Crystal growth of hexaferrite architecture for magnetoelectrically tunable microwave semiconductor integrated devices

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Abstract

Hexaferrites (i.e., hexagonal ferrites), discovered in 1950s, exist as any one of six crystallographic structural variants (i.e., M-, X-, Y-, W-, U-, and Z-type). Over the past six decades, the hexaferrites have received much attention owing to their important properties that lend use as permanent magnets, magnetic data storage materials, as well as components in electrical devices, particularly those operating at RF frequencies. Moreover, there has been increasing interest in hexaferrites for new fundamental and emerging applications. Among those, electronic components for mobile and wireless communications especially incorporated with semiconductor integrated circuits at microwave frequencies, electromagnetic wave absorbers for electromagnetic compatibility, random-access memory (RAM) and low observable technology, and as composite materials having low dimensions. However, of particular interest is the magnetoelectric (ME) effect discovered recently in the hexaferrites such as SrScxFe12-xO19 (SrScM), Ba2–xSrxZn2Fe12O22 (Zn2Y), Sr4Co2Fe36O60 (Co2U) and Sr3Co2Fe24O41 (Co2Z), demonstrating ferroelectricity induced by the complex internal alignment of magnetic moments. Further, both Co2Z and Co2U have revealed observable magnetoelectric effects at room temperature, representing a step toward practical applications using the ME effect. These materials hold great potential for applications, since strong magnetoelectric coupling allows switching of the FE polarization with a magnetic field (H) and vice versa. These features could lead to a new type of storage devices, such as an electric field-controlled magnetic memory.

A nanoscale-driven crystal growth of magnetic hexaferrites was successfully demonstrated at low growth temperatures (25-40% lower than the temperatures required often for crystal growth). This outcome exhibits thermodynamic processes of crystal growth, allowing ease in fabrication of advanced multifunctional materials. Most importantly, the crystal growth technique is considered theoretically and experimentally to be universal and suitable for the growth of a wide range of diverse crystals. In the present experiment, the conical spin structure of Co2Y ferrite crystals were found to give rise to an intrinsic magnetoelectric effect. Our experiment reveals a remarkable increase in the conical phase transition temperature by ~150 K for Co2Y ferrite, compared to 5-10 K of Zn2Y ferrites recently reported. The high quality Co2Y ferrite crystals, having low microwave loss and magnetoelectricity, were successfully grown on wide bandgap semiconductor GaN. The demonstration of the nanostructure materials-based “system on a wafer” architecture is a critical milestone to next generation microwave integrated systems. It is also practical that future microwave integrated systems and their magnetic performances could be tuned by an electric field because of the magnetoelectricity of hexaferrites.
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Chapter 1 Introduction

1.1. Background
1.2. Ferrite materials
1.3. Wide band semiconductor substrates
1.4. Current status of ferrite film growth on semiconductor substrates
1.1 Background

Hexaferrites (i.e., hexagonal ferrites), discovered in 1950s, exist as any one of six crystallographic structural variants (i.e., M-, X-, Y-, W-, U-, and Z-type). Over the past six decades, the hexaferrites have received much attention owing to their important properties that lend use as permanent magnets, magnetic data storage materials, as well as components in electrical devices, particularly those operating at RF frequencies. Moreover, there has been increasing interest in hexaferrites for new fundamental and emerging applications. Among those, electronic components for mobile and wireless communications especially incorporated with semiconductor integrated circuits at microwave frequencies,\(^1\) electromagnetic wave absorbers for electromagnetic compatibility, random-access memory (RAM) and low observable technology, and as composite materials having low dimensions.\(^2\)\(^3\) However, of particular interest is the magnetoelectric (ME) effect discovered recently in the hexaferrites such as SrSc\(_{x}\)Fe\(_{12-x}\)O\(_{19}\) (SrScM), Ba\(_{2-x}\)Sr\(_{x}\)Zn\(_{2}\)Fe\(_{12}\)O\(_{22}\) (Zn\(_{2}\)Y), Sr\(_{4}\)Co\(_{2}\)Fe\(_{36}\)O\(_{60}\) (Co\(_{2}\)U) and Sr\(_{3}\)Co\(_{2}\)Fe\(_{24}\)O\(_{41}\) (Co\(_{2}\)Z), demonstrating ferroelectricity induced by the complex internal alignment of magnetic moments.\(^4\) Further, both Co\(_{2}\)Z and Co\(_{2}\)U have revealed observable magnetoelectric effects at room temperature, representing a step toward practical applications using the ME effect. These materials hold great potential for applications, since strong magnetoelectric coupling allows switching of the FE polarization with a
magnetic field (H) and vice versa. These features could lead to a new type of storage devices, such as an electric field-controlled magnetic memory.

Both traditional and modern microwave components require hexaferrites due to their moderate to high values of magnetization, tunable magnetocrystalline anisotropy field, high permeability, high permittivity, and low-losses at RF frequencies. Additionally, these hexaferrite materials also provide non-reciprocal behavior that is essential for many device applications in radar and communications systems such as in isolators, circulators, etc. It is noteworthy that the microwave electronics community has long sought to integrate microwave passive devices, such as circulators, isolators, phase shifters, filters, etc. with semiconductor device platforms such as GaN thus allowing for system-on-a-wafer architectures.\(^5,6\) Such an achievement would address the demands of ever increasing systems integration while enhancing performance and functionality and concomitantly reducing device profile,\(^7\) volume, and weight.\(^8\) Previous attempts to integrate ferrite materials onto Si and GaAs failed in that the high temperatures required for the processing of low microwave loss ferrite materials resulted in the degradation of microwave performance. It is clear that a low temperature ferrite growth technique is key to realizing planar microwave semiconductor integrated devices including those ideally tuned by electric fields based on the room temperature magnetoelectric effect.

A novel attempt to integrate single crystal Y-type hexaferrite heterostructures on wideband semiconductor substrates is proposed. We show such structures demonstrate the ME effect allowing for E field tuning at
microwave frequencies. Single-crystal Co$_2$Y, \textit{i.e.}, Ba$_2$Co$_2$Fe$_{12}$O$_{22}$, ferrites are an important class of microwave ferrites that are widely used in microwave and mm-wave filters and phase shifters. Wide band gap semiconductor materials, \textit{e.g.}, SiC and GaN,\textsuperscript{9,10} have demonstrated advantages in power handling at high frequencies and received great interest from the semiconductor device community due to their attractive thermal conductivities, band gap energies, breakdown voltages, and permittivity, among other properties.\textsuperscript{11} Additionally, these materials share the same hexagonal crystal symmetry and comparable lattice parameters as hexagonal ferrites and possess the high temperature stability that enables epitaxial growth of high quality microwave ferrites.

We propose that the preparation of single crystal Y-type hexaferrite having thicknesses in the 10’s or even 100’s of micronson lattice mismatched semiconductor substrates is challenging.\textsuperscript{12} Since the 1960s, synthesis techniques for the growth of ferrite single crystals include the melt salt method,\textsuperscript{13} liquid phase epitaxy (LPE) and floating zone method.\textsuperscript{14,15} Among these, floating zone method and LPE growth involves complicated liquid phase control and expensive experimental set up, while the salt melting method, although simple to execute and scalable, involves long cooling cycles and etching of the crystals out from the crucible. A 4 µm thick Co$_2$Y ferrite film has been successfully grown on MgAl$_2$O$_4$ substrate at low temperature,\textsuperscript{16} but it is still too thin to be used in many practical devices. The development of low temperature epitaxial ferrite thick films or crystals with low microwave loss remains a problem whose solution will have a wide-ranging impact upon the microwave device community.
A GaN/Al₂O₃ substrate was employed with the thickness of GaN of ~30 µm. In the case of Y type ferrite films grown on GaN, there is a relatively large lattice mismatch of 6.2% between the GaN (001) substrate and the Co₂Y(001) film thus requiring a buffer layer to mediate interfacial strain and realize epitaxial growth. Further complicating growth is that GaN is thermally unstable in vacuum at temperatures near 950 °C at which typical pulsed laser deposition (PLD) growth of ferrite film seeds are grown. In order to mitigate both interfacial strain and surface reactivity, a layer of MgO, having (111) crystallographic orientation, was grown on the GaN substrate. Following the preparation of the MgO (111) buffer layer, BaFe₁₂O₁₉ (BaM) was deposited between Co₂Y and MgO (as step 1 shown in Fig. 1).¹⁷ Later in this experiment, as step 2, we demonstrate the use of ~20 nm diameter Co₂Y powder positioned atop a GaN/Al₂O₃ substrate to realize epitaxial growth of an 80–500 µm thick film of Co₂Y at temperatures as low as ~1050 to 1150 °C without flux.¹⁸
Ultimately, the designed architecture consisted of five layers: (001) sapphire (Al₂O₃), (001) GaN, (111) MgO, (001) BaM and (001) Co₂Y.

In this dissertation, we will introduce the project background, ferrite materials and semiconductor substrates in Chapter 1. Epitaxial growth methods and sample characterization experiments details will be discussed in Chapter 2. Epitaxial growth of the ferrites films will be provided in Chapter 3. The
theoretical analysis of the melting temperature dependence on particle size will be shown in Chapter 4. Summary of the research result and potential study of the project will be covered in Chapter 5.
1.2 Ferrite materials

Ferrites are a group of magnetic oxide materials. Most ferrites “grow” in either spinel, garnet or magnetoplumbite crystal structure. The crystal structure and the atomic configuration determine their intrinsic magnetic, chemical and mechanical properties. In general, they are mechanically hard, chemically stable and have high electrical resistivity, and high permeability and high permittivity compared to other materials. Because of the low eddy current losses associated with high electrical resistivity, these materials are widely used in high frequency electronic and microwave devices. Ferrites with low dielectric and magnetic loss tangents in the frequency range from DC to millimeter wave can be readily produced. Here, we briefly discuss several key types of ferrites as well as their magnetic properties and applications in microwave devices.

Spinels

Spinels have the chemical formula $\text{Me}^{2+}\cdot \text{Fe}^{3+}_2\text{O}_3$, where $\text{Me}$ represents divalent magnetic ions and Fe can be replaced by other trivalent magnetic ions, crystallize in a cubic structure. The cations occupy either tetrahedral (A) or octahedral (B) sites and, therefore, form two sublattices. The magnetic moment of cations within each sublattice align parallel to each other and anti-parallel to the other sublattice. The normal spinel is described by the inversion parameter, $\delta$, of zero, where $\delta$ is defined as $(\text{Me}_{1-\delta}\text{Fe}_\delta)^\text{tet}[\text{Me}_\delta\text{Fe}_{2-\delta}]^\text{Oct}\text{O}_4$, requiring that divalent...
metal cations occupy 8 out of the possible 64 A sites and trivalent metal ions occupy 16 out of possible 32 B sites. Typically, natural spinel materials (i.e. Fe$_3$O$_4$, CoFe$_2$O$_4$, NiFe$_2$O$_4$, etc.) assume an “inverse” structure, i.e. $\delta=1$, in which 8 divalent cations occupy B sites and 16 trivalent cations distribute equally among A and B sites. Most spinel ferrite can be classified as “mixed” in which the cation distribution is neither purely inverse nor normal but some deviation of the two. No matter which configuration, the magnetism in these structures arises from a super-exchange mechanism$^2$ and the net moment is given by the sum of individual moments of all sites. Fig. 2 shows the cation distribution in a spinel crystal structure along with corresponding magnetic moment directions.

Fig.2 Crystal structure of spinel ferrite, with the magnetic moment direction of each cation indicated.
The inherent flexibility of the spinel crystal structure provides opportunities for manipulating the magnetic properties by either substituting nonmagnetic cations (e. g. Zn in zinc ferrites) for the magnetic ones or by tuning the inversion of normal spinel under non-equilibrium growth. The exchange constant $J_{AB}$ is affected by such manipulations providing an effective tool for controlling material properties, such as saturation magnetization, magnetic anisotropy and Néel temperature. In practice, spinels are successfully used in antennas, inductors, transformers, as well as electromagnetic interference suppression devices because of the high permeability compared to other ferrites.

**Garnets**

Garnets have the chemical formula $\text{M}^{3+}_3\text{Fe}^{3+}_2(\text{Fe}^{3+}\text{O}_4)_3$, in which M is a metal of the lanthanide group, and similarly to spinels, grow in cubic crystal structure. The unit cell consists of twenty four $\text{Fe}^{3+}$ ions at tetrahedral sites (A), sixteen $\text{Fe}^{3+}$ ions at octahedral sites (B) and 24 $\text{M}^{3+}$ ions at dodecahedral sites (C). Fig. 3 shows the crystal structure of the most famous garnet, yttrium iron garnet (YIG).
The crystal structure of Yttrium Iron Garnet (YIG).  

The magnetic momentons of metal ions on both B and C sites are antiferromagnetically aligned with respect to the ions on A sites. Garnets like YIG are easily processed with high crystalline quality. This is possibly because of all metal ions have 3+ state\(^5\) and the oxygen sublattices of garnets structure are completely filled. This is demonstrated in Fig. 3. As a result, the garnet structure is most resistant to defects introduced during the material preparation and film deposition even under condition of large film mismatch with the substrate, which is a challenging problem for the growth of films of other ferrites. For high frequency applications, microwave loss is the key performance parameter and it is determined to a large degree by the crystalline quality of the ferrite film. Not surprisingly, YIG
is the most widely utilized microwave ferrite, dominating in present day commercial microwave applications.

**Hexaferrites**

As the name suggests, hexaferrites grow in a hexagonal crystal structure. It has several structural variations including M, Y, W, and Z types. BaFe$_{12}$O$_{19}$ (M type) ferrite possesses the same crystal structure as the naturally occurring mineral magnetoplumbite and it has attracted much attention in the past few decades. Its unit cell consists of an intergrowth of structural blocks RSR*S*8, shown in Fig.4.

![Fig.4 Barium M-type hexaferrite unit cell structure](image)
The asterisk indicates the block has been rotated by 180° around the crystal c-axis. The S block has the spinel structure with [111] direction parallel to the c-axis. The two S blocks are separated by a hexagonal R block which contains a Ba atom. The overall symmetry of the unit cell is hexagonal since it has a lower symmetry than cubic, which results in large magnetocrystalline anisotropy. The large anisotropy field found in M-type Ba-ferrite is very important for microwave device applications because of its high operational frequency. Additionally, the sole +3 oxidation state of Fe ions in BaM-hexaferrites contributes to better insulating properties compared to spinels, which provides BaM advantages over spinels in the microwave/RF applications that require low eddy current losses.

