that this impurity chemical phase should show no discernible influence on the functional magnetic properties of the multilayer structure.

Figure 5.1. X-ray diffraction of BaM-BST multilayers. BaM and BST phases, as well as the peaks of alumina substrate are indexed.
Magnetization measurements were performed at various temperatures using PPMS. Measurements were done on all samples with magnetic field applied parallel (in-plane) and perpendicular (out-of-plane) to multilayer plane at 10 and 300 K. In figure 5.2(a), the in-plane hysteresis loops measured at 10 and 300 K for samples on alumina and Si are shown. Presence of large coercivity at 10 K ($H_c \approx 1450$ Oe) and at 300 K ($H_c \approx 2300$ Oe) for multilayer on Si and for alumina sample at 10K ($H_c \approx 2200$ Oe) and at 300K ($H_c \approx 1550$ Oe) is consistent with the hard magnetic nature of the BaM.

![Magnetization loops](image)

Figure 5.2. Magnetization of BaM-BST multilayer: (a) Temperature dependence of in-plane magnetization of BaM-BST multilayers., (b) Anisotropy of BaM-BST multilayers at 10K.

Figure 5.2(b)-top shows the magnetization hysteresis loops of the multilayer on Si with applied field parallel (in plane) and perpendicular (out-of-plane) to the film plane. The perpendicular coercivity $H_{c\perp}$ and the in-plane coercivity $H_{c\parallel}$ at 10 K are 1250 Oe and 1450 Oe, respectively and the squareness S (the ratio of remanence magnetization to saturation magnetization) of the perpendicular and parallel loops are 0.45 and 0.6, respectively. The difference in magnetization in two different directions of the multilayer plane indicates that there is a preferential orientation of magnetization along a favored direction, which is a characteristic of barium ferrite thin films. The BST layers and the Si substrate contribute to a diamagnetic background, which is reflected in the negative slopes of the M-H curves at higher fields and had been subtracted in the data shown. In can
be seen that with increasing temperature $H_c$ increases and the magnetization decreases. This trend is opposite to the expected behavior in bulk magnetic materials where larger coercivities are generally observed at lower temperature. In contrast, sample on alumina (figure 5.2(b)-bottom) shows no such deviation upon changing orientations of the magnetic field, because polycrystalline alumina substrate does not allow any crystallite orientation. The value of $H_c$ as a result remains the same in both directions and the value of $H_{c\perp}=H_{c\parallel}$ at 10 K is 2600 Oe. The results presented above are consistent with those reported for pure BaM films deposited using PLD heated in situ at 900°C on Si(100) substrates [85]. The $H_c$ values of various multilayer samples at 10 and 300 K are summarized in table 5.2.

The increase in $H_c$ in the present case with temperature may be due to the competition between the shape and magnetocrystalline anisotropies. The theoretical coercivity of a random array is shown in table 5.3 [74].

$$H_C = 0.48 \cdot (2K/M_S - N \cdot M_S)$$

Table 5.3. Dependence of thin film coercivity on anisotropy

As $M_S$ decreases with increase in temperature, the contribution from the shape anisotropy decreases and $H_c$ increases with temperature. The shape of the BaM crystallites depends very much on the type of substrate and substrate deposition temperature [85]. The films
here were grown at moderate temperatures (≈ 350°C) and not sufficiently high enough to cause crystallization. This temperature-dependent growth and crystallite structure of BaM may explain the variations in coercivity values observed here.
5.2 Thin Film Multilayers Sputtered at UCF

Following the inspiring results from the sputtering of the BaM/BST multilayers at ORNL, several research trips to UCF-AMPAC were made in order to deposit more thin films using RF magnetron sputtering. This facility did not have an option of heating the substrate during the deposition, thus several other deposition and postannealing methods were tried out. The table 5.5 lists the deposition parameters used in this process.

<table>
<thead>
<tr>
<th>UCF magnetron sputtering deposition parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF magnetron sputtering unit from AJA International.</td>
</tr>
<tr>
<td>Power: BaM = 70W, BST = 80W.</td>
</tr>
<tr>
<td>Gas pressure: 20 mtorr, 80% Ar + 20% O₂.</td>
</tr>
<tr>
<td>Substrate temperature = ambient temperature.</td>
</tr>
<tr>
<td>Targets: 3&quot; powder-pressed BaM and BST.</td>
</tr>
<tr>
<td>Substrates: 10 mm x 10 mm one-side polished C-sapphire, A-sapphire and (100) MgO.</td>
</tr>
<tr>
<td>Substrate-target distance = 2 cm.</td>
</tr>
<tr>
<td>Postannealing in furnace at 800°C - 1100°C in flowing O₂.</td>
</tr>
<tr>
<td>Films thickness varies 0.5 - 1.5 microns.</td>
</tr>
</tbody>
</table>

Table 5.4. UCF magnetron sputtering deposition parameters

Thin film multilayers of different total thickness were deposited. This time, instead of alumina substrates, oriented sapphire (C- and A-orientation) and (100) MgO substrates were used. BaM was always deposited first on sapphire substrate, while BST was the first layer on MgO. Oriented thin films grown on these substrates using sputtering were reported by several authors [57, 58, 75, 93, 95]. Unfortunately, in all these studies substrate was heated during the deposition to promote film growth and film adhesion. In order to overcome this, postannealing was done at several temperatures and at various annealing and heating/cooling times. In addition, very thin seed-layers (a few nm) of the first layer were deposited, then annealed, followed by a deposition of a multilayer, which again was postannealed. There were no problems with the film adhesion that was seen in earlier depositions on Si, or with formation of different phases. The multilayers had in general
sharp transitions without much integration as seen from the SEM scan of one sample on sapphire in figure 5.3.

![Figure 5.3. Cross-sectional SEM scan of BaM-BST multilayer on sapphire.](image)

The main problem in the film preparation was the crystallization. Most of the films were amorphous or showed poor crystallization even after annealing. The table 5.5 outlines some of the results of these experiments.

<table>
<thead>
<tr>
<th>Layer</th>
<th>&gt; 1.5 μm</th>
<th>≈ 1.0μm</th>
<th>&lt; 0.5 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>C/BaM/BST</td>
<td>BaM mostly 001-oriented</td>
<td>No BaM peaks</td>
<td>Very good BaM 001 orientation</td>
</tr>
<tr>
<td></td>
<td>BST polycrystalline with strong 110 peak</td>
<td>BST weakly polycrystalline</td>
<td>No BST peaks</td>
</tr>
<tr>
<td>MgO/BST/BaM</td>
<td>BST 100-orientation</td>
<td>BST strong 100 orientation</td>
<td>BST very good 100 orientation</td>
</tr>
<tr>
<td></td>
<td>BaM mostly 110 oriented</td>
<td>BaM weak 110 peak</td>
<td>No BaM peaks</td>
</tr>
</tbody>
</table>

Table 5.5. Partial results from sputtering at UCF. All films were postannealed in O2.

As it can be seen, most of the films were polycrystalline or even weakly polycrystalline (only very small and broad peaks detected by the XRD scan), some even amorphous. These results indicate that substrate heating plays very important role in obtaining high quality films, and it can not be replaced by using seed-layers and postannealing.

### 5.3 Summary

Thin film multilayers of BaM and BST were sputtered onto different substrates under various conditions. The films deposited on heated alumina and Si were polycrystalline and
showed some unusual magnetization properties that were explained as competition between magnetocrystalline and shape anisotropy. The sputtered films on sapphire and MgO at ambient temperature showed poor crystallinity, even after annealing. The main conclusion is that the deposition temperature, choice of substrate as well as presence of BST strongly influence the structural and magnetic properties of BaM films.
CHAPTER 6
PULSED-LASER DEPOSITED BAM-BST BILAYERS AND COMPOSITE THIN FILMS

The results from the previous chapter showed that substrate heating as well as the substrate choice are essential factors for obtaining high quality oriented thin films. In addition to RF magnetron sputtering, pulsed laser ablation (PLD) is another successful technique for deposition of quality thin films with excellent stoichiometry [25]. In this chapter, the results from the PLD deposition of BaM/BST bilayers and composite thin films are presented. The deposition was done at the Laboratory for Advanced Materials and Technology (LAMSAT) at USF, and all characterization was done at USF facilities. The table 6.1 lists the typical deposition parameters used in this study.

<table>
<thead>
<tr>
<th>Pulsed-laser deposition parameters</th>
</tr>
</thead>
</table>
| Excimer laser KrF $\lambda = 248\text{nm}$.
| Energy density = 4 - 9 J/cm$^2$.
| PLD rate increased gradually from 1 to 10 pps in first 10 minutes.
| Substrate temperature = 650$^0$ C (with silver paste).
| Gas: high purity O$_2$ at 250 mtorr.
| Targets: 2" powder-pressed BaM, BST and BaM-BST (50%-50% by weight).
| Substrates: 10 mm x 10 mm one-side polished C-sapphire, A-sapphire and (100)-MgO.
| Substrate-target distance = 5.5 cm.
| Films cooled after deposition in 1 atm O$_2$ at 5$^0$C/min.
| Postannealing in furnace at 900$^0$C in flowing O$_2$.
| Total film thickness about 1 micron.