The structure of Y type hexaferrite has space group (R̅3m) and is often designated as—(TS)’’|(TS)(TS)’|(TS)’’|(TS)—, where the prime means the block is rotated 120° around the c-axis. The structure consists of three Y blocks (formula units). Each Y block consists of twolayered spinel S block and four-layered antiferromagnetic T block, shown in Fig. 5. The metallic cations in the blocks occupy either tetrahedral or octahedral sites between the oxygen polyhedra. The knowledge of the distribution of cations is utmost importance in understanding their physical and chemical properties.
Microwave applications of ferrites

Ferrites have a unique nonreciprocal property which makes them key component in a wide variety of microwave devices. In these devices, the transmission or absorption of electromagnetic waves depends on the wave direction with respect to the magnetic field direction inside the ferrite. For most applications the ferrite has to be biased by an external magnetic field provided by permanent
magnets. The magnets serve to saturate the ferrite as well as to make the ferrite interact with the electromagnetic wave.

Since 1990, ferrite materials and device development have progressed towards higher frequencies of operation (K- and Q-band). The zero field FMR frequency of spinel and YIG ferrites typically falls near or below 2 GHz. Using large magnetic fields to bias YIG ferrites to operate at or above X-band frequencies is impractical. The FMR frequency is strongly dependent on the anisotropy field, $H_a$; M-type hexaferrites (e.g., BaM BaFe$_{12}$O$_{19}$) is 16 kOe, 1000 times greater than the cubic spinels. The zero field FMR frequency for single crystal Barium ferrites is near 46 GHz. Therefore, hexaferrites naturally become the material of choice for high frequency applications eliminating the need for high external biasing field as with spinel or garnet ferrites. In addition, the substitution of Fe by other cations in Ba-ferrite unit cell provides remarkable flexibility of tailoring the magnitude of the anisotropy field, and thus, the corresponding operating frequency. For example, the substitution of Sc or In for Fe reduces the anisotropy field allowing for applications from C-, X-, Ku-, K-, to Ka-bands. On the other hand, substitutions of Al or Ga increase the value of $H_a$ and allows for device applications up to U-, E-, and W-bands. Therefore, BaM hexaferrites and their substitutional companion systems can host a wide range of device applications ranging from 1 to 100 GHz.

In addition to tunability over a wide frequency band, the large magnetocrystalline anisotropy $H_a$ gives rise to a unique potential to hold an intrinsic remnant magnetization in the absence of external magnet. The remnant
magnetization enables the realization of self-biased devices without the need of external magnets. For above reasons, given the advanced preparation techniques, BaM-hexaferrite is now one of the most promising ferrite materials of choice for future microwave applications in the wide frequency range of operation. In the following chapters, we will focus on the research of M-type Ba hexaferrite films on semiconductor substrate.
1.3 Wide band semiconductor substrates

Let us move on to another important and, perhaps, more familiar family of materials - semiconductors. Any material that has the electrical conductivity in between that of a conductor and an insulator is referred to as semiconductor. In the early 1940s, the demand for crystal detectors in radar systems motivated intensive research into the preparation of pure elemental semiconductor materials like silicon and germanium. This research eventually led to the invention of the junction transistor by Shockley in 1951 and the start of the modern electronics era. Interestingly, initial semiconductor research was motivated by the requirements of developing microwaves technology. Nowadays, semiconductors are the most widely used materials in consumer, industrial and military electronics.

Semiconductor classes

The semiconductor family can be classified into 3 groups, which include 1) single element semiconductors like Si and Ge in the IV Group, 2) compound semiconductors like SiC in the IV – IV Group, GaAs, GaN, InP in the III-V Group, and ZnO, CdTe in the II-VI Group, and 3) alloys like AlxGa1-xAs and SiGe. Si has by far been the most dominating material since the inception of semiconductor technology, due in part to a well established fabrication technology and economic considerations. For decades driven by the massive consumer electronics market as well as efforts of thousands of engineers, the Si industry has made tremendous
integrated circuit fabrication progress to realize smaller, cheaper, and faster devices from generation to generation. This progress is accurately captured by Moore’s law. However, as Si processing (45nm) pushed to the processing limit (25nm) or fundamental physical limit (22 nm), alternative ways other than size reduction of devices are needed for future development.

Since the discovery of semiconductors, scientists have been searching for advanced materials besides Si20. For instance, III-V compounds like GaAs exhibiting superior electrical properties, and special optical properties that have been utilized in high frequency MMIC applications for some time. The use of SiGe as a replacement for classic silicon bipolar is also attracting a lot of attention22. However, regardless of their success in some special applications, both materials suffer from limited power handling capabilities.

The ultimate semiconductor material has to meet the challenge of both high speed and high power requirements. Johnson has argued that the basic limitation on various transistor characteristics is set by the product of the breakdown electric field and the saturated electron drift velocity. The combination of these two variables which was called Johnson’s figure of merit (JFOM) will determine cutoff frequency and maximum power ability of the chosen material. Keys later suggested including another highly desirable parameter, thermal conductivity, into his figure of merit (KFOM). The properties of several semiconductor materials, along with their respective figures of merit, are listed in the Table 1 below.
Table 1. The properties of the most common semiconductor materials.

In Table 1, SiC and GaN with their associated figures of merit have significant advantages over other semiconductor materials including Si and GaAs. In fact, the only material with better properties than these two is diamond, which of course, is not presently a practical material for devices in the foreseeable future.

Wide band gap semiconductor material GaN

Gallium nitride (GaN) is a binary III/V direct bandgap semiconductor commonly used in bright light-emitting diodes since the 1990s. The compound is a very hard material that has a Wurtzite crystal structure, shown in Fig. 6. Its wide band gap of 3.4 eV affords it special properties for applications in optoelectronic, high-power and high-frequency devices. For example, GaN is the substrate which
makes violet (405 nm) laser diodes possible, without use of nonlinear optical frequency-doubling.

Its sensitivity to ionizing radiation is low (like other group III nitrides), making it a suitable material for solar cell arrays for satellites. Military and space applications could also benefit as devices have shown stability in radiation environments. Because GaN transistors can operate at much higher temperatures and work at much higher voltages than gallium arsenide (GaAs) transistors, they make ideal power amplifiers at microwave frequencies.

Fig.6 GaN unit cell structure
1.4. Current status of ferrite film growth on semiconductor substrates

Ferrites for microwave applications were first synthesized and studied during the 1940s by Snoek’s group at Philips Laboratories. These pioneering achievements inspired comprehensive investigations of the spinel, garnet and hexagonal ferrite systems. Although ferrites are successfully used in discrete elements as bulk materials, for the microwave and millimeter-wave applications, there is increasing interest in using ferrites as films rather than bulk for several reasons. First, thin films provide greater uniformity surface than bulk. Second, thin films provide lower cost, smaller size, and enhanced compatibility with planar circuit designs compared with discrete forms. Film quality, whether being polycrystalline or single crystal, is a key concern for integrated microwave applications. The research on high quality ferrite films for microwave and millimeter-wave applications was limited and far behind the semiconductor film development. In 1970s, driven by rapid development of various forms of magnetic recording and bubble memory technology, the extensive work on preparing yttrium iron garnet (YIG) films was started and later extended to other ferrite films. As a consequence, YIG films became the first group of ferrite films which could be prepared to near perfect crystalline quality and applied in tunable microwave filters and magneto static wave devices.

In today’s technology, emerging electronic systems, such as wireless and satellite communications (GPS, Bluetooth, WLAN, automotive Radar, etc) are in growing demand, and higher frequencies of operation are needed. It is
recognized that when the frequency shifts into the microwave range, the integration of microwave devices with semiconductor electronics holds significant advantages in the realization of higher performance, higher speed, higher power and smaller size devices. However, could semiconductor devices replace microwave devices altogether? Earlier researchers demonstrated an imposition of a static magnetic field on semiconductor to create magneto plasma to obtain nonreciprocity. MMIC active circulator based on MESFET and HEMT were also reported. In fact, semiconductor transmit/receive modules are widely employed in the mobile phone, and in some cases, semiconductor switches are used as replacement for ferrite phase shifters for electronically steerable phase array radars.

It seems that semiconductor counterpart devices will continue to be successfully utilized in some applications due to the established fabrication technology as well as economic reasons. However, at high frequencies and broader bandwidth applications, which operate in the mm wave range up to 100 GHz, insulating materials are essential to ensure low loss propagation of electromagnetic fields. In addition, no semiconductor device has the power handling ability comparable to ferrite devices. For example, ferrite circulators have proven to be indispensable and far advantageous in the performance over any other technology. As an ultimate goal, we will explore the film-based BaM circulator integration on the wide band gap semiconductor substrate.

In the following, we will review the current status of ferrite film growth on different semiconductor substrates. Furthermore, we will discuss the potential approach of Monolithic Integrated Circuit (MIC) fabrication including
recent studies on ferrite thin film processing and ferrite film patterning in efforts to realize the integration of microwave ferrite devices and semiconductor substrates.

**Preparation of ferrite films on Si**

The growth of ferrite materials on semiconductor substrates was first driven by the potential memory and recording applications. BaM for decades was considered among the top candidates for magnetic recording media because of its high anisotropy field, high coercivity, mechanical hardness, and chemical stability. For longitudinal recording, high coercivity and small grain size are highly desirable. In 1993, Sui reported that coercivity as high as 4100 Oe was achieved in the BaM film grown on Silicon by RF sputtering technique. In 1994, Hylton found that doping Cr$_2$O$_3$ can reduce the grain size down to the order of 20nm while maintaining the coercivity in excess of 4000 Oe.

In contrast, when metallic alloy-based thin film longitudinal recording medium approaches the physical limit, the corresponding small magnetic grains become thermally unstable. In addition, while the recording density of metallic alloy thin film media surpasses 60 Gbits/in2, the saturation magnetization reduces to below 300emu/cm$^3$, which is close to that of BaM thin film. As a result, BaM became more attractive as a candidate material for perpendicular recording medium, which requires c-axis orientation normal to the film plane. In 1985, Matsuoka reported the growth of BaM/ZnO/SiO$_2$/Si structure for perpendicular
recording application. In 1997, Morisako reported the improvement of the c-axis orientation and the alleviation of Barium and Iron diffusion by amorphous Ba-Fe-O buffer layer. In 2001, Lisfi and Lodder claimed the BaM films grown directly on SiO$_2$/Si exhibit a granular structure with two easy axes (in-plane and perpendicular) and strong magnetic coupling. It was noticed that a ZnO underlayer promoted the orientation of the c-axis perpendicular to the film plane and a low exchange coupling was achieved by separating the grains. In 2002, Morisako reported the grain size of BaM films deposited on an AlN underlayer was suppressed to 50 nm. Later in 2004, He reported a better result by using Al$_2$O$_3$ as the buffer layer instead of the previous AlN.

For microwave applications, the deposition of ferrite films on silicon seems more challenging than for the recording industry due to the requirements of high crystal quality and c-axis orientation (normal to the film plane or in the film plane depending on the application), and greater film thickness. The crystal quality of the ferrite film directly relates to the microwave loss, which is among the most important factors to evaluate device performance at high frequency. The loss mechanism can be explained by the ferromagnetic resonance (FMR) which stems from the dampened precession of the magnetic moments of the metal ions. Loss is closely related to the FMR linewidth. The smaller the FMR linewidth, the lower the microwave loss in its host microwave devices. Currently, it remains a great challenge to find the best ferrite film growth technique to ensure high crystal quality. In 1991, Lacroix proposed using SiO$_2$, ZnO, GGG, and Al$_2$O$_3$ as buffer layer, among them ZnO gave rise to the best BaM film orientation for in situ
crystallized barium hexaferrite films grown on Si by PLD. However, the best grown BaM film was still not suitable for LPE seed layer according to the author. In 2000, Wane et al. reported the growth of BaM film used for the integrated permanent magnets in MMIC circulator by e-beam evaporation. It was also reported that a layer of Au or Cu was in need to improve the adhesion of the film on Si. In 2004, Berre reported the growth of 10µm thick BaM for passive isolator with 3.3 dB/cm of loss at 50 GHz. In 2005, Liu reported the growth of barium ferrite thin films by pulsed laser deposition on MgO buffered Si substrates for microwave application. Besides BaM ferrite, spinel and garnet ferrites have also been explored for the integration on silicon. In 1995, Adam first reported the growth of 100 micron thick YIG film on Si for the monolithic integration of an X-band circulator. The film was grown at 500°C, followed by rapid annealing at 850 °C for 20 seconds. In 2004, Xi et al. reported on polycrystalline NiZn-ferrite films fabricated on Si (111) substrates by PLD and observed an preferential (400) orientation of the films. In 2005, Sorescu investigated NiZn and Zn-ferrite films deposited on silicon (100) substrates. In 2006, Calle et al. studied NiZn ferrite films deposited on (100) Si substrates using magneto-optical Kerr effect. In 2008, Chen et al. addressed the polycrystalline BaM films with thicknesses of 100-150 µm deposited on Al₂O₃/Si or SiO₂/Si substrates by screen printing technique. Due to a relatively low density and misalignment of grains, the BaM films exhibited large microwave linewidths that still need to be lowered to meet the requirements of practical microwave devices.
Preparation of ferrite films on GaAs

Even though it is the most dominating material in the semiconductor industry, Si has limited applications in the microwave range due to relatively high conductivity compared to other semiconductor materials such as GaAs. The conductivity translates into high loss in the form of eddy current and is not favorable for high frequency microwave applications. From this point of view, GaAs is a better candidate for use in microwave frequency. In 1987, Abe fabricated a microstrip junction circulator using NiZn ferrite films deposited by electro-plating and spin-spray coating onto GaAs. In 1990, Yoo and Talisa demonstrated the spin-spray deposition and the patterning of NiZn ferrite film on a portion of a GaAs wafer containing several MMIC circuits. For practical device applications, thick films with low losses are in demand. A 25 microns thick Ni-Zn ferrite film was achieved by a multiple deposition method with intermediate drying processes. Unfortunately, low resistivity and high dielectric loss at microwave frequencies was observed due to the poor film crystal quality. In 1995, Buhay reported the deposition of YIG films using high rate PLD on GaAs. The poor microwave performance (high attenuation) was explained by poor surface morphology and severe cracking of thick YIG films. In 1996, Adam reported the development of K-band circulators operating at 20 and 35 GHz that were monolithically integrated with both GaAs and epitaxial GaAs-on-Si wafers. The device and its scattering parameters are shown in Fig. 7.
Fig. 7 Photograph of a completed GaAs-on-Si wafer showing 20 and 35 GHz circulators on gold ground planes along with test matching sections. The insertion loss and isolation of a 20 GHz circulator as a function of frequency.

Despite all these efforts, no practical devices were ever achieved. As we discussed earlier, poor crystal quality of the films has a detrimental effect on the
device performance. As a matter of fact, the produced films mentioned above are mostly polycrystalline, or even amorphous, resulting in poor device performance compared with competing technologies. In polycrystalline ferrites, the impurity defects, random local anisotropy fields and residual porosity, broaden the FMR linewidth and increase the microwave loss. This is a serious obstacle, especially in circulator design and fabrication. To ensure better microwave performance, single crystal films are needed. However, successful single crystal ferrite film growth requires high temperature processing, which is beyond the tolerance of Si and GaAs substrates. In case of GaAs, even by introducing SiO₂ and Si₃N₄ as protective layers, GaAs cannot be exposed to temperatures approaching 900 °C without degradation. Such temperatures, however, are required for the growth of high quality BaM films. It is well known that GaAs dissociate at ~400 °C and silicon easily alloys under long heating. So, even the trial of a two-step deposition of BaM at temperature under 500 °C, followed by annealing, was not successful in obtaining high film quality. The trial of rapid thermal annealing for several seconds also failed because it is not effective to transfer polycrystalline hexaferrite into good single crystal hexaferrites.
Chapter 2 Growth and characterization of ferrite films

2.1. Pulsed laser deposition (PLD)
2.2. X-ray diffraction (XRD)
2.3. Scanning electron microscopy (SEM)
2.4. Vibrating sample magnetometer (VSM)
2.5. Ferromagnetic resonance (FMR)
2.1. Pulsed Laser Deposition (PLD)

Pulsed laser deposition (PLD) is a well-established and powerful tool to grow semiconductors, dielectrics, ferroelectrics, ferrites (YIG, spinel, hexaferite), high temperature superconducting oxides and other films with complex composition and structures. In PLD, high energy Excimer laser pulses, impinging upon a homogeneous target, produce a vapor flux, also known as a plume. The content of the plume, including ions, atoms, molecules, clusters, and other species, is condensed on the nearby substrate to form the film. The principle may seem similar to a flash evaporation technique. But, it has two major intrinsic advantages over any other conventional evaporation. First, high energy (several hundred milliJoule) transferred into the target during the short time (nanosecond) of interaction with the laser pulse can generate extremely high heating rate on a small target spot, which cause the evaporation of the target material irrespective of the evaporating point of the constituent elements. Secondly, using external laser allows deposition to take place in a reactive or inert atmosphere, depending on the composition and the stoichiometry of the desired film. These two advantages make PLD an efficient tool for the growth of stoichiometric, epitaxial, high temperature superconducting oxide films in 198780. In 199081, Vittoria et al. first proposed to grow ferrite films using PLD.

Despite the success of PLD in many applications, the growth of
epitaxial BaM on wide band gap semiconductor substrates has proven challenging. Numerous unexpected challenges were encountered as research progressed. Before going into experimental details, let us first go over the basics of the PLD technique. For convenience, we separate the PLD process into four steps: *ablation, transportation, deposition, and growth*. A PLD set up in the chamber was shown in Fig. 1.

![Fig. 1 PLD set up in the chamber](image)

*Ablation* is the first step of PLD processing. The physics of the complex laser–solid interaction is presently not fully understood. However, it is generally agreed that it is a far from equilibrium process. With high energy laser pulses impinging upon a small target area, part of the energy is absorbed immediately by the target material and transformed into electronic excitation energy, lattice thermal energy, and hydrodynamic energy. This complex interaction causes the target ablation, in other words, creates a dense vapor of particles extracted from the target. The target that was used in our experiment was shown in Fig.2. In addition, part of the laser energy from the pulses is
absorbed by the formed vapor, which results in the increase of the vapor pressure and temperature as well. Therefore, the vapor quickly expands into the surrounding vacuum. The majority of vapor’s contents are ionized particles formed by laser-solid and laser-plume interaction. The ionized particles have been long recognized a major positive impact relative to the film growth and is believed critical for oxygen stoichiometry preservation in the metal oxides films. The high degree of ionization is indeed an important advantage of the PLD process attributed to the high energy density delivered by the laser. In addition to the ions, the vapor contains many other species including photons, electrons, neutral atoms, molecules, clusters, and particulates. With regard to the film quality, particulates are the most undesirable portion of plume content. In fact, particulates “splashing” from the target are the main cause for the inhomogenous film growth, responsible for defects as well as loss of epitaxy. Typically, there are several types of splashing associating to PLD processing, which include surface boiling and exfoliation. Surface boiling occurs when the time of energy transfer from the laser into the target is shorter than the time needed to evaporate target surface layer with thickness of material’s skin depth. Since this phenomenon probably results from the film strain, it can often be observed in high Young’s modulus materials, such as high melting metals and hard oxides.
Splashing becomes a major obstacle preventing the application of PLD technique in industry. Usually, a low laser energy density can effectively alleviate splashing at the expense of deposition rate. However, this is detrimental to the film quality as the film growth is sensitive to laser energy density. Fortunately, particulates have larger size from 0.1 to several microns and move slower (less than 50 m/s) compared with other species (100-5000 m/s) in the plume. So, one could apply a flux screening or a mechanical velocity selector technique to sieve out undesirable particulates.

In the transport phase, we discuss the phenomena involved after the interaction of the incident laser beam with the vapor in the vicinity of the target surface. It is reasonable to assume that an isothermal temperature is maintained since a dynamic equilibrium exists between the plasma absorption and the energy transfer from thermal to kinetic. As a result, plume species obtain velocities in the range of 104 to 106 m/s and high energies of 1 to 100 eV, except for particulates. In the process of vapor expansion, particles’ kinetic energy is attenuated due to multiple collisions within the plume or with
background gas molecules until the particles are deposited on the substrate surface. Within the plume, the frequency of particle collisions is determined by the particle size and the pressure of the background gas. It is recognized that the kinetic energy determines the particle diffusivity as well as absorption and desorption probability at the film surface. Since the kinetic energy is adjustable through ambient pressure, it provides an effective way to control the thin film growth and may be the key factor in pursuit of epitaxial growth in low temperature regime (e.g. low pressure growth). Several models, like the drag force and the shock wave, have been proposed to calculate kinetic energy in both low and high ambient pressure environments.

In addition to the kinetic energy, species distribution is another critical factor that controls the film growth process. The expansion of the vapor containing numerous species was described by forward peaking guided by the laws of gas dynamics. The target-to-substrate distance and the working gas pressure are two additional important parameters that influence the angular distribution of the plume intercepted by the substrate. An uneven particle distribution is detrimental to the film's uniformity, especially, in the case for large wafer substrates. As a fact, the uniformity limitations imposed by the angular distribution of particles in the plume are among the major downsides that hinder the wide acceptance of PLD as a commercial film growth tool.

Now, let us consider the third stage of the deposition which occurs near the substrate surface. When the energetic species arrive at the substrate, a collision region is formed between the incident flux and the desorpted atoms
from the film surface. This region serves as a source for the particles condensation at the film surface. When the condensation rate is higher than the particles arriving rate, thermal equilibrium condition is met and film growth proceeds on the substrate surface fueled by the direct flow of the ablation particles. This is common to other evaporation-based film growth methods; however, the short duration of laser pulse give rise to PLD an unique effect on the subsequent film nucleation and growth.

The deposition can be seen as instantaneous for every pulse and this instantaneous deposition is followed by a relative long time interval, where no deposition takes place. During this time interval, the adatoms relax on the surface by migration and subsequent incorporation through nucleation and growth. This adatom rearrangement can be considered as an anneal process and has significant consequences in deposition, especially in alternating target laser ablation (ATLAD), which will be discussed in the later chapter. As a matter of fact, the short duration high power density pulses give PLD another advantage of high deposition rate over other physical vapor deposition techniques. Take an example of BaM, a typical deposition rate is 0.01-0.1 nm/pulse with deposition pulse duration of 10 ns. As a result, the instaneous deposition rate can be converted to as high as 10^6-10^5 nm/s. This value is much higher compared to other PVD techniques whose typical deposition rates are in order of 10^-2-10^-1 nm/s. The instantaneous deposition rate is mainly determined by the laser energy density, target-to-substrate distance and the ambient gas properties. Additionally, the average growth rate
is regulated by the pulse repetition rate and can be varied far from the instantaneous deposition rate.

Nucleation and growth is the final and the most important stage in PLD process. Nucleation occurs whenever local fluctuations from equilibrium arise in a thermodynamically stable system, which leads to a phase transition from gas to solid phase. In other words, a supersaturated gas phase is a prerequisite for the formation of nuclei, while the formation probability is determined by the activation energy. Here, we use three different mechanisms to describe the process of film growth as following:

1. Three dimensional islands growth (Volmer-Weber),
2. Two dimensional full-monolayer growth (Frank-van der Merwe),
3. Two dimensional growth of full-monolayers followed by three dimensional islands growth (Stranski-Krastino).

How a substrate-film system selects the growth mode is determined by the thermodynamics of the surface energies and the interfacial energies among three phases of substrate, the condensing cluster and the vapor. The system energy results in a strong bonding between film and substrate. Therefore, two dimensional full-monolayer (Frank-van der Merwe) formation will take place. This could be treated as two independent processes in which nucleation causes the formation of surface steps and subsequent growth causes the lateral development of these steps. This condition is always self-satisfied for a perfect homoepitaxy; in general, full monolayer nucleation will be
promoted by the strong film substrate bonding, low film surface energy and high substrate surface energy.

In last, three dimensional islands nucleation on two dimensional full monolayers often occurs in heteroepitaxial growth. There, the lattice mismatch between the substrate and the film will introduce biaxial strain, resulting in an increase in elastic energy. This elastic energy grows along with the increase of the layer thickness and changes the growth mode at a critical thickness, where elastic energy is comparable to the increase in the interfacial energy. Unlike LPE and MBE, PLD is far from thermodynamic equilibrium, thus nucleation and growth are more complicated and strongly affected by the kinetic energies of the species. The theory of poly-layer growth of thin films was proposed to describe the complex film formation in the PLD process. In this theory, it is assumed that the building of a thin solid film is accomplished by the simultaneous filling of several monolayers and the supersaturation dependence can be determined by concrete model considerations. As a result, depending on many combined parameters, such as laser density, substrate temperature, kinetic energy, ionization degree, as well as the type of the condensing material and the physical-chemical properties of the substrate, thin films of single crystalline, poly crystalline or amorphous structures can be synthesized by PLD.
2.2 X-Ray Diffraction (XRD)

X-ray Diffraction (XRD) is a tool used for identifying the atomic and molecular structure of a crystal, in which the crystalline atoms cause a beam of incident X-rays to diffract into many specific directions. By measuring the angles and intensities of these diffracted beams, a crystallographer can produce a three-dimensional picture of the density of electrons within the crystal. From this electron density, the mean positions of the atoms in the crystal can be determined, as well as their chemical bonds, their disorder and various other information. Since many materials can form crystals—such as salts, metals, minerals, semiconductors, as well as various inorganic, organic and biological molecules—X-ray crystallography has been fundamental in the development of many scientific fields. In its first decades of use, this method determined the size of atoms, the lengths and types of chemical bonds, and the atomic-scale differences among various materials, especially minerals and alloys. The method also revealed the structure and function of many biological molecules, including vitamins, drugs, proteins and nucleic acids such as DNA. X-ray crystallography is still the chief method for characterizing the atomic structure of new materials and in discerning materials that appear similar by other experiments. X-ray crystal structures can also account for unusual electronic or elastic properties of a material, shed light on chemical interactions and processes, or serve as the basis for designing pharmaceuticals against diseases.

In a single-crystal X-ray diffraction measurement, a crystal is
mounted on a goniometer. The XRD from Rigaku is shown in Fig.3. The
goniometer is used to position the crystal at selected orientations. The crystal is
bombarded with a finely focused monochromatic beam of X-rays, producing a
diffraction pattern of regularly spaced spots known as reflections. The two-
dimensional images taken at different rotations are converted into a three-
dimensional model of the density of electrons within the crystal using the
mathematical method of Fourier transforms, combined with chemical data
known for the sample. Poor resolution (fuzziness) or even errors may result if
the crystals are too small, or not uniform enough in their internal makeup.

Fig. 3 Rigaku XRD

X-ray crystallography is related to several other methods for
determining atomic structures. Similar diffraction patterns can be produced by
scattering electrons or neutrons, which are likewise interpreted by Fourier
transformation. If single crystals of sufficient size cannot be obtained, various
other X-ray methods can be applied to obtain less detailed information; such methods include fiber diffraction, powder diffraction and (if the sample is not crystallized) small-angle X-ray scattering (SAXS). If the material under investigation is only available in the form of nanocrystalline powders or suffers from poor crystallinity, the methods of electron crystallography can be applied for determining the atomic structure.

For all above mentioned X-ray diffraction methods, the scattering is elastic; the scattered X-rays have the same wavelength as the incoming X-ray. By contrast, inelastic X-ray scattering methods are useful in studying excitations of the sample, rather than the distribution of its atoms.

Crystals are regular arrays of atoms, and X-rays can be considered waves of electromagnetic radiation. Atoms scatter X-ray waves, primarily through the atoms' electrons. Just as an ocean wave striking a lighthouse produces secondary circular waves emanating from the lighthouse, so an X-ray striking an electron produces secondary spherical waves emanating from the electron. This phenomenon is known as elastic scattering, and the electron (or lighthouse) is known as the scatterer. A regular array of scatterers produces a regular array of spherical waves. Although these waves cancel one another out in most directions through destructive interference, they add constructively in a few specific directions, determined by Bragg's law (shown in Fig. 4):

$$2d \sin \theta = n\lambda$$

Here $d$ is the spacing between diffracting planes, $\theta$ is the incident angle, $n$ is
any integer, and \( \lambda \) is the wavelength of the beam. These specific directions appear as spots on the diffraction pattern called \textit{reflections}. Thus, X-ray diffraction results from an electromagnetic wave (the X-ray) impinging on a regular array of scatterers (the repeating arrangement of atoms within the crystal).

![Fig. 4 X-Ray analysis of crystal](image-url)
2.3 Scanning electron microscope (SEM)

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons, shown in Fig. 5. The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image. SEM can achieve resolution better than 1 nanometer. Specimens can be observed in high vacuum, in low vacuum, in dry conditions (in environmental SEM), and at a wide range of cryogenic or elevated temperatures.