Table 6.1. Pulsed-laser deposition parameters

Bilayers as well as composite BaM/BST films were deposited onto polished sapphire (A- and C-oriented) and (100-oriented) MgO substrates. Prior to the deposition, the as-

1The contents of this chapter are published in [50, 51]
received substrates were ultrasonically cleaned in acetone, rinsed with methanol, and dried with nitrogen. KrF pulsed excimer laser was used to ablate the material from the rotating target to the substrate, as illustrated in the figure 3.2. The laser energy density was focused to about 8.7 J/cm$^2$ for BaM, 4.3 J/cm$^2$ for BST and 6.5 J/cm$^2$ for the composite target. The composite target was made by mixing 50% by weight BaM and BST powders, and pressing the mixture into a 1” pallet. The substrates were positioned 5.5 cm away from the target and parallel to the target surface. The ideal deposition temperature for BaM on sapphire is reported to be around 920$^0$C [105, 107], while the ideal deposition temperature for BST varies from 775$^0$C to 820$^0$C [19, 62]. The maximum deposition temperature with this set-up was 650$^0$C using a quartz lamp, thus this temperature was also chosen as the deposition temperature. A thin layer of silver paste was carefully applied to the back of the substrates in order to promote uniform heat flow from the substrate heater to the deposited film during the heated deposition. Before deposition, the chamber was evacuated for several hours to a pressure below 10$^{-5}$ torr, and then high purity oxygen (99.999%) was introduced. All depositions were done at constant O$_2$ pressure of 250 mtorr. After the deposition, the films were slowly cooled \textit{in-situ} to room temperature at almost 1 atm gas pressure. All films were also postannealed \textit{ex situ} in a quartz tube furnace in flowing O$_2$. After several postannealing trials, the most successful annealing procedure in terms of crystallographic structure was determined to be as following:

- Increase the temperature from room temperature to 900$^0$C in 3 hrs.
- Anneal at 900$^0$C for 8 hrs.
- Decrease the temperature from 900$^0$C to room temperature in 3 hrs.

All subsequent PLD films were prepared this way. At the beginning of the deposition, the laser pulse rate was increased from 1 pps to 10 pps gradually over a time period of 10 min. This step was needed to promote initial crystal growth as reported by other authors.

\footnote{Due to the age and the quality of the laser system and the optics, the real laser energy could have been less than reported here.}
After that, the rate was kept at 10 pps. Depending on the target materials and desired film thickness, the total number of pulses varied. When depositing more than one layer, the chamber had to be opened, the target was changed, and the above procedure was repeated.

The texture and surface morphology analysis was performed in order to study the structural quality of the films. The magnetization measurements were also studied using PPMS. These results are presented for each film type in the following sections.

The crystal structures of BaM and BST were already described in the chapter 2, BST having a cubic and BaM having a hexagonal crystal structure. Depending on the crystallographic orientation of the substrates and the underlying thin films, the growth orientations of the film on the top varied. The reason is that during the initial stage of the deposition, the film orientation is adjusted to the substrate to minimize lattice mismatch. Some typical orientations of the cubic and hexagonal crystal lattices are shown in figure 6.1. Depending on the preferred film orientation, Bragg-reflections from different planes are visible in the X-ray pole-plot.

![Figure 6.1. Crystal plane orientations: (a) cubic lattice (b) hexagonal lattice.](image)
6.1 BaM-BST bilayer on C-sapphire

BaM/BST bilayers were deposited on C-oriented sapphire substrates and compared with pure BaM films deposited on the same substrate. Figure 6.2 illustrates the arrangement of layers and shows their preferential orientation. The first layer (BaM) was deposited using 45,000 pulses, resulting in a thickness of $\approx 500$ nm, and the second layer (BST) needed 61,000 pulses for the same thickness. The pure BaM film was deposited using 46,000 pulses. Four samples were deposited simultaneously and used for different studies. The as-deposited films were crystalline, but it was determined that postannealing further improved the crystallographic structure.

![Figure 6.2](image-url)  
Figure 6.2. PLD deposited thin films on C-sapphire substrate: (a) BaM single layer (b) BaM-BST thin film bilayer.

The X-ray diffractograms of the C/BaM/BST bilayer are shown in figure 6.3. The main figure shows a $\Theta - 2\Theta$ scan of the sample. Each peak is labeled according to its crystallographic orientation. In case of the BaM film, the “third” index is usually omitted for simplification (e.g. (006) instead of (0006)). It can be seen that all peaks come either from the substrate, BaM or BST. The BaM film shows only peaks belonging to the (00l) group of peaks, indicating that the c-axis of the hexagonal structure grows out of the thin film plane. On the other hand, the two sharp BST peaks (111) and (222) show a strong alignment in the (hhh) direction. The analysis of the degree of film alignment from the $\omega$-scans (rocking curves) reveals low dispersion and epitaxial nature of the bilayers: the full-width-at-half-maximum is FWHM = 0.37° for BaM (008) peak and 0.41° for BST (111) peak. These values correspond to highly oriented epitaxial films. BaM thin films deposited under similar conditions but at higher temperatures show slightly lower values of FWHM (around 0.15°) [105, 107]. The BST layer, as it will be seen later, also influences
the orientation of the BaM film at the interface. BST has a cubic crystal structure as described in chapter 2.2, with the lattice parameter around 3.95 Å. Its crystal structure is similar to MgO that has a lattice parameter around 4.2 Å (in next section it will be seen that BST grows epitaxially on MgO). It was shown in [110] that MgO thin film deposited on a C-oriented sapphire substrate grows in preferential (111) orientation, with FWHM of 2.4°, indicating large mosaicity. This suggests that if MgO (111) grows on C-sapphire, and BaM (001) grows epitaxially on C-sapphire, that BST (111) would also grow on BaM (001), which is indeed the case here. In addition, both C-oriented BaM as well as (111) BST films have been successfully grown on (111) MgO [89, 91, 94], thus it was intuitive to try growing (111) BST films of C-oriented BaM. It has also been reported that (111) BST films exhibit similar properties as (100) films at microwave frequencies [91].

The small FWHM in the rocking curve of the BST films suggests a better lattice match compared to the MgO grown on C-sapphire, probably due a smaller difference in the lattice parameter. Growth conditions play a significant role as well in determining the overall quality of the films. The values of FWHM of this BST film are even better than the FWHM values of the BST film grown directly on (100) MgO as seen in the next section (0.47°) and BST films grown on (100) and (110) MgO (0.54° and 0.51°, respectively) reported by [90].

The figures 6.4(a and b) reveal the crystallographic texture analysis of the C/BaM/BST bilayer. Because (001) planes of BaM crystallites and (111) planes of BST crystallites are parallel to the film surface, a different set of planes needs to be chosen for the pole plot and φ-scan [105]. Figure 6.4(a) is an XRD pole plot of BaM (107) peak and BST (200) peak, both being the strongest peaks in the θ−2θ scan of the X-ray diffraction pattern [2, 3]. The figure 6.4(b) is a φ-scan at Ψ = 35° for BaM and at Ψ = 55° for BST. There are six peaks in the pole plot of the BaM film and also six peaks in the pole plot of the BST film. (111)-BST has a three-fold symmetry about the axis perpendicular to the plane [110]. Occurrence of six poles in the BST film indicates presence of two sets of epitaxial single crystallites rotated by 60° to each other - [(200), (020), (002), (200), (200), (200)]. This phenomenon is called
twinning and develops during film growth, or cooling from high-temperature deposition
to room temperature, when there is a large lattice mismatch [70]. The \( \phi \)-scans, which
are performed at higher resolution, actually confirm this and show an additional set of
three poles separated by 120°. This result indicates that the BST film is not purely single
crystalline, but epitaxially polycrystalline. One set of three poles and one set of six poles
of BST(111) film grown on MgO(111) was also observed by [91]. In the case of BaM film,
the six peaks come from the six sets of (107) planes associated with the six faces of the
hexagon. Every time the sample is rotated by 60° a Bragg’s condition is satisfied, resulting
in a peak. This is consistent with epitaxial growth of BaM, with crystalline axis of BaM
being parallel to the (0001) axis of sapphire, also reported by [57, 105]. The \( \phi \)-scan reveals
that there are also two sets of three peaks separated by 120° - one at (-120°, 0°, 120°), and
the other, very small one at (-60°, 60°, 180°). This was also observed in the single layer
BaM film (not shown here). This indicates a presence of other sets of crystallites, tilted
from the C-axis due to the twinning, as will be evident in the magnetic properties of the
sample. This defect most likely has to do with insufficient temperature during deposition
process. Other films grown at higher temperatures do not show this [57, 105, 107].
temperatures above 900°C, the lattice mismatch between the BaM and sapphire substrate is less than at the room temperature. The lattice parameters of the a-axis of BaM and sapphire are 5.89 Å and 4.75 Å, respectively, while the expansion coefficients are $\alpha_a = 9.99$ ppm/°C for BaM and $\alpha_a = 4.9$ ppm/°C (at room temperature) and $\alpha_a = 15.6$ ppm/°C (at 500°C) for sapphire [33]. The lattice parameter expansion coefficient of sapphire is much smaller than for BaM at room temperature, but it increases with temperature, and only at elevated temperatures, the gap between the lattice parameters starts to shrink. Due to the capabilities of commercial substrate heaters, maximum temperatures for thin film deposition are usually around 900-1000°C, thus this range was also established by others as optimal growth temperature for BaM films [105, 107].

Figures 6.5(a and b) present room temperature magnetic hysteresis loops (M-H curves) of the BaM single layer (a) and the BaM/BST bilayer (b), with magnetic field applied parallel (in-plane) and perpendicular (out-of-plane) to the film surface. The diamagnetic contributions (manifested by a negative slope in the M-H curves) coming from the substrate and BST film have been subtracted. A large out-of-plane anisotropy is observed, typical for out-of-plane grown crystallites, with easy magnetization axis perpendicular to the film
Figure 6.5. In-plane and out-of-plane magnetization of PLD deposited thin films on C-sapphire substrate: (a) single layer BaM thin film (b) BaM-BST thin film bilayer.

plane. The in-plane magnetization does not reach the saturation at the maximum field of 12 kOe, because of large anisotropy field, which is around 17 kOe [77]. The squareness and the coercivity of the out-of-plane loop of the single layer are small (≈ 0.22 and 545 Oe, respectively), making it magnetically soft, which is good for low loss high-frequency applications. The bilayer is magnetically harder, with squareness of 0.62 and coercivity of 1850 Oe. This is most likely caused by the BaM/BST interface and is also noticed in the bilayer grown on A-oriented sapphire samples. A possible explanation is given in section 6.3. The M-H loops of a single layer BaM film are comparable with the data by [105] in figure 6.8-right panel, although their films were deposited at a higher temperature. A slight broadening of the in-plane hysteresis loop is observed in both single BaM as well as BaM/BST bilayer. This is caused by a presence of a small amount of in-plane oriented crystallites, also evident from the X-ray diffraction analysis.

The atomic force micrographs in figures 6.7 reveal the surface morphology of BaM single layer thin film. Hexagonal crystallites are seen growing out of the film plane, consistent with the magnetization studies. One can also observe the presence of small “particles” at the crystallite edges, roughly 2-5 nm in diameter. These are likely BaM atomic clusters, coming from unstable growth and “mound” formation during deposition process, as illustrated in figure 6.6. The mounds occur when the diffusing adatoms are reflected from the descending
step edges and attach to the ascending steps [35]. The BaM film grown at 920°C as reported by [105], experiences large shear due to the lattice distortion of BaM at the interface with the substrate. This creates screw locations that propagate from the interface all the way to the film surface, creating spirally winding steps and terraces (see figure 6.8, left panel at the bottom). The film grows by depositing BaM atoms onto these steps. Due to the lower deposition temperature in this case, some of these atoms seemed to have nucleated at the crystallite edges.

Figure 6.6. Bilayer thin film growth during deposition [35].

Growth and characterization of PLD deposited BaM thin films on C-oriented sapphire was thoroughly investigated by [105], and it is very comparable with the data presented here, considering that the growth temperature here was around 650°C, and the films were postannealed at 950°C. The magnetization from figure 6.5(a) for single layer BaM film fits well with the data in figure 6.8 - between figures (c) and (d), on the right panel. The AFM scans in figure 6.7 showing out-of-plane grown crystallites also correspond well with the AFM scans in the left panel and illustrations in the middle panel of figure 6.8 for the temperature between 700°C and 920°C. This shows repeatability of the film preparation, even with some small adjustments in the growth conditions.
Figure 6.7. Atomic force microscope scan of single layer BaM thin film on C-oriented sapphire substrate: (a) 2.5 µm x 2.5 µm area scan, (b) 1.0 µm x 1.0 µm area scan.

Figure 6.8. Results from PLD deposited BaM films on C-sapphire by [105].
6.2 BaM-BST bilayer on (100)-MgO

Next sample is a BST/BaM bilayer grown on (100)-oriented MgO substrate under same conditions. MgO is an excellent dielectric substrate for microwave applications with dielectric constant $\epsilon = 9.5$ and loss tangent $\tan\delta = 1 \times 10^{-5}$ being lower than other substrates used for BST growth (LaAlO$_3$, alumina, sapphire). It has a cubic crystal structure with lattice parameter of $a = 4.214\AA$, and represents a relatively good substrate match to BST, which has $a = 3.947\AA$, although a 6.4% lattice mismatch suggests that the epitaxial growth might be difficult to achieve. High quality BST films grown on (100)-MgO have been reported by others [20, 22, 62, 90, 99]. First a 0.5 $\mu$m BST layer was deposited on the MgO substrate using 60,000 pulses, and subsequently a BaM layer of same thickness was deposited using 45,000 pulses.

![Diagram](image.png)

Figure 6.9. BST-BaM bilayer thin films on 100-MgO.

The $\theta - 2\theta$ scan in figure 6.10 reveals only $(h00)$ peaks in the BST film and $(00l)$ peaks coming from the BaM film. No secondary orientations were observed, suggesting that the films are unidirectional and single phase. The $\omega$-scans shown in the inset confirm a good degree of out-of-plane orientation - FWHM of BaM (008) peak is $0.55^0$ and of FWHM of BST (200) peak is $0.47^0$.

Figure 6.11 shows a texture analysis of the BST film. BaM film could not be analyzed because reflections from all possible planes lie too close to the reflections of the BST planes, which are much larger in magnitude. The pole plot of the (220) BST peak at $2\theta = 67.012^0$ indicates a presence of two sets of four poles, one at $\Phi = 25^0$ and the other at $\Phi = 45^0$, consistent with the calculation of the interplanar angles. For a cubic system, the angle between the atomic planes can be expressed as [37]:

73
Figure 6.10. Θ - 2Θ scan of BST-BaM bilayer on (100) MgO substrate. Inset: rocking curves of BaM (008) and BST (200) peaks.

\[
\phi = \cos^{-1}\left(\frac{h_1h_2 + k_1k_2 + l_1l_2}{\sqrt{(h_1^2 + k_1^2 + l_1^2)(h_2^2 + k_2^2 + l_2^2)}}\right)
\]

There are only two sets of four poles satisfying this relationship for the given \(\phi\) angles - \([(220), (2\overline{2}0), (\overline{2}20), (\overline{2}00)]\) and \([(200), (\overline{2}20), (020), (0\overline{2}0)]\). The \(\phi\)-scan in figure 6.11(b) taken at \(2\theta = 67.012^0\) and \(\Phi = 45^0\) indicates excellent in-plane epitaxy, as no additional peaks are observed. Both pole plot and \(\phi\)-scan confirm that the BST film grows epitaxially on the MgO substrate.

Even though the X-ray diffraction scans show good quality BaM film with the c-axis growing out of film plane, the in-plane and out-of-plane magnetization loops in figure 6.12 do not show a large preferential orientation, as it was seen earlier for the BaM film deposited on C-oriented sapphire. The saturation magnetization along the axis perpendicular to the film plane is only slightly smaller than along the axis parallel to the film plane. This can be explained by looking at the components contributing to the magnetic anisotropy. There is a competition between crystal anisotropy trying to align the magnetization perpendicular to the plane and the shape anisotropy trying to align the magnetization in the film plane.
The AFM scan in figure 6.13 shows a presence of acicular shaped BaM crystallites, oriented in the film plane. This kind of crystallite growth in BaM films has also been observed by others [24, 64, 82, 84, 112, 119], and typically occurs when the growth is not epitaxial, e.g. on substrates such as Si/SiO$_2$, Pt, polycrystalline alumina, etc. It was also reported by [82, 112] that the presence of these elongated in-plane oriented crystallites favors magnetization parallel to the film plane. The effective anisotropy can be calculated from the areas enclosed by the hysteresis loops [97]:

$$K_{eff} = K_\perp - K_\parallel = \int H_\perp dM - \int H_\parallel dM = 0.52 \times 10^6 \text{erg cm}^{-3}$$

where $H_\perp$ and $H_\parallel$ are magnetic fields applied perpendicular and parallel to the film plane, respectively. The magnetocrystalline anisotropy constant can be expressed as:

$$K_1 = K_{eff} + 2\pi M_s^2 = 0.52 \times 10^6 \text{erg cm}^{-3} + 0.6 \times 10^6 \text{erg cm}^{-3} = 1.12 \times 10^6 \text{erg cm}^{-3}$$

with $M_s \approx 315 \text{emu cm}^{-3}$ being the saturation magnetization, after a rough estimate of the volume of the sample $V = 7 \times 10^{-6} \text{cm}^3$. A large difference between $K_{eff}$ and $K_1$ indicates
that the shape anisotropy plays an important role in determining overall magnetization response in this thin film [97]. Approximate values of the magnetization parameters (coercive field and squareness) for in-plane and out-of-plane hysteresis loops are given in table 6.2:

<table>
<thead>
<tr>
<th></th>
<th>$H_c$ (Oe)</th>
<th>$M_r/M_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>IN-PLANE</td>
<td>2045</td>
<td>0.63</td>
</tr>
<tr>
<td>OUT-OF-PLANE</td>
<td>2000</td>
<td>0.58</td>
</tr>
</tbody>
</table>

Table 6.2. Magnetic characteristics of BST/BaM bilayer grown on MgO substrate.