Fig. 5 SEM
The most common mode of detection is by secondary electrons emitted by atoms excited by the electron beam. On a flat surface, the plume of secondary electrons is mostly contained by the sample, but on a tilted surface, the plume is partially exposed and more electrons are emitted. By scanning the sample and detecting the secondary electrons, an image displaying the topography of the surface is created. Since the detector is not a camera, there is no diffraction limit for resolution as in optical microscopes and telescopes.

The types of signals produced by a SEM include secondary electrons (SE), back-scattered electrons (BSE), characteristic X-rays, light (cathodoluminescence) (CL), specimen current and transmitted electrons. Secondary electron detectors are standard equipment in all SEMs, but it is rare that a single machine would have detectors for all possible signals. The signals result from interactions of the electron beam with atoms at or near the surface of the sample. In the most common or standard detection mode, secondary electron imaging or SEI, the SEM can produce very high-resolution images of a sample surface, revealing details less than 1 nm in size. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. This is exemplified by the micrograph of pollen shown above. A wide range of magnifications is possible, from about 10 times (about equivalent to that of a powerful hand-lens) to more than 500,000 times, about 250 times the magnification limit of the best light microscopes.

Back-scattered electrons (BSE) are beam electrons that are reflected
from the sample by elastic scattering. BSE are often used in analytical SEM along with the spectra made from the characteristic X-rays, because the intensity of the BSE signal is strongly related to the atomic number (Z) of the specimen. BSE images can provide information about the distribution of different elements in the sample. For the same reason, BSE imaging can image colloidal gold immuno-labels of 5 or 10 nm diameter, which would otherwise be difficult or impossible to detect in secondary electron images in biological specimens. Characteristic X-rays are emitted when the electron beam removes an inner shell electron from the sample, causing a higher-energy electron to fill the shell and release energy. These characteristic X-rays are used to identify the composition and measure the abundance of elements in the sample.

In a typical SEM, an electron beam is thermionically emitted from an electron gun fitted with a tungsten filament cathode (shown in Fig. 6). Tungsten is normally used in thermionic electron guns because it has the highest melting point and lowest vapour pressure of all metals, thereby allowing it to be heated for electron emission, and because of its low cost. Other types of electron emitters include lanthanum hexaboride (LaB₆) cathodes, which can be used in a standard tungsten filament SEM if the vacuum system is upgraded and FEG, which may be of the cold-cathode type using tungsten single crystal emitters or the thermally assisted Schottky type, using emitters of zirconium oxide.
The electron beam, which typically has an energy ranging from 0.2 keV to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 nm to 5 nm in diameter. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the x and y axes so that it scans in a raster fashion over a rectangular area of the sample surface.

When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to approximately 5 µm into the surface.
The size of the interaction volume depends on the electron's landing energy, the atomic number of the specimen and the specimen's density. The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors. The beam current absorbed by the specimen can also be detected and used to create images of the distribution of specimen current. Electronic amplifiers of various types are used to amplify the signals, which are displayed as variations in brightness on a computer monitor (or, for vintage models, on a cathode ray tube). Each pixel of computer video memory is synchronized with the position of the beam on the specimen in the microscope, and the resulting image is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen. In older microscopes image may be captured by photography from a high-resolution cathode ray tube, but in modern machines image is saved to computer data storage.
2.4 Vibrating sample magnetometer (VSM)

A vibrating sample magnetometer (shown in Fig. 7) or VSM is a scientific instrument that measures magnetic properties, invented in 1955 by Simon Foner at Lincoln Laboratory MIT. The paper about his work was published shortly afterward in 1959. A sample is placed inside a uniform magnetic field to magnetize the sample. The sample is then physically vibrated sinusoidally, typically through the use of a piezoelectric material. Commercial systems use linear actuators of some form, and historically the development of these systems was done using modified audio speakers, though this approach was dropped due to the interference through the in-phase magnetic noise produced, as the magnetic flux through a nearby pickup coil varies sinusoidally. The induced voltage in the pickup coil is proportional to the sample's magnetic moment, but does not depend on the strength of the applied magnetic field. In a typical setup, the induced voltage is measured through the use of a lock-in amplifier using the piezoelectric signal as its reference signal. By measuring in the field of an external electromagnet, it is possible to obtain the hysteresis curve of a material. The vibrating sample magnetometer measures the magnetization of a small sample of magnetic material placed in an external magnetizing field by converting the dipole field of the sample into an ac electrical signal. The idea of vibrating sample came from D. O. Smith's Vibrating Coil magnetometer.
When an external magnetic field is applied to a ferromagnet such as iron, the atomic dipoles align themselves with it. Even when the field is removed, part of the alignment will be retained: the material has become magnetized. Once magnetized, the magnet will stay magnetized indefinitely. To demagnetize it requires heat or a magnetic field in the opposite direction. This is the effect that provides the element of memory in a hard disk drive.

The relationship between field strength \( H \) and magnetization \( M \) is not linear in such materials, shown in Fig. 8. Starting at the origin, the upward curve is the *initial magnetization curve*. The downward curve after saturation, along with the lower return curve, is the main *loop*. The intercepts \( h_c \) and \( m_{rs} \) are the coercivity and saturation *remanence*. If a magnet is demagnetized (\( H=M=0 \)) and the relationship between \( H \) and \( M \) is plotted for increasing levels of field strength, \( M \) follows the initial magnetization curve. This curve increases rapidly at first and then approaches an asymptote called
magnetic saturation. If the magnetic field is now reduced monotonically, $M$ follows a different curve. At zero field strength, the magnetization is offset from the origin by an amount called the remanence. If the $H$-$M$ relationship is plotted for all strengths of applied magnetic field the result is a hysteresis loop called the main loop. The width of the middle section is twice the coercivity of the material.

![Theoretical model of magnetization $m$ against magnetic field $h$.](image)

A closer look at a magnetization curve generally reveals a series of small, random jumps in magnetization called Barkhausen jumps. This effect is due to crystallographic defects such as dislocations. Magnetic hysteresis loops are not exclusive to materials with ferromagnetic ordering. Other magnetic orderings, such as spin glass ordering, also exhibit this phenomenon.
The phenomenon of hysteresis in ferromagnetic materials is the result of two effects: rotation of magnetization and changes in size or number of magnetic domains. In general, the magnetization varies (in direction but not magnitude) across a magnet, but in sufficiently small magnets, it does not. In these single-domain magnets, the magnetization responds to a magnetic field by rotating. Single-domain magnets are used wherever a strong, stable magnetization is needed (for example, magnetic recording).

Larger magnets are divided into regions called domains. Within each domain, the magnetization does not vary; but between domains are relatively thin domain walls in which the direction of magnetization rotates from the direction of one domain to another. If the magnetic field changes, the walls move, changing the relative sizes of the domains. Because the domains are not magnetized in the same direction, the magnetic moment per unit volume is smaller than it would be in a single-domain magnet; but domain walls involve rotation of only a small part of the magnetization, so it is much easier to change the magnetic moment. The magnetization can also change by addition or subtraction of domains (called nucleation and denucleation).
2.5 Ferromagnetic resonance (FMR)

Ferromagnetic resonance, or FMR, is a spectroscopic technique to probe the magnetization of ferromagnetic materials. It is a standard tool for probing spin waves and spin dynamics. FMR is very broadly similar to electron paramagnetic resonance (EPR), and also somewhat similar to nuclear magnetic resonance (NMR), except that FMR probes the sample magnetization resulting from the magnetic moments of dipolar-coupled but unpaired electrons, while NMR probes the magnetic moment of atomic nuclei that are screened by the atomic or molecular orbitals surrounding such nuclei of non-zero nuclear spin.

A modified Varian electron paramagnetic resonance (EPR) spectrometer is used with a klystron to do ferromagnetic resonance (FMR) spectroscopy in the X-band (9.53 GHz), shown in Fig. 9. The magnetic sample to be measured is placed between the poles of an electromagnet, at the end of a shorted waveguide or centered in a cavity. An incident microwave signal couples to the sample and is partially absorbed. A crystal detector then measures the reflected microwave signal. This signal from the crystal detector is then input into the lock-in amplifier where it is compared with the reference signal. The output voltage from the lock-in amplifier vs. the external magnetic field corresponds to the derivative of the absorption curve. The half power linewidth and magnetic resonance field can be then found easily.
The dominant loss mechanism within ferrites at RF frequencies is associated with processional damping. This damping is commonly described by a damping coefficient, commonly referred to as $\alpha$ in the Landau–Lifshitz equation, or in terms of the half–power ferromagnetic resonance (FMR) linewidth $\Delta H$. These two quantities are related to each other by

$$\alpha = \frac{\gamma' \Delta H}{4\pi f'}$$  \hspace{1cm} (1)$$

where $f'$ is the frequency at which the swept field linewidth is measured and $\gamma' = 2.8$GHz/kOe. Fundamentally, $\Delta H$ is defined as the width of the imaginary part of the on–diagonal components of the susceptibility tensor $[\chi]$, which relates $M$ and $H$ [Pozar]. One
of these components, $\chi_{xx}$, is plotted as a function of the internal field of the ferrite in Fig. 10.

![Diagram](image)

Fig.10 The definition of the linewidth $\Delta H$

It is our interest to find the half-power linewidth of the absorbed power $P_{\text{abs}}$ curve, the slope of $P_{\text{abs}}$ as a function of $H_{\text{dc}}$ is known from measurement i.e. $dP_{\text{abs}}/dH_{\text{dc}}$. A typical plot of $dP_{\text{abs}}/dH_{\text{dc}}$ is shown in Fig.11.
A typical plot of $\frac{dP^{\text{abs}}}{dH_{\text{dc}}}$ as a function of $H_{\text{dc}}$.

The peak–to–peak linewidth $\Delta H_{pp}$ is defined as the spread between these two peaks, and it holds the relation that

$$\Delta H = \sqrt{3}\Delta H_{pp} \quad (2)$$

To determine the half power linewidth, one simply needs to measure the slope of $P^{\text{abs}}$ as a function of field strength and determine the peak–to–peak linewidth from the data; the half power linewidth is simply computed using Eqn. (2).

The convenient way to express the FMR condition which can be applied to most or all cases of interest is as equ (3):

$$\left(\frac{\omega}{\gamma}\right)^2 = (H + 4\pi M)(H - H_A) = H_1 H_2 \quad (3)$$
The permeability parameters $H_1$ and $H_2$ for various magnetic fields are shown in Table 1. In our later experiments, we will use the thin film M and Y type ferrites FMR condition to evaluate the microwave properties of our sample.
<table>
<thead>
<tr>
<th>Field Configuration</th>
<th>$H_1$</th>
<th>$H_2$</th>
</tr>
</thead>
</table>
| M-type hexaferrites (saturated case) | $H + 4\pi M$  
$H_A + 4\pi M,$  
$H_A = 2|K_u|/M,$  
$K_u < 0.$ | $H - H_A,$  
$H - H_A,$  
$H - H_A$  
$H - H_A$  
$H - 4\pi M,$  
$H - H_A - 4\pi M,$  
$H_A = 2|K_u|/M,$  
$K_u < 0.$ |
| M-type hexaferrites (Unsaturated case) | $H + H_A + 4\pi M,$  
$H_A = 2|K_u|/M,$  
$K_u < 0.$ | $H + H_A$  
$H + H_A$  
$H + H_A$  
$H + H_A$  
$H + H_A$  
$H - H_A - 4\pi M,$  
$H_A = 2|K_u|/M,$  
$K_u < 0.$ |

Table 1 The permeability parameters $H_1$ and $H_2$ for various magnetic fields
<table>
<thead>
<tr>
<th>Field Configuration</th>
<th>$H_1$</th>
<th>$H_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>M-type hexaferrites</strong></td>
<td>$H + H_A - 4\pi M$, $H + H_A \geq 4\pi M$, $H_A = 2</td>
<td>K_u</td>
</tr>
<tr>
<td><strong>Nanowires</strong></td>
<td>$H + H_A + N_1 M$, $N_1 \cong \frac{4\pi}{1 + b/a}$, $c &gt;&gt; a &gt; b$</td>
<td>$H + H_A + N_2 M$, $N_2 \cong \frac{4\pi}{1 + a/v}$, $H_A = 2</td>
</tr>
<tr>
<td><strong>Nanoparticles</strong></td>
<td>$H + (N_x - N_y)M$, $N_x \cong \frac{4\pi}{1 + t/L + t/w}$, $N_y \cong \frac{4\pi}{1 + t/L + t/w}$</td>
<td>$H + (N_x - N_y)M$, $N_x \cong \frac{4\pi}{1 + t/L + t/w}$, $N_y \cong \frac{4\pi}{1 + t/L + t/w}$</td>
</tr>
<tr>
<td><strong>Nanoparticles</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>M-type hexaferrites (oriented compacts)</strong></td>
<td>$\frac{(H_A - 4\pi M)^2 - H^2}{H_A - 4\pi M}$, $H \leq H_A - 4\pi M$</td>
<td>$H_A = 4\pi M$, $H_A = 2</td>
</tr>
<tr>
<td>Field Configuration</td>
<td>$H_1$</td>
<td>$H_2$</td>
</tr>
<tr>
<td>---------------------------</td>
<td>-----------------------------------------------------------------------</td>
<td>---------------</td>
</tr>
</tbody>
</table>
| Cubic crystals $<101>, H <001>$ | $H + H_C + 4\pi M,$  
$H_C = 2|K_1|/M,$  
$K_1 < 0.$                  | $H + H_C$      |
| Cubic crystals $<100>, <010>$ | $H + H_C/2 + 4\pi M,$  
$H_C = 2|K_1|/M,$  
$K_1 < 0.$                  | $H - H_C$      |
| Cubic crystals $<001>, <111>, H <001>$ | $H + 2/3 H_C + 4\pi M,$  
$H_C = 2|K_1|/M,$  
$K_1 < 0.$                  | $H + 2/3 H_C$  |
| Y-type hexaferrites       | $H + H_A + 4\pi M,$  
$H_A = 2|K_u|/M,$  
$K_u > 0.$                  | $H$           |
| Y-type hexaferrites       | $H - H_A - 4\pi M,$  
$H > H_A + 4\pi M$  
$K_u > 0.$                  | $H - H_A - 4\pi M$ |

Table 1 continued
Chapter 3 Epitaxial growth of the hexaferrites films on semiconductor substrate GaN