These values indicate that the film has a high degree of magnetic hardness, both in parallel and perpendicular direction of the magnetic field, and these values are well comparable to the other reported values of isotropic BaM thin films [97, 105, 113].

The crucial result of this section is that a good quality BaM film with hard magnetic properties can be grown on high quality BST film. It will be seen in the next chapter that this bilayer BST/BaM film shows large electrical tunability in the frequency range 1-65 GHz, and magnetic tunability in the range 40-60 GHz.
Figure 6.12. M-H loop of BaM-BST bilayer on (100) MgO substrate.

Figure 6.13. Atomic force microscope scan of BST/BaM bilayer on MgO substrate - the top layer seen here is BaM. Scan area = 2.5 µm x 2.5 µm.
6.3 BaM-BST bilayer on A-sapphire

Another BaM/BST bilayer film was grown on A-oriented sapphire substrate under same conditions as the bilayer on C-sapphire substrate in section 6.1. It was reported by [57, 131] that the BaM film deposited on this substrate has its c-axis in the film plane, exactly opposite to the BaM film grown on C-sapphire.

Figure 6.14. PLD deposited thin films on A-sapphire substrate and their crystallographic orientation: (a) BaM single layer (b) BaM-BST thin film bilayer.

Figure 6.15. Θ - 2Θ scan of BaM-BST bilayer on A-sapphire substrate. Inset: rocking curves of BaM (200) and BST (211) peaks.

The appearance of large (h00) type diffraction peaks for BaM in the Θ - 2Θ scan indicates highly oriented single-phase BaM layer. The diffraction peaks of BST (100, 111, 211, and 222) reveal a polycrystalline nature of the BST layer, with 211 peak being the most prominent. Planar orientation was examined using rocking curve (ω-scan) analysis -
Figure 6.16. Crystallographic texture analysis of the BaM-BST bilayer on A-sapphire substrate: (a) XRD pole figure of BaM (220) peak at $2\theta = 63.060^0$ and BST (200) peak at $2\theta = 45.944^0$, (b) azimuthal ($\phi$) scan of BaM (220) peak at $\Phi = 30^0$ and BST (200) peak at $\Phi = 65^0$.

see inset of figure 6.15. Full width half maximum of the BaM (200) peak is 0.50 and 0.89$^0$ for BST (211) peak. This confirms a fairly good orientation of both layers.

The pole plot and the $\phi$-scan in figure 6.16 describe the crystallographic texture of the bilayer. The BaM has one set of two large peaks at $\phi = 90^0$ and $270^0$, as it is expected from crystallites with c-axis in the film plane - there are only two possible reflections from the planes parallel to (0001) and (0001) planes, see figure 6.1. There is also another set of two smaller peaks coming from another set of in-plane oriented crystallites rotated by 70$^0$. This is also confirmed in the $\phi$-scan. No out-of-plane orientation was recorded, indicating a very good crystallographic quality of the BaM film. The pole figure of the BST film shows a presence of multiple crystallites, consistent with the $\theta - 2\theta$ scan. Obviously, there is a poor lattice match between the BaM (100)-plane and the BST, causing a creation of multiple crystallites.

The figures 6.17(a and b) show in-plane and out-of-plane magnetization of single layer BaM film (a) and the BaM-BST bilayer (b). A similar trend can be seen as in figure 6.5, with the difference that in this case the easy axis of magnetization lies in the film plane,
consistent with the orientation of the BaM C-axis. Large out-of-plane magnetic anisotropy is observed, comparable to the results of [130]. Large squareness is also noticeable in the in-plane hysteresis loops (0.87 for the single layer and 0.91 for the bi-layer), making them both magnetically hard in the film plane. A comparison between the out-of-plane magnetization of the single BaM layer and the BaM/BST bilayer, shows that there is some difference in the magnetization characteristics, just like in the case of the bilayer on C-sapphire. It appears that the BST layer has an influence on the shape of the M-H curve again. For example, the coercivity of the bilayer is higher compared to that of the single BaM layer. The coercivities of the in-plane M-H loops are about 1820 Oe and 1870 Oe for single and bilayer, while the coercivities of the out-of-plane M-H loops are 230 Oe and 1525 Oe for the single and the bilayer, respectively. This is an important finding, indicating possible interaction of the layers presumably mediated by strain at the BaM/BST interface. The bottom of the BST layer likely influences the orientation of the BaM crystallites close to its interface causing them to be different (i.e. c-axis oriented out-of-plane) compared to the overall nature of the BaM growth (as seen in the XRD and also AFM images) which favors the in-plane geometry.

The atomic force microscope surface scan is shown figure 6.18. It is not as easy to recognize the crystal structure as in the previous two cases, yet in-plane orientation of the crystallites can be clearly seen.
Figure 6.17. In-plane and out-of-plane magnetization of PLD deposited thin films on A-sapphire substrate: (a) single layer BaM thin film (b) BaM-BST thin film bilayer.

Figure 6.18. Atomic force microscope scan of single layer BaM thin film on A-oriented sapphire substrate - scan area = 2.5 µm x 2.5 µm.
6.4 **BaM-BST composite on C-sapphire**

This and the following section describe the properties of the composite BaM/BST films deposited on C- and A-oriented sapphire substrates. The composite deposited on the MgO substrate was amorphous even after annealing.

The composite film was deposited onto C-sapphire substrate by two different methods. In the first method, the composite film was directly deposited using 62,000 pulses under same conditions as described before (deposition and annealing), resulting in an approximate thickness of 0.5 \( \mu m \). The second method involved a deposition of a seed layer - a thin BaM layer (\( \approx 20 \) nm) deposited at 650\(^\circ\)C using 1100 pulses, then the composite thin film was deposited using 62,000 pulses. The results of these two methods are compared with each other and with the results obtained for bilayer thin films.

The deposition of a seed layer made a large impact on the crystallographic properties of the composite thin films. Additional crystallographic phases were seen in the composite films without the seed layer, which disappeared in the composites grown on the seed layer. The following X-ray diffraction analysis contains only the results of the composite films with the seed layer. The \( \Theta - 2\Theta \) scan in figure 6.20 shows a (00\(l\)) oriented BaM film and (hhh) oriented BST film, with exception of some additional peaks: (203) BaM and (211) BST. The rocking curve of the BaM (008) peak in the inset shows nearly similar results for the BaM/BST bilayer (FWHM = 0.39\(^\circ\)), see figure 6.3. The \( \omega \)-scan of the BST (111) peak shows a larger degree of planar distribution (FWHM = 0.97\(^\circ\)).

The pole plots of the composite thin film are also comparable with the results of the bilayer BaM/BST film on C-sapphire in figure 6.4. There is one set of six poles and one set of three poles coming from BaM and one set of six poles coming from BST. The one
Figure 6.20. Θ - 2Θ scan of BaM-BST composite on C-sapphire substrate. Inset: rocking curves of BaM (008) and BST (111) peaks.

set of three poles of BaM has much stronger reflections than in the bilayer, probably due to a presence of larger amount of BaM crystallites tilted with respect to the C-axis. The occurrence of a (203) BaM peak in the Θ - 2Θ scan could also have an impact on magnetic properties described below. The pole plot and the φ-scan coming from the BST are nearly the same as in the bilayer. These are very interesting results, indicating that BaM and BST favor a particular growth in both composite and the bilayer form. Most likely, there is a presence of separate BaM and BST regions inside the composite films. In these regions, BaM and BST grow separately, but their orientation is influenced by their interface and the interface with the substrate. Thus the growth of both BaM and BST might be controlled by the interface, indicating a possibility of a deposition of multilayers consisting of several alternating layers of BaM and BST, an idea which might be pursued in a separate study.

Figure 6.22 shows the M-H loops of the composites without (a) and with (b) the BaM seed layer, with magnetic fields applied in and out of the film plane. Even though the crystallographic analysis of the composite with the seed layer does not show much difference compared to the bilayer film, the magnetization properties show a significant change. The composite film without the seed layer shows a small anisotropy similar to the multilayer on
MgO, while the film on the seed layer shows a larger anisotropic behavior, very similar to the C/BaM/BST bilayer in figure 6.5. A distinct feature clearly seen in all M-H loops is a presence of a double-hysteresis. This was also reported for sputtered polycrystalline composite BaM/BST thin films on alumina in chapter 4. Occurrence of the double-hysteresis loop in BaM films grown on (0001) sapphire and Si/SiO$_2$/Pt under different conditions was also reported by [84, 111]. Their explanation was a presence of two different types of BaM crystallites - platelet-shaped crystallites preferring out-of-plane orientation and acicular crystallites preferring in-plane orientation. In the previous case reviewed here, the BaM grown on C-sapphire has out-of-plane oriented platelet-crystallites, BaM grown on A-sapphire has in-plane oriented platelet-crystallites, and BaM grown on MgO/BST has in-plane oriented acicular crystallites, but none of these films have both platelets and acicular crystallites. This is probably only the case in the composite films. A deeper understanding requires a more detailed study of the microstructure, and there are no indications of the presence of a second magnetic phase that could explain this.
Figure 6.21. Crystallographic texture analysis of BaM-BST composite on C-sapphire substrate with the BaM seed layer: (a) XRD pole figure of BaM (107) peak and BST (200) peak, (b) azimuthal (\(\phi\)) scan of BaM (107) and BST (200) peaks.

Figure 6.22. In-plane and out-of-plane magnetization of PLD deposited composite thin films on C-sapphire substrate: (a) composite film (b) composite film with 20 nm BaM seed layer.
6.5 BaM-BST composite on A-sapphire

The BaM/BST composite thin film was also deposited onto A-oriented sapphire substrate under same conditions described in the previous section, both without and with the BaM seed layer.

The X-ray diffraction analysis in figures 6.24 and 6.25 reveals that the composite with the seed layer also has nearly same crystallographic properties as the BaM/BST bilayer from section 6.3, while the composite without the seed layer (not shown here) has other crystalline phases. The BaM peaks from the Θ - 2Θ scan show a distinct (h00) orientation, while BST has a strong (211) peak. The rocking curves are also similar to the bilayer, with small FWHM of BaM (200) peak and a broader FWHM for BST (211) peak. Since the total thickness is about 1/2 µm, the effect of the substrate and the seed layer is dominant, particularly for the growth of BaM constituent. The pole and azimuthal scans are also very similar to the bilayer, although in this case the BaM shows three sets of two poles, suggesting a larger amount of different in-plane oriented crystallites. The peaks in the pole plot and the φ-scan are also much broader than in the bilayer, indicating a poorer texture quality of the films.

The magnetization properties in figure 6.26, just as in the previous section, show a large difference between the composite films without and with the seed layer, as well as compared to the BaM/BST bilayer on the same substrate. Here also, there is a clear presence of a double-transition hysteresis loop. The composite without the seed layer looks nearly the same as the composite on C-sapphire without seed layer in figure 6.22(a), indicating that internal distribution of the BaM and BST regions in the composites without the seed layer

Figure 6.23. BaM-BST composite thin film on A-sapphire
and the interaction between them plays a greater role in determining the overall magnetic response than the effect of the substrate.

Obviously in the composite films, the microstructure and the magnetic properties are highly connected, allowing customization of magnetic properties through controlled changes in the microstructure (this was also observed in the sputtered composites in chapter 4. This opens a possibility of creating artificial single-layer ferrimagnetic-ferroelectric thin films through controlled deposition. If the BaM and BST regions can be controlled (e.g. deposition through a mask), it might be possible to custom-design some of the magnetic (and ferroelectric) properties, and even explore a possibility of magnetoelectric coupling. Such effects were observed in ferroelectric-ferromagnetic nanostructured composite thin film in [133].
Figure 6.25. Crystallographic texture analysis of BaM-BST composite thin film on A-sapphire substrate with BaM seed layer: (a) XRD pole figure of BaM (220) peak at $2\theta = 63.02^\circ$ and BST (200) peak at $2\theta = 45.94^\circ$, (b) azimuthal ($\phi$) scan of BaM (220) peak at $\Phi = 30^\circ$ and BST (200) peak at $\Phi = 65^\circ$.

Figure 6.26. In-plane and out-of-plane magnetization of PLD deposited composite thin films on A-sapphire substrate: (a) composite film (b) composite film with 20 nm BaM seed layer.
6.6 Summary

This chapter described crystallographic, structural and magnetic properties of single layer, bilayer and composite BaM and BST thin films fabricated by pulsed laser deposition. High quality BaM-BST bilayers were grown on C- and A- sapphire and MgO. The measured properties are consistent with the results from the literature for single layer films. The composite films grown on sapphire showed a presence of a double-transition hysteresis loop.
CHAPTER 7
MICROWAVE PROPERTIES OF BAM-BST BILAYERS AND COMPOSITE THIN FILMS

This chapter presents tunable electrical and magnetic properties of PLD deposited thin film samples described earlier. The data was taken in the range 1-65 GHz using the experimental set-up described in chapter 3.4.

7.1 Coplanar Waveguide Phase Shifters

Coplanar waveguide phase shifter is a device that includes a substrate, tunable dielectric material and a coplanar waveguide, and changes the transmission phase angle (phase of $S_{21}$) of the propagating wave by electric, magnetic or mechanical control. Phase shifters find largest applications in phased array antenna systems [44, 126]. Phased array antennas are part of a radar system in which the phase of a large array of antennas is controlled so that the radiation is reinforced in one and suppressed in the other direction. Electrical control of the phase shift can be realized by using nonlinear dielectrics such as barium-strontium-titanate, in which the dielectric properties vary with the change of applied voltage. For magnetic control, materials like yttrium-iron-garnet or barium-hexaferrite can be used. The physical properties of these materials change in magnetic field at microwave frequencies. Mechanical tunability is achieved by physical movement of specific parts of the transmission line (e.g. in MEMS). All of these three types of phase shifters have limitations and drawbacks in terms of amount of shift, losses, power handling, response time and manufacturing costs. Recently, there has been an increase in research and development of new class of tunable microwave devices, some of it was mentioned in chapter 1.1.

\footnote{The contents of this chapter are published in [50, 51]}
Phase shifters incorporating ferroelectric [12, 19, 20, 22, 40, 63, 72, 86, 92, 104, 127, 126] or ferrimagnetic [32, 55, 73, 96, 121, 134, 135] materials have been studied in the past. Their operation is based on the dependence of the sample’s permittivity and permeability on the applied electric and magnetic fields, as explained in chapter 2.

There are two ways how electrical and magnetic properties of a device can be tuned. One is by applying electric field to tune the electrical properties, and applying magnetic field to tune the magnetic properties. The other way, which is a new and growing research topic is by tuning magnetic properties with electric field and vice versa. This is based on the magnetoelectric effect [38]. An example of a possible use of magnetoelectric effect is tuning ferrimagnetic resonance by electric field [14, 15]. Electrical tuning of FMR at microwave frequencies could potentially lead to development of new types of microwave devices.

Thus, looking at the frequency dispersion of the phase shift with applied electric and magnetic fields not only gives the information about the electrical and magnetic tunability, but it could also provide a method to detect novel magnetoelectric phenomena. The data presented in the following sections describes the phase shift of pure ferrite films, ferrite-ferroelectric bilayers and ferrite-ferroelectric composite thin films under applied electric and magnetic fields.

The phase shift of the transmission coefficient $S_{21}$ is described as [68, 90]:

$$\Delta \phi = \phi_2 - \phi_1 = \frac{360 \cdot f \cdot l}{c} \cdot \left(\sqrt{\epsilon_{2 \text{eff}}^2 \mu_{2 \text{eff}}^2} - \sqrt{\epsilon_{1 \text{eff}}^2 \mu_{1 \text{eff}}^2}\right), \quad (7.1)$$

with $f$ the operating frequency, $l$ the length of the cpw line, $c$ the speed of light, and “1” and “2” are the two different states (e.g. without and with bias field). It can be seen that the phase shift increases with increasing frequency, line length, and the difference in effective material permittivities ($\epsilon_{\text{eff}}$) and permeabilities ($\mu_{\text{eff}}$).
7.2 Electrical Tunability

Electrical tunability of the coplanar waveguides was determined by measuring the scattering parameters while electric bias between the central and the ground conductor was applied using the bias tees - see figures 3.13(a) and 7.1. These measurements were performed at the USF WAMI Laboratory on a probe station capable of measurements up to 65GHz. Before the measurement, SOLT calibration on a calibration substrate was performed in the range 1-65 GHz. Even though interdigital capacitors were designed and fabricated, they were not tested due to some fabrication and measurement difficulties. Only the phase shift of the coplanar waveguides was measured. Before and after the measurements under applied electric field, the resistance was measured between the central and the ground connector using a bias tee and a multimeter. Figure 7.1 illustrates how a bias electric field is applied in the CPW geometry using a bias tee. A bias tee is a device used to apply both DC and RF signals to a device under test (DUT). The voltage was applied in four steps - 12.5 V, 25.0 V, 37.5 V, and 50 V, and these values were transformed into kV/mm by dividing by the width of the gap, which was 5 µm.