3.1. BaM thin film grown on MgO substrate
3.2. Crystal growth of Y type hexaferrite
   3.2.1 Flux based single crystal Zn₂Y growth in crucible
   3.2.2 Single crystal Zn₂Y grown on MgO substrate
   3.2.3 Single crystal BaM grown on GaN substrate
   3.2.4 Single crystal Co₂Y growth on GaN substrate
   3.2.5 Magnetization of the thick single crystal Co₂Y ferrite film dependence on temperature
3.1 BaM thin film grown on MgO substrate

In the case of Y type ferrite films grown on GaN, there is a relatively large lattice mismatch of 6.2% between the GaN (001) substrate and the $\text{Co}_2\text{Y}$ (001) film thus requiring a buffer layer to mediate interfacial strain and realize epitaxial growth. Further complicating growth is that GaN is thermally unstable in vacuum at temperatures near 950 °C at which typical pulsed laser deposition (PLD) growth of ferrite film seeds are grown. In order to mitigate both interfacial strain and surface reactivity, a layer of MgO, having (111) crystallographic orientation, was grown on the GaN substrate. Following the preparation of the MgO (111) buffer layer, $\text{BaFe}_{12}\text{O}_{19}$ (BaM) was deposited between $\text{Co}_2\text{Y}$ and MgO (as step 1 shown in Fig. 1). Now, let us take a close look at how we realize the first step to grow BaM on MgO substrate.
The hexagonal Ba M-type (BaM) hexaferrites are of great interest for microwave devices applications because of their large and tunable magnetic anisotropy fields, high resistivity at high frequencies, high coercivity, and high hysteresis loop squareness, that make them suitable for self-biased device applications\textsuperscript{20}, magnetic memory\textsuperscript{21}, as well as permanent magnet materials. The magnetic properties of BaM hexaferrite\textsuperscript{22} can be
tailored by the substitution of ions for $\text{Ba}^{2+}$ or $\text{Fe}^{3+}$. It is well known that the large uniaxial magnetocrystalline anisotropy of $\text{BaM}$ can be reduced by the substitution of $\text{Me–Ti}$ or $\text{Me–Sn}$, where $\text{Me}=\text{Zn}, \text{Co}, \text{Mn}$; such, substitutions for $\text{Fe}^{3+}$ are desirable for magnetic recording-media-application \textsuperscript{23}. To date, bulk ceramic samples with substitutions for $\text{Fe}^{3+}$ have been widely studied.\textsuperscript{24} The effect of the substitution $\text{Fe}^{3+}$ on the magnetocrystalline anisotropy is spectacular and results in a change of anisotropy filed. The substitution content of Zr and Zn were chosen to be 0.5, according to the reference\textsuperscript{25}, the $\text{H}_a$ is about 8000 Oe. The reduction of the strong magnetic anisotropy makes hexaferrites suitable for perpendicular magnetic recording and microwave applications. Here, $\text{BaFe}_{11}\text{Zn}_{0.5}\text{Zr}_{0.5}\text{O}_{19}$ (or $\text{Ba(Zr,Zn)M}$) thin films were deposited by pulsed laser deposition (PLD) \textsuperscript{26} on MgO (111) substrates\textsuperscript{27}. We demonstrate the success epitaxial growth of $\text{Ba(Zr,Zn)M}$ single crystal thin film with (00l) preferred orientation. The samples were annealed after deposition to achieve improved crystallization as judged by rocking curve full width at half maximum linewidths. Low perpendicular anisotropy fields were achieved around 7500± 10% Oe (46% lower than the $\text{BaM}$ parent compound) while maintaining a relatively high $4\pi\text{Ms}$ or $\sim3080 \pm 7\% \text{ G}$ at room temperature. The magnetization dependence of the sample was examined from 25 to 350 °C, indicating a Curie temperature of 320°C and a compensation temperature around 250 °C. $\text{Ba(Zn,Zr)M}$ ferrite films having a comparatively low $K_1 \sim 0.920 \times 10^6 \pm 12.2\% \text{ erg/cm}^3$ have attracted new interest in the field of microwave devices especially for X (8-12 GHz) and Ku band (12-18 GHz) applications. The ferromagnetic resonance peak-to-peak derivative linewidth at 9.55 GHz was 120 Oe demonstrating properties that satisfy the needs of self-biased microwave device applications\textsuperscript{28}. 
A BaFe_{11}Zn_{0.5}Zr_{0.5}O_{19} target was made by conventional ceramic techniques of repeated firing and grinding until X-ray diffraction confirmed a pure phase hexaferrite structure existed. Ba(Zn,Zr)M films were then deposited on MgO (111) by pulsed laser deposition (PLD) from this target. The Excimer laser was excited by KrF gas with λ=248 nm of an average laser density of 400 mJ/cm². The base pressure in the deposition chamber was 5x10^{-6} Torr; During deposition a dynamic pressure of oxygen was maintained during the course of deposition from 5 mTorr to 10 mTorr. The substrate temperature was adjusted from 850 to 950 °C. The Ba(Zn,Zr)M samples were annealed after deposition at temperatures and times of 1000 to 1150 °C for 2 to 20 minutes, respectively. Crystal structure and texture of the resulting films were studied by room temperature X-ray diffraction (XRD) using Cu Kα radiation in a θ-2θ geometry. The surface morphology was observed by atom form microscopy (AFM). Rocking curve scans for the (006) peak was performed by XRD to determine the crystal quality of the thin films. The magnetic properties of the films were determined using vibrating sample magnetometry (VSM). The magnetic temperature dependence for the thin films was measured within the VSM instrument. The microwave properties were measured by FMR at 9.55 GHz.

X-ray diffraction (XRD) spectra for the Ba(Zn,Zr)M films deposited on MgO (111) substrates were collected at room temperature using Cu Kα radiation in 0-2θ geometry. The XRD pattern of the Ba(Zn,Zr)M film grown on MgO (111) substrate at 950 °C and under 5 mTorr O₂ pressure is illustrated as Fig.2 (a). It is noticed that the Ba(Zn,Zr)M film remains as a pure phase structure possessing a (00l) preferred orientation. Additionally, the thickness of the films was determined to be 296.3 ± 15%
nm by surface profilometry; this result is consistent with the result ~285.7 ± 12% nm derived from the Jade™ XRD analysis software, which is based on Scherrer Equation.

\[ B(2\theta) = \frac{K \lambda}{L \cos \theta} \]  

Here, \( B \) is the peak width, and \( K \) is a constant with value of 0.94. \( \lambda \) refers to the wavelength of the incident X-ray beam and \( L \) is the thickness. The peaks near 37.1 and 78.6 degree (in \( 2\theta \)) correspond to the MgO substrate. The peaks at 23.03\(^\circ\), 30.5\(^\circ\) and 54.6\(^\circ\) correspond to (006) and (008) and (0014) planes of the Ba(Zn,Zr)M film, respectively. Lattice constants of the doped BaM were also obtained by analysis of the XRD data and resulted in c-axis of 23.3 Å and a-axis of 5.91 Å, which is slightly larger than the undoped BaM. The lattice constant of MgO and the BaM crystal is 4.213 and 5.893 Å, respectively. The lattice mismatch between (111) MgO~5.957 Å and BaM crystallographic planes is ~1.07%; This is a critical factor in achieving epitaxial growth. The rocking curve of the Ba(Zn,Zr)M film around the (006) diffraction peak is shown as Fig.2(b). The full width at half maximum (FWHM) of the (006) rocking curve diffraction obtained was about 0.183\(^\circ\) (~658.8 arcseconds), which is comparable to BaM thin films deposited on sapphire substrate\(^{29}\).
Fig. 2 (a) XRD patterns for Ba(Zn,Zr)M films deposited at 950 °C under 5 mT oxygen pressures. Diffraction peaks have been identified with either the Ba(Zn,Zr)M film or the MgO (111) substrate. (b) Rocking curve of single crystal Ba(Zn,Zr)M thin film was measured around (006) diffraction peak.

The surface morphology for the Ba(Zn,Zr)M films on MgO substrates was observed by atomic force microscopy (AFM), shown in Fig. 3(a). The surface roughness is about 2.541 nm with a uniform grain size of 200~300 nm.

The chemical composition of the ablated BaM films was determined using energy-dispersive X-ray spectroscopy (EDXS). Findings indicate a close match exists between the film composition and that of the target composition of BaFe_{11}Zn_{0.5}Zr_{0.5}O_{19}. Since these values are close to the nominal ratios used in designing the target composition, preferential ablation and deviation from ideal sticking coefficients do not play a major role in film growth.
Fig. 3(a) AFM images of Ba(Zn,Zr)M thin film. Fig. 3(b) Hysteresis loop of Ba(Zn,Zr)M thin film with in plane and out of plane magnetic field applied.

The magnetic properties of Ba(Zn,Zr)M films were measured using a vibrating sample magnetometer (VSM) at room temperature with a magnetic field strength ranging from -10 kOe to 10 kOe. Both in plane and out of plane hysteresis loops are presented in Fig. 3(b). It is shown that the easy axis of the Ba(Zn,Zr)M film aligns out of the film plane consistent with the crystallographic c axis aligning perpendicular\(^{30}\) to the sample plane. The hysteresis loop collected with the applied magnetic field aligned along the crystallographic c axis perpendicular to the film plane experiences a saturation magnetization \((4\pi M_s)\) of \(3080 \pm 7\% \text{ G}\) with a magnetic anisotropy field of \(7500 \pm 10\%\)
A coercive field of ~80 Oe was measured along the magnetic hard axis. Low coercivity along the hard direction reflects the less effective pinning of domain walls from the defected interface volume and has phenomenologically been linked to low microwave losses in BaM films. These results match other high quality BaM films deposited on lattice matched oxide substrates.

The temperature dependence of the magnetization of Ba(Zn,Zr)M films on MgO (111) is shown in Fig.4. At an applied of H=5000 Oe, magnetization was measured from 25 to 350 °C. The magnetization of Ba(Zn,Zr)M films was first decreased as temperature was increased, reaching the first minima at 250 °C. Then the magnetization abruptly rises again and reaches a high value of 1.7 kG at 270 °C followed by another drop to near zero at 320°C. The behavior reveals a compensation temperature where the net magnetization vanishes at a temperature of 250°C and a Curie temperature where the individual sublattice magnetizations vanish at 320°C. This behavior is consistent with two spin sublattices in a ferrimagnetic in which they lose their magnetism at different temperature rates. The Curie temperature is around 320°C which is lower than pure BaM which is reported to be ~450°C. The substitution of Fe³⁺ results in a weakening of the magnetic interactions, which is observable by a diminution of the Curie temperature. The number of the magnetic ions Fe³⁺ decreases after the substitution of Zn²⁺ and Zr⁴⁺, which results in the decrease of the number of exchange magnetic ion pairs in the materials. The exchange effect is relatively weak so as to lead the decrease of Curie temperature.
The microwave properties were measured by FMR as the power derivative as a function of applied magnetic field as plotted in Fig. 5 for an annealed Ba(Zn,Zr)M sample. The FMR linewidth at 9.55 GHz, $\Delta H$, is measured to be $\sim$120 Oe, which is comparable with other BaM thin films deposited on oxide substrate\textsuperscript{35}. Compared to the as-deposited films, the FMR linewidth was reduced by 57.9% upon annealing. The improvement after annealing indicates assorted defects within the film have been eliminated by the heat treatment process. The theoretical resonance condition is expressed as:

$$f = \gamma' \sqrt{H(H - H_A + 4\pi M_s)}.$$
Here $\gamma'$ refers to the effective electron gyromagnetic ratio, and its value is $2.8 \times 10^6$ Hz/Oe, and the DC magnetic field is in the film plane. The calculated anisotropy field is around 8204 Oe, which matched in the range of the results obtained from VSM measurement.

![Graph](image)

**Fig.5** FMR measurement of Ba(Zn,Zr)M films on MgO (111) at 9.55 GHz.

In summary, BaFe$_{11}$Zn$_{0.5}$Zr$_{0.5}$O$_{19}$ was grown as films on MgO (111) substrates by pulsed laser deposition. In order to optimize the growth of Ba(Zn,Zr)M films, variation of deposition temperature, pressure and laser energy were explored. Room temperature $\theta$–$2\theta$ X-ray diffraction measurements indicate all diffraction features correspond to
reflections indexed to a single crystalline phase having space group $P63/mmc$ with (00l) preferred orientation. Atomic force microscopy images reveal smooth uniform surface with a grain size of 200–300 nm. The resulting Ba(Zn,Zr)M films had an anisotropy field value of 7500 Oe (representing a 46% lower over pure BaM thin films), while retaining a relatively high $4\pi M_s$ of 3080 ± 7% G. The best films have an FMR power derivative linewidth of 120 Oe at 9.55 GHz.

Later in this experiment, as step 2, we demonstrate the use of ~20 nm diameter Co$_2$Y powder positioned atop a GaN/Al$_2$O$_3$ substrate to realize epitaxial growth of an 80–500 µm thick film of Co$_2$Y at temperatures as low as ~1050 to 1150 ºC without flux. $^{36}$
3.2 Crystal growth of Y type hexaferrite

Single crystal or quasi-single crystal ferrites have as advantages high crystalline orientation, low microwave loss and compact size, and high efficiency in device applications. Earlier steps, such as traditional Pt crucible-based crystal flux growth, liquid phase epitaxy, screen printing, solid-state quasi-crystal growth and floating zone techniques were employed to grow low microwave loss ferrite materials. However, those methods require long firing and/or cooling cycles, often complicated laboratory instrumentation and protocols, and expensive chemical materials consumption and waste. Furthermore, traditional growth methods typically involve complicated liquid phase mixtures, strict temperature and growth diffusion rate control, and the use of highly toxic fluxes of the Bi$_2$O$_3$ and/or PbO type (among others). These characteristics often result in a higher likelihood of failure, the detrimental introduction of impurities and environmental pollution.

The methods of synthesis of the single crystal from melts have been listed in table 1 to show the advantages and drawbacks. The BaO-Na$_2$O-Fe$_2$O$_3$ system has the advantage of low volatility, low viscosities, low melting T, and negligible corrosive effect on Pt crucible. However, it involves long cooling circle, and long time to etch the crystal out from crucible, as well as parallel intergrowths of several phases. Similar results could also be found
from BaO-B₂O₃-Fe₂O₃ melts system. By adding Add PbO or PbF₂ to the BaO-
Na₂O-Fe₂O₃ system, large crystal may be obtained, but Pb is of high volatility
and density which has corrosive effect on Pt crucible. Also, Pt is of toxicity and
can sometimes substituted Ba ferrite could be formed.