![Image of biasing setup]

Figure 7.1. An illustration of the biasing of the CPW phase shifter. The bias field is applied between the central and ground conductors via a bias tee.

The main problem during the measurement of the bilayers with BST on top (sapphire/BaM/BST), was that the resistance between the central and the ground conductors
would start dropping when the bias voltage was turned on, and the metal layer would appear to start oxidizing and degrading (the waveguide conductor layer would literally become brownish and greenish near the contacts with the probes, and if the voltage is not turned off immediately, it will continue across the whole area of the waveguide). The reason for this is probably occurrence of the leakage current that is one of the main failure mechanisms in high-permittivity thin films [13, 102]. After the measurement was done, and the bias voltage turned off, the resistance was immediately measured across the gap using the bias tee. It was noted that the value was much lower than before the measurement, and it was rising slowly toward the initial value. Such resistance degradation and its return to nearly initial values has been reported in BST films by others [13, 83, 102]. Due to the fatigue effect, the resistance does not return completely back to its original value. Although leakage currents have not been fully understood yet, it is believed that the electrode/ferroelectric interface plays a significant role.

For the bilayers with BST on top, the resistance over the 5µm gap was in the order of MΩs before the measurement. The bilayer with BaM on top (MgO/BST/BaM) did not show any drop in resistance after the measurement even after the maximum applied voltage of 50V, and no degradation of the metal layer was observed. The resistance was in the order of GΩs. Thus, this experimental scheme has resulted in an important observation showing that a highly insulating layer with low microwave losses can be deposited on the top of the BST and a good tunability can still be obtained, minimizing the leakage currents.

Another method was demonstrated in [66], where instead of applying metalization directly on the BST film, a 0.1 µm SiO₂ layer was used as a buffer layer, which reduced the possibility of creating large current crowding depths inside the BST that increase the losses [21]. That paper did not address the leakage currents, but obviously their idea of a low-dielectric buffer layer might have reduced the leakage currents similar to the geometry with the BaM on top.

Increased care during the manufacturing process was also necessary to eliminate some problems caused by residual photoresist on the film surface in between the electrodes. Very
small microscopic amount of the photoresist can remain in the CPW gap after processing, increasing the risk of device failure. The samples needed to be thoroughly cleaned in ultrasonic cleaner, RF Plasma Etcher, and visually inspected under the microscope. The limited development time and longer baking times (explained in chapter 3.4.3) could be a cause for this.

Another important matter is that the BST layer (due to its large permittivity) caused the line impedance to be much lower than 50Ω. When the circuits were designed, the optimum dimensions were calculated using only the substrate properties, and the influence of the films was not taken into account. Due to this large mismatch between the DUT and the microprobes ($Z_{in} = 50Ω$), the reflection loss ($S_{11}$) was large, and therefore the transmission coefficient ($S_{21}$) was very small. The pure BaM samples did not experience such large impedance mismatch, mainly due to the absence of the ferroelectric layer.

Phase shifters are usually characterized by a figure of merit (FOM) which is defined as [118]:

$$FOM = \frac{\text{(phase shift in degrees)}}{\text{(magnitude of insertion loss in dB)}}$$

(7.2)

Only when a network is well matched, the insertion loss is equal to $S_{21}$ [100]. Since there is a large impedance mismatch, using $S_{21}$ for insertion loss would result in lower values of the FOM. Despite that, in order to compare these results with the existing data from the literature, a figure of merit of bilayer films is calculated using $S_{21}$ values and plotted in figures 7.2(a, b, and c). If the dimensions of the circuits were designed to adjust for the impedance mismatch due to the BST, thus minimizing the mismatch, the reflection coefficient would have been smaller and the propagation coefficient would have been larger - the dB values of the $S_{21}$ would have been smaller. This would make the correct FOM probably twice as large as the estimates here. The highest FOM is seen in the MgO/BST/BaM bilayers, in which the BST layer is deposited directly on the MgO substrate, and experiences the best quality in terms of the crystallographic texture, as seen in the previous chapter. Its preferred orientation was (100). The BST film deposited on C/BaM, showed an excellent crystallographic orientation in (111) direction, although the
FOM is somewhat smaller. The BST film deposited on A/BaM was polycrystalline and showed a lesser degree of texture. It was also having problems with metal degradation and resistance drop when voltage was applied, as discussed earlier. This bilayer showed smaller degree of electrical tunability. It was shown in [91] that the (111) oriented BST film shows less tunability than (100) oriented film, but with improved dielectric quality factor. It is also important to notice that the FOM in figures (a) and (b) have a flat response in the frequency region from 20-50 GHz, above which the calibration becomes bad. This could be important in possible practical applications.

Maximum values of FOM found in the literature for BST-based phase shifters are around 40-50 deg/dB [20, 68, 79, 90]. The theoretical estimates based on calculation of losses in a ferroelectric device predict that the figure of merit could be further increased by a factor of three if the losses are minimized [118]. The sources of losses include energy dissipation in a ferroelectric, losses in conducting electrodes, and external losses of the circuit design. The main source of losses in this case comes from the circuit design, causing a large impedance mismatch, which can be easily fixed by redesigning the circuit dimensions. In addition, it has been recently reported that the small gap size ($\approx 5 \mu m$) can further increase losses in the metal electrodes [20, 118]. Larger gap size with this film thickness (0.5 $\mu m$) would result in less losses in metal conductors but also in decrease in tunability. It would be interesting to study the effect of the increase of the CPW-gap and film thickness on the figure of merit.

Figures 7.3 show a more accurate plot of the tunability effect as a phase shift per unit length (deg/cm). As described by equation 7.1, the phase shift increases with frequency and applied voltage (increase in permittivity difference). The data is noisy above 50 GHz, probably due to calibration issues. Due to a small size of the CPW gap (5 $\mu m$), a very large phase shift was obtained with a relatively small voltage (10 kV/mm corresponds to 50 V). Other reports on BST based CPW phase shifters use much large voltages due to larger gap size (up to 250 V) [20, 68, 79]. Even though a smaller gap size introduces additional losses, it provides a benefit of using smaller bias fields. The phase shift of A-BaM-BST structure
in figure 7.3(c) shows a wavy nature of the curve. The reason behind this is either dielectric resonances in the substrate-BaM-BST structure or poor impedance match. Phase shifter should be manufactured directly on the substrate, and the microwave measurements should be performed to see if there are any dielectric resonances due to the substrate.

Scattering parameters of the bilayer thin films are displayed in the figure 7.4. It can be seen that the reflection loss $S_{11}$ is large due to poor impedance match, ultimately causing the transmission coefficient $S_{21}$ to be very small. Another trend, that has been reported by others [68, 79, 90], is that the insertion losses of MgO-BST-BaM and C-BaM-BST films increase with frequency and improve with increased applied voltage. The A-BaM-BST bilayer shows an opposite trend, probably due to the problems with metal degradation.

Another way to minimize the dielectric, interface and conductor losses is by measuring the properties at cryogenic temperatures. Bilayer structures incorporating the superconducting materials such as YBa$_2$Cu$_3$O$_{7-3}$, ferroelectric/paraelectric and ferrimagnetic materials hold a great promise for development of cryogenic microwave devices [17, 39, 53, 60, 78, 81].

There is also an important issue that was raised by [42], and addresses the question whether materials in microwave devices should be used in ferroelectric or paraelectric state. So far, exclusively paraelectric materials have been utilized for tunable devices, but there are doubts whether at upper GHz frequencies these materials are in paraelectric state at all. Also, very little research has been done on measurements of microwave properties of materials in ferroelectric (polar) state. The main reason for using paraelectrics is that below 10 GHz, ferroelectrics in polar state experience large losses due to piezoelectric transformations, domain wall movements and hysteresis effects. It turns out that at millimeter frequencies, piezoelectric transformations and domain wall movements do not contribute to the high frequency losses (an example is ferroelectric Na$_{0.5}$K$_{0.5}$NbO$_3$ [9]). In addition, ferroelectrics below Curie temperature have much higher permittivities than in the paraelectric state. This indicates that ferroelectrics in polar state could be used for microwave tunable devices above 10 GHz. It would be interesting to measure microwave proper-
ties of other compositions of Ba$_{1-x}$Sr$_x$TiO$_3$, below and above x=0.3, which corresponds to ferroelectric-paraelectric boundary at room temperature and has a maximum peak of permittivity [80]. Also cryogenic microwave measurements of Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ below Curie temperature could be performed to study the impact of losses at microwave and millimeter wave frequencies.

Another study of a dual-tunable device (also mentioned in chapter 1.1), reports on the electrical and magnetic tunability of BST film deposited on YIG substrate [67]. The phase shift from BST film was only about 170/cm at 10 GHz with 2.1 kV/mm, which is much smaller than the data obtained here. The gap of their coplanar waveguide was 19 µm, which could account for low tunability, given the small thickness of the film (500 nm). A poor impedance match, resulting in high reflection and insertion losses was also reported.

Microwave characterization of composite thin films was also performed, but these films were having very low resistance across the gap (in kΩs), and no electrical tunability could be measured. The reason for this is probably large leakage currents that also caused degradation of the electrodes, as mentioned previously. In addition, there is a possibility that some other faces were formed in small quantities (e.g. Fe$_3$O$_4$) that have semiconducting features, but were not detected in the X-ray diffraction scan. Further investigations are needed to understand the origin of the low resistivity in the composites and to improve their quality.
Figure 7.2. Figure of merit for electrical tunability of BaM-BST bilayers: (a) MgO/BST/BaM, (b) C-sapphire/BaM/BST and (c) A-sapphire/BaM/BST.
Figure 7.3. Phase shift of BaM-BST bilayers with applied electric field: (a) MgO/BST/BaM, (b) C/BaM/BST and (c) A/BaM/BST.
Figure 7.4. S-parameters of bilayer thin films under bias electric fields: (a) Mgo/BST/BaM, (b) C/BaM/BST, (c) A/BaM/BST.
7.3 Magnetic Tunability

For the measurements of the phase shift under bias magnetic fields, the CPW structure illustrated in figure 7.5 was used. The right-angle bents allow for probing from the sides. A similar method was also used by [27] for study of ferromagnetic resonance in a ferromagnetic metal. In this set-up, the magnetic field is always perpendicular to the magnetic component of the microwave field that is propagating along a waveguide (see also figures 3.9, 3.10 and 3.12). This arrangement of AC and DC magnetic fields is mandatory for studying ferrimagnetic resonance.

![Applied Magnetic Field](image)

Figure 7.5. Set-up for magnetic tunability measurement

The main problem in this experiment was that the cables and the probes are of “SMA-type” (SubMiniature version A), which is rated only for use up till about 24 GHz. Above this frequency, higher modes of propagation are excited, increasing the return loss. Despite this drawback, an SOLT calibration was performed from 1-65 GHz on a calibration substrate, and scattering parameters of the thin films were recorded at different applied magnetic and electric fields. The phase shift measures the difference in the phase of $S_{21}$ with and without the bias field. It turns out that the phase of $S_{21}$ is unaffected by the increased return losses due to exceeding usable range of the cables and connectors. Additional losses due to impedance mismatch (as described in the previous section) are seen in the bilayer films. Because of that, the main focus is directed toward the monolayer BaM films, and some results of the bilayers and the composite films will be presented.
Figure 7.6 shows magnetic tunability of the BaM thin film on the A-oriented sapphire substrate. It is shown in chapter 6.3 that the easy-axis of magnetization of this film lies in the film plane. The reflection coefficient $S_{11}$ shown in 7.6(a) is almost unaffected by the magnetic field, and seems quite noisy above 20 GHz due to previously mentioned reasons. The transmission coefficient $S_{21}$ at zero field shows a large increase of losses at about 50 GHz in figure 7.6(b), indicating the presence of the natural ferrimagnetic resonance. A typical shift of the FMR peak position to higher frequencies at applied magnetic fields is also noticeable (see also figure 7.6(d)).

The frequency of the ferrimagnetic resonance for anisotropic thin films with in-plane magnetization is given by [122, 131]:

$$102$$
\[ f = \frac{\gamma}{2\pi} \sqrt{(H_R + H_A + 4\pi M_S)(H_R + H_A)} \]  

(7.3)

where \( \gamma \) is the gyromagnetic ratio, \( H_R \) is the resonant magnetic field (applied field), \( H_A \) is the anisotropy field, and \( M_S \) is the saturation field. The peak position follows a straight line as seen in figure 7.6(d), and it could be easily fitted if the anisotropy field \( H_A \) were known. This value can be obtained using torque magnetometer measurements, a set-up not available at the time of this writing. A similar fit of 7 \( \mu \)m PLD grown thick BaM film was reported by [131]. For a rough estimate, one can take the anisotropy field to be 17 kOe, and \( \gamma/2\pi=2.72 \text{ GHz/kOe} \) [131], and the saturation magnetization is estimated to be (see also figure 6.17(a)):

\[ M_s = 3.2 \cdot 10^{-4} \text{emu} \approx \frac{3.2 \cdot 10^{-4} \text{emu}}{2.0 \cdot 10^{-6} \text{cm}^3} \approx 160 \text{ emu/cm}^3 \]

Then \( 4\pi M_S \approx 2 \text{ kOe} \), and using the equation 7.3, one can fit the position of the resonant frequency in figure 7.6(d). Even though this is an approximation, the real values of \( H_c \) and \( 4\pi M_S \) are probably not much different, and the calculated data seems to agree well with the experimental, see figure 7.7. This demonstrates that the ferrimagnetic resonant frequency can be precisely determined using measurements of \( S_{21} \).

![Figure 7.7. Resonant frequency vs. applied field for BaM thin film deposited on A-oriented sapphire - experimental and calculated data.](image-url)
The focus of the study is actually directed toward the phase shift as seen in 7.6(c). The plot of the phase shift vs. frequency at different fields shows the great potential of this experiment. Even though the frequency exceeded the recommended limits of the cables and connectors, and as it will be seen later in the case of the bilayers, the return loss was large due to impedance mismatch, the phase shift was nearly unaffected by this. After a thorough literature search, it was concluded that this is probably the first look at the phase shift near the FMR frequencies, as the magnetic field is varied. A more detailed quantitative analysis that relates the phase shift to FMR is needed.

Microwave response in bare sapphire substrates was also measured (not shown here) and no shift with applied electric or magnetic fields was seen.
The figures 7.8(a-c) show the microwave properties of BaM single layer film deposited on the C-oriented sapphire, and having the easy magnetization axis perpendicular to the film plane. Even though the effect of the applied magnetic field can not be clearly seen in the measurement of $S_{11}$ and $S_{21}$ parameters, the phase shift shows a clear change with magnetization. In this case, the field was first applied in one direction, then brought to zero, then applied in oposite direction, and brought back to zero again. It can be seen from the figure 7.8(c) that the effect is repeatable in both directions of applied magnetic field, and also that there is no effect of remanent magnetization. This is mainly due to the fact that it is hard to fully magnetize this film in the plane direction. Another visible effect is the difference in the shape of the phase shift compared to the previous example with the in-plane oriented BaM. The explanation lies in the different orientation of the thin film magnetizations with respect to the oscillating magnetic field. Modeling of such longitudinally biased magnetic phase shifter would involve calculation of TEM wave propagation through an anisotropic medium, given the values for the anisotropy field $H_A$, saturation magnetization $M_S$, demagnetization factors $N_{\parallel}$ and $N_{\perp}$, FMR line width $\Delta H$, effective g-factor ($g_{eff}$), permittivity $\epsilon$ and the circuit dimensions, as well as taking into account different magnetostatic modes [134]. Some of these values were not available at the time of this writing.