<table>
<thead>
<tr>
<th>Theory</th>
<th>By adding flux to the mixer to lower the melting point</th>
<th>and crystallization top seeding or spontaneous nucleation by very slow cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Advantages</strong></td>
<td><strong>Drawbacks</strong></td>
<td></td>
</tr>
<tr>
<td>1. BaO-Na₂O-Fe₂O₃ melts</td>
<td>Low volatility, low viscosities, low melting T, and negligible corrosive effect on Pt crucible</td>
<td>Long cooling circle, and long time to etch the crystal out from crucible. Parallel intergrowths of several phases.</td>
</tr>
<tr>
<td>2. BaO-B₂O₃-Fe₂O₃ melts</td>
<td>Same as above</td>
<td>Same as above</td>
</tr>
<tr>
<td>3. Add PbO or PbF₂ to 1.</td>
<td>Large crystal may be obtained</td>
<td>high volatility and density, corrosive effect on Pt crucible, toxicity, substituted Ba ferrite formed</td>
</tr>
</tbody>
</table>

Table 1 Synthesis from melts (three compositions)

The methods of synthesis of the single crystal from salt melts have been listed in table 2 to show the advantages and drawbacks. The BaCO₃-
FeOOH in alkali metal melts (NaCl, KCl) system features low volatility, low
viscosities, low melting T, and negligible corrosive effect on Pt crucible, but
long cooling circle, and long time to etch the crystal out from crucible were found as the drawbacks. Also, parallel intergrowths of several phases may happen as well. \( \text{BaCO}_3-\text{Fe}_2\text{O}_3-\text{Na}_2\text{SO}_4, \text{K}_2\text{SO}_4 \) melts share similar advantage but it required excess Ba which would form poorly soluble \( \text{BaSO}_4 \).

<table>
<thead>
<tr>
<th>Theory</th>
<th>Advantages</th>
<th>Drawbacks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1. \text{BaCO}_3-\text{FeOOH} in alkali metal melts (NaCl, KCl)</strong></td>
<td>Low volatility, low viscosities, low melting points, and negligible corrosive effect on Pt crucible</td>
<td>Long cooling circle, and long time to etch the crystal out from crucible, parallel intergrowths of several phases.</td>
</tr>
<tr>
<td><strong>2. \text{BaCO}_3-\text{Fe}_2\text{O}_3-\text{Na}_2\text{SO}_4, \text{K}_2\text{SO}_4 melts</strong></td>
<td>Same as above</td>
<td>Required excess Ba forms poorly soluble ( \text{BaSO}_4 )</td>
</tr>
</tbody>
</table>

Table 2 Synthesis from salt melts

**Floating zone method:**\(^{10}\) The floating zone method was worked out with the use of either carbon-arc or xenon-arc image furnaces in order to improve the Bridgnzan method. Heating of the sample is carried out by means of the Costello method. A halogen lamp is placed on one focal point and the ample on the other in a closed elliptical reflector. The light produced by the halogen lamp is focused and cast on the sample from every direction. An
outline of the apparatus is shown in Fig. 6. The enlarged figure image of molten zone is projected on the screen through the lens. The molten zone and optical system are separated by a quartz tube, and high-pressure gas flows through the tube. The maximum pressure is 30 atm. A metal tube is set up in a part situated above the molten zone in the quartz tube. The vapor of oxide flows through the metal tube. No deposition takes place on the quartz tube. The reflector is cooled with water and the lamp with air. Temperatures at the surface of the sample, which was set up at the focal point of the closed reflector, were measured in order to obtain the information of the distribution and the fluctuation of the temperature in the melt zone.
In the preparation of crystals, the seed crystal and ceramic rod were rotated in opposite directions to each other (30 r/min) and moved downward at zone speed of 10 mm/h, 10 minutes after the molten zone became stationary. When a ferrite single crystal was prepared from the ceramic ferrite rod having uniform composition, the composition of the crystal varied with position. The sample was grown with the zone speed of 10 mm/h on the seed crystal having the same composition as that of the rod.

**Pulling Technique and LPE:** Growth experiments were performed in a vertical Kanthal furnace containing a 7-cm-diam heating element. An alumina end plug with an opening 3 cm in diameter was placed on the top of the furnace to allow observation of growth progress and provide for entry of the crystal puller's seed holder (Fig. 7). Temperature control and programming was achieved by a West digital controller modified by gearing the set point helipot to a timing motor with interrupter. Temperature deviations in the melt were typically ±0.5°C and cool-down rates could be varied from 2° to 0.01°C/h. Standard-form 60-cc platinum crucibles, filled to approximately three-fourths of their volume were used. All growth runs were made in a vertical temperature gradient of 10°C/cm, the temperature being highest at the bottom of the crucible.
The procedure used for pulling hexagonal ferrite crystals from a flux was as follows. The constituent oxides and carbonates were mixed together and premelted in a platinum crucible by induction heating. The loaded crucible was placed in the furnace and held at a temperature of 1200°C for 24 h. The temperature was then slowly decreased until surface nucleation was observed. Once the liquidus temperature was approximately determined by this method, a rotating seed crystal (60-100 rpm) was lowered until it contacted the melt surface. A furnace cool-down was then initiated at rates of 0.1 ° to 0.2°C/h while the seed crystal was simultaneously withdrawn from the melt at 0.025 to 0.075 mm/h. Crystals which grew on seeds oriented in the (IOiO) and (1120) directions were generally inferior in quality to crystals grown in the (0001)
direction. Some typical crystals were grown in the (0001) direction.

### 3.2.1 Flux based single crystal Zn$_2$Y growth in crucible

To realize the thick single crystal Zn$_2$Y growth on BaM, several methods have been tried. The very first one was using the bulk single crystal as seed, mixing with other chemical powders, and then put on top of the substrate for future epitaxial growth. The chemical oxides that were used to grow single crystal Zn$_2$Y were shown in Fig. 8.

![Chemical composition of the mixture](image)

**The chemical composition of our mixture**

- Zn$_2$Y: Ba$_2$Zn$_2$Fe$_{12}$O$_{22}$
- $\text{Na}_2\text{CO}_3$: 26.3%
- $\text{Fe}_2\text{O}_3$: 44.22%
- ZnO: 14.74%
- $\text{BaCO}_3$: 14.74%

**Total weight of 20 g mixed powder**

- $\text{Na}_2\text{CO}_3$: 4.16 g
- $\text{Fe}_2\text{O}_3$: 10.12 g
- $\text{BaCO}_3$: 3.99 g
- ZnO: 1.72 g

*Fig. 8 Chemical oxides used to grow Zn$_2$Y single crystal*

The chemicals were first measured and then ball milled with alcohol in the ball milling system, and then dried in hot plate. The powder was then put
into the alumina crucible, shown in Fig. 9. The crucible was then put into furnace to heated 1150~1200 °C for 7~8 hours, and then Cooling rate was 1~4 °C/hr to room temperature.

Fig. 9 Experimental set up of the Zn2Y single crystal growth

The single crystal was examined by microscopy shown in Fig. 10, and hexagon shaped crystals with size of 0.3~0.5 mm were clearly showed, which indicated the success growth of the hexaferrites.
The crystals were then examined by XRD, and the XRD spectrum was shown in Fig. 11. From the XRD, it indicates the crystal has multiply phases, including both M and Y type ferrite available in the crystals.
Fig. 11 XRD spectrum of the hexaferrites

The magnetic properties of the films were measured using a vibrating sample magnetometer (VSM) at room temperature with a magnetic field strength ranging from -10 kOe to 10 kOe. Both in plane and out of plane hysteresis loops are presented in Fig.12. The VSM indicated the crystal has anisotropy in C axis, and it suggested that the main phase for the yield crystal is M type.
The VSM indicated the crystal has anisotropy in C axis, and it suggested that the main phase for the yield crystal is M type. The chemicals that were used to make Y type ferrite yielded M & Y type. The EDAX results of the sample indicating the ratio of Ba$^{2+}$ to Fe$^{3+}$ is $\sim$1:6, which is M type ferrite. For Y type, the ratio of Ba$^{2+}$ to Fe$^{3+}$ =1:3 (2:6), indicating Ba$^{2+}$ lost during the baking procedure.

By doping BaCO$_3$ by 1.5 times, 2 times and 2.5 times to the original amount, same temperature recipe was employed. But there were no crystal yielded afterwards. A Completely New idea was going to be tried out!
3.2.2 Single crystal Zn$_2$Y growth on MgO substrate

The present microwave integrated circuit design paradigm has passive circuit elements, e.g., ferrite-based isolators, circulators, phase shifters, etc., fabricated on dielectric substrates. A long sought goal of the microwave device community has been the fabrication of reduced size, weight, and costs of ferrite components, while concomitantly enhancing performance and functionality. Single crystal or quasi-single crystal ferrites have as advantages high crystalline orientation, low microwave loss and compact size, and high efficiency in device applications. Earlier steps, such as traditional Pt crucible-based crystal flux growth, liquid phase epitaxy, screen printing, solid-state quasi-crystal growth and floating zone techniques were employed to grow low microwave loss ferrite materials. However, those methods require long firing and/or cooling cycles, often complicated laboratory instrumentation and protocols, and expensive chemical materials consumption and waste. Furthermore, traditional growth methods typically involve complicated liquid phase mixtures, strict temperature and growth diffusion rate control, and the use of highly toxic fluxes of the Bi$_2$O$_3$ and/or PbO type (among others). These characteristics often result in a higher likelihood of failure, the detrimental introduction of impurities and environmental pollution. To this end, a technique that realizes epitaxial thick crystalline ferrite film growth on dielectric substrates having a benign environmental impact, low cost, rapid and simple experimental setup and
protocols is sought. Such a technique will have a wide-ranging impact on the field of microwave devices, components, and systems.

Single-crystal Zn₃Y, i.e., Ba₂Zn₂Fe₁₂O₂₂, ferrites are an important class of microwave ferrites that are widely considered and used in the design of microwave and mm-wave filters and phase shifters (among other devices). However, it is often difficult to grow Y-type hexaferrites especially with thicknesses in the 10’s of microns on lattice matched supporting substrates. In the present work, a method for growing large area, i.e., >1 cm², Zn₃Y ferrite crystalline films on single-crystal (111) MgO substrates with thicknesses ranging from 25 to >100 µm is demonstrated. In this technique, a ferrite oxide precursor (FOP) mixture of BaCO₃, ZnO and Fe₂O₃ with mole ratio of 1:1:3 was ball milled for 2 hours in alcohol followed by drying at 90°C in air to eliminate the solvent. The FOP and anhydrous sodium carbonate are then melted on the surface of an MgO single crystal substrate so that the molten solution spreads over the surface as a uniform layer. The solution is maintained at 1050-1150°C for 5-15 h in order to vaporize the anhydrous sodium carbonate, thus depositing the ferrite film. Ferrite films grow with the same crystallographic orientation as the substrate. The side views of various approaches of applying the FOP and Na₂CO₃ to the substrate are shown in Fig. 13 a). In each experiment, the weight ratio of salt to FOP was maintained at 1:1 and the surface loading of the FOP was 1 mg/mm². The magnetic properties of the films were measured using a vibrating sample magnetometer (VSM) at room temperature with a magnetic field strength ranging from -10 kOe to 10 kOe.
Both in plane and out of plane hysteresis loops are presented in Fig. 13 b). In method A (see Fig. 13 a) and Table 3), a dry mixture of FOP and anhydrous Na$_2$CO$_3$ was used, resulting in secondary nucleation and polycrystalline deposits. No obvious magnetic anisotropy was observed in the hysteresis loops of sample A that indicated the sample grew without a preferred crystalline orientation. In method B, an alumina ring was introduced to assist in confining the reactant powders: The salt was packed on the bottom and the FOP loosely placed atop the salt. But most crystallization took place on the walls of the alumina ring, leaving little ferrite yield on the substrate. Resulting films demonstrated similar in plane and out of plane hysteresis loops with magnetization values lower than published results for Zn$_2$Y. In method C, dry anhydrous Na$_2$CO$_3$ was spread loosely atop the substrate and covered with dry FOP. This approach resulted in relatively poor control of the ferrite concentration as well as an uneven ferrite film thickness. The VSM results indicated a slight in plane anisotropy and relatively low $4\pi M_s$. Method D, which gave the best results, involved the compaction of a bilayer of dry anhydrous Na$_2$CO$_3$ and dry FOP; the disk was then placed on the MgO substrate. VSM results show that the easy axis of the film aligns in the film plane, with a saturation magnetization ($4\pi M_s$) of $2.5 \pm 0.1$ kGauss. The out of plane magnetic anisotropy field $H_A$ is of $8.9 \pm 0.1$ kOe. All values are consistent with those reported in the literature for Zn$_2$Y.
The ferrite nominal composition and representative firing conditions are listed in Table 3. The thickness of the ferrite films was largely dependent upon the thickness of the liquid layer formed on the MgO. The FOP surface loading, temperature, firing time, and weight ratio of salt to FOP, are four key factors affecting the epitaxial growth of ferrite films. In general, the best films, as judged by both crystallinity and magnetic properties, were produced by using the lowest temperature that would facilitate complete melting of the FOP and

Fig. 13 a) Images of the experimental set-up for each sample growth approach, and b) hysteresis loops of \( \text{Zn}_2\text{Y} \) ferrite thick films grown under different conditions with in-plane and out-of-plane applied magnetic field orientation.
salt mixture. For the case of the weight ratio of 1:1 between salt and FOP, if the melt had a low viscosity and low surface tension, as is the case for low FOP surface loading and/or high firing temperatures, the ferrite films were thin or the mixture was subject to excessive evaporation. At temperatures of 1100 °C, where thicker liquid layers were stable, the thickness of the ferrite film could be controlled by varying the surface loading density. Crystalline films of 50~100 µm in thickness were grown. When the firing temperature was reduced to 1050 °C, the mixture did not completely melted and no crystal was formed. But if the powder was over loaded, even under the same circumstances, the excess melt would run off the substrate, leading to incomplete crystal growth. When the ratio of salt to FOP was 7:3, for example, the evaporation rate was much higher than the 1:1 mixture. Discontinuous films resulted when the maximum temperature was 1100 °C, and crystalline films of ~25 µm resulted when T_{max}=1050 °C.

<table>
<thead>
<tr>
<th>Exp. Condition</th>
<th>FOP Weight %</th>
<th>FOP Surface loading (mg/mm²)</th>
<th>Time (hour)</th>
<th>Temp. (°C)</th>
<th>Film Thickness (µm)</th>
<th>Comments</th>
</tr>
</thead>
</table>


<table>
<thead>
<tr>
<th>Surface Loading</th>
<th>50</th>
<th>1.67</th>
<th>15</th>
<th>1100</th>
<th>N/A</th>
<th>Excess melts run off substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50</td>
<td>1.33</td>
<td>15</td>
<td>1100</td>
<td>~100</td>
<td>Uniform surface</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>1</td>
<td>15</td>
<td>1100</td>
<td>~80</td>
<td>Uniform surface</td>
</tr>
<tr>
<td>Firing Time</td>
<td>50</td>
<td>0.5</td>
<td>15</td>
<td>1100</td>
<td>&lt;1</td>
<td>Evaporation of charge</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.5</td>
<td>7.5</td>
<td>1100</td>
<td>~50</td>
<td>Uniform surface</td>
</tr>
<tr>
<td>Firing Temp.</td>
<td>50</td>
<td>1</td>
<td>15</td>
<td>1150</td>
<td>&lt;1</td>
<td>Evaporation of charge</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>1</td>
<td>15</td>
<td>1100</td>
<td>~80</td>
<td>Uniform surface</td>
</tr>
<tr>
<td>Flux Ratio</td>
<td>50</td>
<td>1</td>
<td>15</td>
<td>1100</td>
<td>~80</td>
<td>Uniform surface</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>1</td>
<td>15</td>
<td>1100</td>
<td>N/A</td>
<td>Discontinuous film</td>
</tr>
</tbody>
</table>

Table 3 Ferrite thick film growth conditions.

The mechanism for the growth can be interpreted by Marangoni convection\textsuperscript{64}. The system is viewed as a shallow liquid layer heated from below, supported below by a rigid plane and above with a free surface whose surface tension depends linearly upon temperature.\textsuperscript{65} A toroid convection pattern develops in which the fluid is observed to rise along the surface of the
spherical droplet and to accelerate downwards in the interior towards the liquid/solid contact point. The internal dynamics arise due to the presence of a vertical temperature gradient leading to a gradient in surface tension that in turn drives fluid away from the contact point along the interface. Two time scales associated with two flow scales of the Marangoni and buoyant convection are expected for such a system. The ratio of flow scales is estimated as follows:

\[
\frac{U_M}{U_B} \sim \frac{\tau_B}{\tau_M} \sim \frac{\alpha \Delta T}{\Delta \rho ga^2} \sim \frac{a}{\alpha \rho ga^2}
\]  

(1)

Here, convective time scales for flow driven by density gradients and for flow driven by surface tension gradients are \(\tau_B\) and \(\tau_M\), the characteristic velocity of Marangoni flow scales is \(U_M\), and the characteristic velocity associated with buoyancy-driven convection is \(U_B\). In the present case, gravity \(g\) is 9.8 m·s\(^{-2}\), density \(\rho\) is \(~5.3 \times 10^3\) kg·m\(^{-3}\), change in surface tension due to temperature \(\alpha = \partial \sigma / \partial T\) is \(~0.05\sim 0.13 \times 10^{-3}\) kg·s\(^{-2}\)·K\(^{-1}\), the coefficient of thermal expansion is \(~17\sim 20 \times 10^{-6}\) K\(^{-1}\) and characteristic radius \(a\) of the droplets is about 5 mm. Therefore, the right side of equation (1) can be estimated to be 2.18\sim 5.67, yielding \(U_M/U_B > 1\). This indicates that Marangoni flow is the leading current so as to enhance the circulation within the liquid layer and to evaporate the flux. In our case, a low-density salt compared to the heavier density ferrite powder was chosen to accelerate and assist in Marangoni flow. The flux was packed on the bottom of the interface of substrate, when heated, the flux melts and floats upward and leaves the ferrite fluid deposited
on the bottom. When the diffusion rate is larger than the evaporation rate a crystal forms.

X-ray diffraction (XRD) spectra as the linear intensity versus $\theta-2\theta$, for the best $\text{Zn}_2\text{Y}$ films grown using method D at 1100 °C for 15 hours with the weight ratio of 1:1 between salt and ferrite powder and surface loading of 1.33 mg/mm$^2$, were collected at room temperature using Cu Kα radiation in $\theta-2\theta$ geometry (see Fig. 14 (a)). It is noticed that the $\text{Zn}_2\text{Y}$ film exists as a pure phase structure possessing a strong (00$l$) preferred crystallographic orientation. Peaks near 37.1 and 78.6 degrees in $2\theta$ correspond to the MgO substrate. Peaks at 24.5°, 30.8°, 43.6° and 57° correspond to (0012), (0015), (0021) and (0027) planes of the $\text{Zn}_2\text{Y}$ film, respectively. Lattice constants of the $\text{Zn}_2\text{Y}$ were obtained by analysis of the XRD data and resulted in a $c$-axis of 42.94 Å and $a$-axis of 5.97 Å. The lattice constant $a$ of MgO and the $\text{Zn}_2\text{Y}$ crystal was measured to be 4.21 and 5.88 Å, respectively. However, the lattice mismatch between the atomic spacing on the (111) plane of the MgO (5.96 Å) and the $\text{Zn}_2\text{Y}$ crystallographic planes is ~1.34%; this relatively small mismatch is a critical factor in achieving high quality epitaxial growth. To further characterize the crystal quality of the $\text{Zn}_2\text{Y}$ films, pole figures were collected from the (0015) and (0021) diffraction peaks, and the data are shown as Figs. 14 b) and c), respectively. The reflections in which the angle between the film normal and the vector bisecting the incident and detected x-ray beams, $\phi$, was varied from 0° to 90°, and the azimuthal angle about the bisecting vector, $\xi$, was varied from 0° to 360°. The sharp peak at the center of the (0015) pole
The figure indicates c-axis alignment normal to the film plane with low in-plane dispersion. The six-fold symmetry of low intensity peaks arising from \{113\} Zn$_2$Y planes has similar values in d spacing. With regard to the (0021) peak reflection, three MgO \{200\} reflections in which 2\(\theta\)=43.005° appear with threefold symmetry. These results confirm the epitaxial growth of Zn$_2$Y (00\(l\)) films on MgO (111) substrates.

Fig. 14 a) XRD patterns for Zn$_2$Y films grown at 1100 °C, b) pole figure obtained from the (0015) peak reflections, and c) pole figure obtained from the (0021) peak reflections. During pole figure measurements the angle between the film normal and the vector bisecting the incident and detected x-ray beams, \(\phi\), was varied from 0° to 90°, and the azimuthal angle about the bisecting vector, \(\xi\), was varied from 0° to 360°.
The surface morphology of the best Zn$_2$Y films was observed in scanning electron microscopy (SEM) and presented as Fig. 15 a). Hexagonal crystals, ~1 mm in effective diameter, were clearly visible on the film surface, as shown in Fig. 15 a), qualitatively confirming the orientation of crystals with the crystallographic c-axis aligned normal to the film plane. The thickness of the film was determined by cleaving the MgO substrate and film perpendicular to the plane of the film. The cleavage propagated through both the MgO substrate and the ferrite film so that it was possible to examine both the thickness of ferrite films and the MgO substrate in cross section as shown in Fig. 15 b). The thickness was measured to be ~100 µm. The chemical composition of the Zn$_2$Y films was determined using energy-dispersive X-ray spectroscopy (EDXS). Findings indicate less than 1% of sodium remained in the Zn$_2$Y ferrite films, which confirmed that this growth methodology is relatively simple, cost effective, and an environmentally friendly way of depositing thick ferrite films with high purity and crystalline quality$^{68}$. 
The main FMR linewidth, $\Delta H$, of 62 Oe as the peak-to-peak in the power derivative was measured at a frequency of 9.6 GHz with an external DC magnetic field of 958 Oe applied along the in-plane direction is shown in Fig. 16. The theoretical resonance condition is given by:

$$f = \gamma' \sqrt{H(H + H_A + 4\pi M_s)}$$  \hspace{1cm} (2)

where $\gamma'$ refers to the effective electron gyromagnetic ratio, $2.8 \times 10^6$ Hz/Oe. Substituting the saturation magnetization of 2512 kG and driving frequency 9.6 GHz into the above condition, a magnetocrystalline anisotropy field value was calculated to be 8.797 kOe; this is in good agreement with the 8.9 +/- 0.1 kOe
measured by VSM.

Fig.16 Ferromagnetic resonance measurement as the peak-to-peak in the power derivative measured at a frequency of 9.6 GHz with an external in film plane field of 0.958 kOe for the thick Zn$_2$Y film.

In summary, Zn$_2$Y ferrite films were grown on MgO (111) substrates by a relatively simple, cost effective, and environmentally friendly crystal growth technique. In order to optimize the growth of films, variation of firing time, temperature, weight ratio of salt to FOP, and ferrite surface loading were explored. Room temperature X-ray diffraction measurements indicated all diffraction features correspond to reflections indexed to a single crystalline phase having space group $R-3m$ with (00$l$) preferred orientation. Scanning electron microscopy images reveal large hexagonal crystals of ~ 1 mm in
effective diameter and film thicknesses of ~100 µm. The resulting Zn$_2$Y films had an anisotropy field value of $8.9 \pm 0.1$ kOe, while retaining a relatively high $4\pi M_s$ of $2.5 \pm 0.1$ kG. The best films have an FMR power derivative peak-to-peak linewidth of 62 Oe at 9.6 GHz. These results proved the efficacy of our technique in producing epitaxial growth of thick crystal ferrite films, and lay the foundation for a pathway to realizing thick film based devices that operate at low frequencies (X band to Ku band), and possess the potential to advance microwave device applications.

### 3.2.3 Single crystal BaM growth on GaN substrates

By using similar method discussed in 3.3, we aim to grow thick BaM single crystal films with (00l) preferred orientation on GaN/Al$_2$O$_3$ substrates. The thick films are expected to have a thickness of ~ 100 µm with low microwave loss.

BaCO$_3$ and Fe$_2$O$_3$ chemical powders were mixed together with alcohol and ball milled for 2 hours, and the slurry was dried resulting in ferrite powder. The GaN/Al$_2$O$_3$ substrates, with (00l) orientation, were ultrasonically cleaned in acetone and alcohol followed by a rinsing in DI water and blown dry. These preparation steps were found to result in smooth surfaces on the subnanometer scale, largely free of defects and contamination. A weighted amount of dry anhydrous Na$_2$CO$_3$ and ferrite powder was lightly pressed into disk and placed on the substrate. The ferrite oxides and anhydrous sodium carbonate were
melted on the surface of GaN/Al$_2$O$_3$ substrate so that it spread over the surface as a uniform liquid layer. The solution was maintained at 1050-1150°C for 5-15 h in order to vaporize the solvent and cool slowly to room temperature, thus depositing the ferrite. Crystal structure and texture of the resulting films were studied by room temperature X-ray diffraction (XRD) using Cu K$_\alpha$ radiation in a $\theta$-2$\theta$ geometry. The surface morphology was observed by scanning electron microscopy (SEM), and a thickness of ~100 µm was also obtained. The magnetic properties of the films were determined using vibrating sample magnetometry (VSM).

X-ray diffraction (XRD) spectra for the BaM films deposited on GaN/Al$_2$O$_3$ (00l) substrates were collected at room temperature using Cu K$_\alpha$ radiation in $\theta$-2$\theta$ geometry. The XRD pattern of the BaM film grown at 1100 °C and maintained for 15 hours is illustrated as Fig. 17. The weight ratio of ferrite powders to salt is 1:1 with ferrite powders surface loading density of 1mg/mm$^2$. It is noticed that the BaM film remains as a pure phase structure possessing a (00l) preferred orientation. The peak near 41.6 degree (in 2$\theta$) corresponds to the GaN/Al$_2$O$_3$ substrate. The peaks at 23.03°, 30.5° and 54.6°correspond to (006) and (008) and (0014) planes of the BaM film, respectively. The XRD patterns proved that BaM (001) single crystals are of good quality$^{69}$, and the successful epitaxial growth on GaN(001) /Al$_2$O$_3$ (001) substrate. Lattice constants of the BaM were also obtained by analysis of the XRD data and were measured to be a c-axis of 23.2 Å and a-axis of 5.91 Å, which is consistent with the high quality single crystal BaM$^{70}$. When growth of thick ferrite films of
~100 um, the lattice mismatch between the substrates and the ferrite films plays a less important role for the thin layers of several hundred nanometers. The growth mechanism in this process is super saturation of the melt by the evaporation of the salt solvent. The reaction first took place between the ferrite powders and the molten Na$_2$CO$_3$, and CO$_2$ was evaporated. Then sodium compounds formed slowly via decomposition followed by the vaporization of Na$_2$O. Finally, super saturation and nucleation at the free surface of the melt precipitated epitaxial growth.

Fig. 17 XRD patterns for BaM films grown at 1100 ºC. Diffraction peaks have been identified with either the BaM film or the GaN/Al$_2$O$_3$ substrate.

The surface morphology for the BaM films on GaN/Al$_2$O$_3$ substrates was
observed by scanning electron microscopy (SEM). The hexagonal growth facet was shown in Fig.18, demonstrating an in plane growth along the c axis. The chemical composition of the BaM films was determined using energy-dispersive X-ray spectroscopy (EDXS). Findings indicate less than 1% of salt remained in the epitaxial BaM ferrite films, which demonstrated this growing method is a simple and quick way of depositing thick ferrite films with few defects versus the traditional flux growth methods.

Fig.18 SEM image of the surface of BaM thick films.
The magnetic properties of BaM films were measured using a vibrating sample magnetometer (VSM) at room temperature with a magnetic field strength ranging from -10 kOe to 10 kOe. Both in plane and out of plane hysteresis loops are presented in Fig. 19. It is shown that the easy axis of the BaM film aligns out of the film plane consistent with the crystallographic c axis aligning perpendicular to the sample plane. The hysteresis loop collected with the applied magnetic field aligned along the crystallographic c axis perpendicular to the film plane experiences a saturation magnetization ($4\pi M_s$) of $4.6 \pm 0.28$ kG. A coercive field of $\sim 231$ Oe was measured along the magnetic hard axis. Low coercivity along the hard direction reflects less effective pinning of domain walls from the defected interface volume and has phenomenologically been linked to low microwave losses in BaM films. These results match other high quality BaM thick films deposited on lattice matched oxide substrates. Finally ferromagnetic resonance (FMR) measurement indicates that the thick film has a narrow microwave linewidth of $\sim 100$ Oe at X-band. These results demonstrate a feasibility in the growth of thick crystalline films on semiconductor substrates by means of a simple, inexpensive and fast powder melting technique.
In summary, thick BaM crystalline ferrite films of thicknesses of ~100 µm having $4\pi M_s$ of 4.6 ± 0.2 kG and FMR linewidth of ~100 Oe, have been epitaxially grown on GaN/Al₂O₃ substrates from a molten-salt solution by vaporizing the solvent. Room temperature, 0–2θ X-ray diffraction measurements indicate all diffraction features are found to correspond to reflections indexed to a single crystalline phase having space group $P63/mmc$ with (00l) preferred orientation. SEM images present clear hexagonal growth facets, and both indicate a successful epitaxial growth of high quality crystal growth along the c-axis. These results demonstrate that high crystal quality barium hexaferite
films can be grown on high performance wide band gap semiconductor substrates, specifically GaN. This demonstration provides a pathway to realizing the integration of high performance ferrite microwave passive devices with active circuit elements on a common semiconductor substrate: a necessary step in creating “system on a wafer” architectures.