The following figures 7.9 and 7.10 show the tunability of the bilayers on the A-oriented sapphire and MgO. The bilayer on the C-oriented sapphire showed a very small phase shift and the data was very noisy, and it will not be presented here. It can again be noticed that even though there is very little change in the magnitude of the S-parameters with the applied magnetic field, the phase of $S_{21}$ shows a significant change. The phase shift of BaM-BST bilayer on A-oriented sapphire in figure 7.9(c) looks quite different than for the single layer BaM film in figure 7.6(c). This can be related to the existance of some out-of-plane grown BaM crystallographic phases, creating a mixture of the phase shift response seen in figures 7.6(c) and 7.8(c). It was observed that there is an increase of the out-of-plane remanent magnetization in figure 6.17. Obviously, there is a strong influence
Figure 7.9. Microwave properties of BaM-BST bilayer on A-oriented sapphire substrate under bias magnetic and electric field: (a) $S_{11}$, (b) $S_{21}$, (c) phase shift under varying magnetic fields, and (d) phase shift under electric and magnetic fields.

of interfacial effects between the BaM and BST layer. Such effects could be important if one is looking for magnetoelectric coupling, otherwise, these effects should be minimized to reduce unwanted response in microwave devices. One way to do this is by introducing intermediate (buffer) layers, which could reduce the lattice mismatch between the layers. Figure 7.9(d) shows a dual-tunability effect (electrical and magnetic). First, the phase shift was measured with applied magnetic field of 5.5 kOe, then while the magnetic field was on, the electric field of 25 V was applied and the data was measured again. The effects of the electrical and magnetic shift in figures 7.3(c) and 7.9(c) get superimposed, creating a dual-tunable phase shifter. This is believed to be the first demonstration of dual tunability in this class of materials. The electric field does not seem to change the FMR position, thus
Figure 7.10. Microwave properties of BST-BaM bilayer on MgO substrate under bias magnetic and electric field: (a) $S_{11}$, (b) $S_{21}$, (c) phase shift under varying magnetic fields, and (d) phase shift under electric and magnetic fields.

There is likely no magnetoelectric coupling between the layers. Unfortunately, no higher electric fields could be applied due to the leakage current problems mentioned earlier.

The phase shift of the BST-BaM bilayer on MgO substrate, figures 7.10(c and d), exhibits somewhat similar behavior, although the magnetic phase shift looks more like the one from the single layer BaM film on the A-sapphire substrate. This bilayer film shows nearly anisotropic magnetic behavior as seen in figure 6.12, thus there is no preferred axis of magnetization. The dual tunability at 5.5 kOe and various electric fields also shows a superposition of electrical and magnetic effect. It also confirms the previous measurements of electrical tunability done on different sample and with different CPW structure (“straight” vs. “bent” CPW) - compare with the figure 7.3(a).
Finally, the magnetically tunable phase shift was also measured in BaM-BST composite thin films. Even though the effect is quite small and noisy, it still demonstrates that even the smallest changes in magnetization at microwave frequencies can be picked up by looking at the phase shift.

7.4 Simulations Using Commercial Software Packages

Simulations of measured data (S-parameters) of CPW circuits was attempted using two commercial software packages - HP Advanced Design System (ADS) and Ansoft High Frequency Structure Simulator (HFSS). Due to the presence of BST, the effective dielectric constant of the structure (substrate + bilayer) was large, and neither ADS nor HFSS were able to handle simulations with large dielectric constant. Despite this lack of quantitative analysis and modeling, the results obtained here are well comparable to the results obtained by others for both BaM and BST films.
7.5 Microwave Measurements at Oakland University

This section presents the results of microwave measurements performed at Professor G. Srinivasan’s laboratory at the Oakland University Physics Department. The author is not an expert in these measurements and no detailed interpretation of the data will be presented. The intent is rather to show the magnetic tunability performed on a different experimental set-up. In this experiment, the samples were placed at the metal short end of a U-band waveguide-coaxial adapter and the reflected power was measured at different external magnetic fields ranging from 0 to 14 kOe using an electromagnet and in the frequency range of 40-60 GHz. Figure 7.12(a) shows the return loss of BaM-BST bilayer deposited on A-sapphire substrate as a function of external magnetic field, while position of the maximum absorption peak (resonant absorption) as a function of field is plotted in figure 7.12(b).

![Figure 7.12](image)

Figure 7.12. Microwave absorption measurements of BaM-BST bilayer on A-sapphire: (a) return loss and b) Position of the resonant absorption as a function of external field.

A noticeable feature in this set of data is that there are distinct jumps in the minimum frequency position at characteristic fields above 8 kOe. These jumps are due to mode repulsion of magnetic and dielectric resonances [51], and more work is needed to interpret these complex features. These features were not observed in single layer BaM films on A-
sapphire. This is another demonstration that these multilayer systems provide rich physics as well as potential applications.

7.6 Summary

This chapter presented the results of the microwave characterization of PLD-deposited single- and bilayer thin films. A coplanar waveguide phase shifter was fabricated and the phase shift of transmission coefficient $S_{21}$ was measured as a function of frequency and applied electric and magnetic fields. Due to the presence of a material with large dielectric constant, the characteristic impedance of the line was smaller than 50Ω, causing a large mismatch at the ports. Electrical tunability was seen in all films, and particularly large values were measured in the MgO-BST-BaM structure, due to an excellent quality of BST. Also the BaM layer on top provided possibility of applying large electric fields without causing damaging leakage currents. Magnetic tunability of the phase was also measured in a custom-made experimental set-up, and a typical phase shift was observed at the ferrimagnetic resonant frequency. Dual tunability of the A-BaM-BST structure was also reported.
CHAPTER 8
CONCLUSION AND FUTURE WORK

This work presented growth, structural, crystallographic, magnetic and microwave analysis of several different types of BaM-BST thin films. The films were grown in composite and multilayer form, using RF magnetron sputtering or pulsed laser ablation. The effect of substrates and deposition temperature was also studied.

Several interesting phenomena were observed. Composite films showed a double-transition hysteresis loop, and magnetic properties in multilayer films were also affected by the presence of the BST. A possibility of customizing magnetic properties through the use of BST was also observed.

High quality BaM-BST multilayers were grown on single crystal sapphire and MgO substrates providing a possibility of designing multifunctional magneto-dielectric thin films.

A novel experimental stage for microwave measurements of thin films was built and electrically and magnetically tunable phase shift was measured in the frequency range 1-65 GHz. It was seen that the ferrimagnetic resonance can also be observed by measuring scattering parameters of a phase shifter.

Future work on these systems might include some of the following ideas:

- Growing of tri- and multilayers of BaM and BST using PLD on single crystal substrates.
- Increasing the thickness of the layers. Thick films are more preferable for possible applications. Also the CPW-gap can be larger in thicker films minimizing potential losses due to the small gap size. The geometric fill factor - ratio of the film size to the total thickness (substrate + film) is larger for thicker films, and the electromagnetic
fields are more contained in the thicker films, having larger effects on the overall electromagnetic wave propagation properties.

- Investigating for a possible magnetoelectric coupling and other phenomena at the interface of the films - neutron scattering, transmission electron microscopy, etc.
- Depositing buffer layers between BaM and BST at the interface to minimize the interfacial effects.
- Increasing the BaM film deposition temperature to optimum reported temperature of 920°C, and finding a optimum deposition temperature for BST in this case.
- More studies of composite thin films, in particular the correlations between microstructure and magnetic effects. Finding a more quantitative explanation of the double-hysteresis loop and a possibility of custom designing magnetic properties through controlled microstructural design.
- Designing the circuits to account for the change in characteristic impedance and repeating the measurements of figure of merit in bilayer films.
- Measuring of electrical and magnetic tunability beyond 65 GHz, as the resonant frequency exceeded 65 GHz in this study. Is there a “cut-off” frequency for electrical tunability?
- Studying the gap-dependent electrical and magnetic tunability, and optimizing the gap size to the film thickness.
- Calculating relative permeability and permittivity and looking for a software that could possibly model a phase shifter with large permittivity and permeability.
- It would be also interesting to use these measurement techniques for testing biological samples at high frequencies and extract their complex permittivity and permeability. Coplanar waveguide phase shifters could be fabricated on high-resistivity substrates and biological samples could be deposited on the top and their parameters measured as a function of frequency, and electric and magnetic fields.
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APPENDICES
Appendix A List of Publications


Appendix A (Continued)

Appendix B List of Conference Presentations

Conference Presentations (oral)

• 50th Magnetism and Magnetic Materials (MMM) Conference 2005, San Jose.
• Ninth International Conference on Ferrites (ICF-9) - August 2004, San Francisco.
• American Physical Society (APS) March Meeting 2003, Austin.
• American Physical Society (APS) March Meeting 2002, Indianapolis.

Contributed Conference Presentations

• American Physical Society (APS) March Meeting 2005, Los Angeles.
• American Physical Society (APS) March Meeting 2004, Montreal.
ABOUT THE AUTHOR

Ranko Heindl was born in Sarajevo, Bosnia-Herzegovina. In 1992, he moved to Germany where he finished High-School and attended Ruhr-University in Bochum for 2 years and obtained “Vordiplom”. In 1998, he came to USA and joined the Physics Department at the University of South Florida (USF). He obtained B.S. and M.S. degrees in physics in 2000 and 2002, respectively. Besides working at USF, he also made research visits to the Oak Ridge National Laboratory and the Advanced Materials Processing and Analysis Center at the University of Central Florida. He published several scientific papers in the field of magnetism. He was awarded Tharp, SURA and IGERT fellowships over the years. When he became a US citizen in 2004, he changed the spelling of his last name from Hajndl to Heindl. He won the NRC Postdoctoral Research Fellowship in Fall 2006, and will join NIST, Boulder in the Spring 2007.