3.2.4 Single crystal Co$_2$Y growth on GaN substrates

A nanoscale-driven crystal growth of magnetic hexaferrites was successfully demonstrated at low growth temperatures (25-40% lower than the temperatures required often for crystal growth). This outcome exhibits thermodynamic processes of crystal growth, allowing ease in fabrication of advanced multifunctional materials. Most importantly, the crystal growth technique is considered theoretically and experimentally to be universal and suitable for the growth of a wide range of diverse crystals. In the present experiment, the conical spin structure of Co$_2$Y ferrite crystals were found to give rise to an intrinsic magnetoelectric effect. Our experiment reveals a remarkable increase in the conical phase transition temperature by $\sim$150 K for Co$_2$Y ferrite, compared to 5-10 K of Zn$_2$Y ferrites recently reported. The high quality Co$_2$Y ferrite crystals, having low microwave loss and magnetoelectricity, were successfully grown on wide bandgap semiconductor GaN. The demonstration of the nanostructure materials-based “system on a wafer” architecture is a critical milestone to next generation microwave
integrated systems. It is also practical that future microwave integrated systems and their magnetic performances could be tuned by an electric field because of the magnetoelectricity of hexaferrites.

A novel attempt to integrate single crystal Y-type hexaferrite heterostructures on wideband semiconductor substrates is proposed. We show such structures demonstrate the ME effect allowing for E field tuning at microwave frequencies. Single-crystal Co$_2$Y, i.e., Ba$_2$Co$_2$Fe$_{12}$O$_{22}$, ferrites are an important class of microwave ferrites that are widely used in microwave and mm-wave filters and phase shifters. Wide band gap semiconductor materials, e.g., SiC and GaN, have demonstrated advantages in power handling at high frequencies and received great interest from the semiconductor device community due to their attractive thermal conductivities, band gap energies, breakdown voltages, and permittivity, among other properties. Additionally, these materials share the same hexagonal crystal symmetry and comparable lattice parameters as hexagonal ferrites and possess the high temperature stability that enables epitaxial growth of high quality microwave ferrites.

We propose that the preparation of single crystal Y-type hexaferrite having thicknesses in the 10’s or even 100’s of micron on lattice mismatched semiconductor substrates is challenging. Since the 1960s, synthesis techniques for the growth of ferrite single crystals include the melt salt method, liquid phase epitaxy (LPE) and floating zone method. Among these, floating zone method and LPE growth involves complicated liquid phase control and expensive experimental set up, while the salt melting method,
although simple to execute and scalable, involves long cooling cycles and etching of the crystals out from the crucible. A 4 µm thick Co$_2$Y ferrite film has been successfully grown on MgAl$_2$O$_4$ substrate at low temperature, $^{80}$ but it is still too thin to be used in many practical devices. The development of low temperature epitaxial ferrite thick films or crystals with low microwave loss remains a problem whose solution will have a wide-ranging impact upon the microwave device community.

In order to realize heteroepitaxial growth, thermal and structural compatibilities of the substrate’s surface and the growing film are key factors. Here, we present an innovative solution that employs the use of ferrite nanoparticles to facilitate the growth of large area, i.e., ~1 cm$^2$, Co$_2$Y (Ba$_2$Co$_2$Fe$_{12}$O$_{22}$) films with thicknesses ranging from 80 to greater than 500 µm on GaN substrates without the need for an enabling flux. The omission of a flux is attractive in that it often introduces contaminates to the growing films leading to unwanted effects to magnetic and microwave properties. In this experiment, we demonstrate the use of ~20 nm diameter Co$_2$Y powder positioned atop a GaN/Al$_2$O$_3$ substrate to realize epitaxial growth of an 80~500 µm thick film of Co$_2$Y at temperatures as low as ~1050 to 1150 ºC without flux. $^{81}$ A GaN/Al$_2$O$_3$ substrate was employed with the thickness of GaN of ~ 30 µm. In the case of Y type ferrite films grown on GaN, there is a relatively large lattice mismatch of 6.2% between the GaN (001) substrate and the Co$_2$Y (001) film thus requiring a buffer layer to mediate interfacial strain and realize epitaxial growth. Further complicating growth is that GaN is thermally unstable
in vacuum at temperatures near 950 °C at which typical pulsed laser deposition (PLD) growth of ferrite film seeds are grown. In order to mitigate both interfacial strain and surface reactivity, a layer of MgO, having (111) crystallographic orientation, was grown on the GaN substrate. Following the preparation of the MgO (111) buffer layer, BaFe$_{12}$O$_{19}$ (BaM) was deposited between Co$_2$Y and MgO. Ultimately, the designed architecture consisted of five layers: (001) sapphire (Al$_2$O$_3$), (001) GaN, (111) MgO, (001) BaM and (001) Co$_2$Y, as illustrated in Fig.20.
Fig. 20 Atom view of the Co$_2$Y film growth on GaN substrate

Synthesis of Co$_2$Y nanoparticles (Co$_2$Y-NPs): The Ba$_2$Co$_2$Fe$_{12}$O$_{22}$ (Co$_2$Y) nanoparticles were prepared by aqueous chemical coprecipitation
Starting powders of BaCl₂, Fe(III)Cl₃, CoCl₂, NaOH, and Na₂CO₃ were mixed in the appropriate stoichiometric ratios, and then were diluted in deionized water independently in 400 mL beakers, after which they were added simultaneously to a larger vessel, which was heated to 951°C and subsequently mixed using a motorized stirrer at 150 rpm for 2 h. Tetra-ethylene glycol was added during the mixing process to serve as a surfactant, which aided in particle formation, shown in Fig. 21.

Fig. 21 Experimental set up for mixing the chemical powder
After precipitation, the resultant powders were filtered utilizing vacuum filtration to remove water and NaCl. These precipitated particles then underwent additional rinsing, including ultrasonic vibration and magnetic stirring before subsequently being vacuum filtered (in Fig. 22) and dried. The dried powders were subsequently sintered at 900°C for 14 h, and then was ball milled with alcohol for 20 hours to reduce the size after synthesized.

![Fig. 22 Experimental set up for filtering the chemical powder](image)

Fabrication of $\text{Co}_2\text{Y}$ hexaferrite / BaM hexaferrite / MgO / GaN / Sapphire heterostructure: A commercial (001)GaN/(001)Al$_2$O$_3$ substrate (Supplied by MTI®, USA) was employed with an area of 10x10 mm$^2$, having the thickness of 30 μm and 0.5 mm for GaN and Al$_2$O$_3$, respectively. It is noticed that there is not only a relatively large lattice mismatch of 6.2% between the GaN (001) substrate and the $\text{Co}_2\text{Y}$ (001) film, but also GaN is thermally unstable in vacuum at high temperatures near 950 °C at which typical
Pulsed Laser Deposition (PLD) growth of seeded ferrite films was employed. Thus, in order to mitigate both interfacial strain and surface reactivity, an 8 nm layer of MgO, having (111) crystallographic orientation, was deposited at 550 °C by PLD on the GaN substrate prior to the growth. Following the preparation of the MgO (111) buffer layer, a BaFe_{12}O_{19} (BaM) seed layer with a thickness of ~200 nm was ablated at 900 °C from a homogeneous BaM target within the same chamber without disrupting vacuum. A KrF Excimer laser of wavelength 248 nm operating at 250 mJ per pulse was used in pulsed laser deposition. An oxygen pressure of 20 mTorr, with a corresponding substrate temperature of 900 °C, was determined to be optimal based upon the structure, magnetic and microwave characterization. Finally, an alumina ring with an inner diameter of 6 mm was placed atop the substrate and filled with the nanoparticulate Co$_2$Y powder, and placed into a box furnace and heated to 1050~1150°C which was shown to result in the melting of the powder. Ramping and cooling rate are at 5 °C/min and 1~3 °C/min, respectively. The Co$_2$Y crystals have a thickness ranging from 80~500 µm, depending upon loading factor of the nanoparticles and growth processing.

Crystal structure and texture of the Co$_2$Y nanoparticles and the resulting Co$_2$Y crystals grown on GaN were studied by room temperature X-ray diffraction (XRD) using Cu Kα radiation in a θ-2θ geometry. The chemical composition of the Co$_2$Y films was determined using energy-dispersive X-ray spectroscopy (EDX). The magnetic properties of Co$_2$Y films were measured using vibrating sample magnetometry (VSM) at room temperature with a
magnetic field strength ranging from -10 kOe to 10 kOe. The microwave properties were measured by ferromagnetic resonance (FMR) as the power derivative as a function of applied magnetic field. Temperature dependences of magnetization were measured by Quantum Design-Physical Property Measurement System (PPMS) over a temperature range from 5-1000 K.

The Co$_2$Y nanoparticles, synthesized by an aqueous chemical coprecipitation method were examined for crystallographic structure and morphology by XRD and SEM, respectively. In Fig. 23 (a), the XRD spectrum, collected using Cu Kα radiation at room temperature in a θ-2θ geometry, display a single phase of hexagonal Co$_2$Y structure, indicating a high crystal quality of nanoparticles. An average grain size of 36 ± 6nm was calculated using the Scherrer equation, whereas the grain size observed in electron microscopy images range from 10-40 nm (Fig.23 (b)). More precise statistical data (Fig.18 (c)) indicates that approximate 60% of the nanoparticles have a grain size less than 30 nm, which is indeed dominant in the distribution of the particle size. It is assumed to play a crucial role in lowering the melting temperature of the Y-type ferrite powder, which will be discussed later in the theoretical section.
Crystal structure and texture of the resulting Co$_2$Y crystals (shown in Fig. 24 c), grown at a low temperature of ~1050 °C, were studied by room temperature X-ray diffraction (XRD). The XRD pattern of the Co$_2$Y thick
ferrite film grown on a GaN/Al₂O₃ substrate is illustrated as Fig. 24 (a). It is observed that the Co₂Y phase remains the dominant phase possessing (00l) preferred orientation. The peak near 41.6 degree (in 2θ) corresponds to that of the substrate. Additionally, peaks at 24.5°, 30.8°, 39.2° and 57° correspond to (0012), (0015), (0019) (0027) planes of the Co₂Y film, respectively. Lattice constants of the doped Co₂Y were obtained by analysis of the XRD data and resulted in a c of 43.62 Å and an a of 5.88 Å. These results are consistent with previous published results for the Co₂Y phase. The lattice mismatch between the (111) MgO, ~5.957 Å, BaM, ~5.89 Å and Co₂Y, ~5.88Å, crystallographic planes are less than ~1%: this is a critical factor in achieving epitaxial growth. To further characterize the crystal quality of the Co₂Y films, a pole figure was obtained from the (0027) diffraction peak. These data are shown as Fig. 24 (b). In collecting these data the angle between the film normal and the vector bisecting the incident and detected x-ray beams, φ, was varied from 0° to 90°, and the azimuthal angle about the bisecting vector, ξ, was varied from 0° to 360°. The peak at the center of the (0027) pole figure indicates c-axis alignment normal to the film plane with low in-plane dispersion. The six-fold symmetry of low intensity peaks arise from the (039) Co₂Y planes having similar values in d spacing. These results confirm the epitaxial growth of Co₂Y (001) on BaM (001)/MgO(111)/GaN(001)/Al₂O₃ (001).
Fig. 24 a) XRD patterns for Co$_2$Y films grown at 1100 °C. Diffraction peaks have been identified with either the Co$_2$Y film or the GaN/Al$_2$O$_3$ substrate; b) Pole figures were obtained from the (0027) peak reflections.c) real image of the sample with thickness of 500 µm.

The surface morphology of the Co$_2$Y films was observed in scanning electron microscopy (SEM) and presented as Fig. 25 (a). Hexagonal growth facets are clearly visible on the film surface, confirming the orientation of crystals with the crystallographic c-axis aligned normal to the film plane. The
chemical composition of the Co$_2$Y films was determined using energy-dispersive X-ray spectroscopy (EDXS). The results indicate a ratio of BaO: CoO: Fe$_2$O$_3$ is $\sim$1:1:3 in the Co$_2$Y ferrite films, which confirms that this growth methodology is a relatively simple, cost effective, and an environmentally friendly (i.e., no toxic flux) method of depositing thick ferrite films with high purity and crystalline quality. The magnetic properties of Co$_2$Y films were measured using vibrating sample magnetometry (VSM) at room temperature with a magnetic field intensity ranging from -10 kOe to 10 kOe. Both in plane and out of plane hysteresis loops are presented as Fig. 25 (b). It is shown that the hard axis of the Co$_2$Y film aligns out of the film plane consistent with the crystallographic c axis aligning perpendicular to the sample plane. The hysteresis loop collected with the applied magnetic field aligned in the film plane experiences a magnetization ($4\pi M$) of $2.2 \pm 0.1$ kG at 10 kOe that matches the properties of high quality Co$_2$Y ferrite. The intrinsic coercivities derived from in-plane and out-of-plane measurements were measured to be 32 Oe and 73 Oe, respectively. Also, an enlarged scale plot of the M-H curve under application of small magnetic fields is presented as the inset to Fig. 25 (b). The Co$_2$Y crystal is seen to possess large magnetic anisotropy. We propose that the magnetization along the hard-axis (i.e. c-axis) consists of two mechanisms as is evidenced by the pronounced inflection in the curve as it approaches saturation. This behavior deviates from the straight-line curve observed in epitaxial films and some reported crystals. We assume that the Co$_2$Y crystals consist of multiple magnetic domains, including non-uniform
domains. We conjecture that domain wall motion is initialized at low magnetic fields resulting in high susceptibility (i.e., large slope of the magnetization curve), followed by spin-rotation.  

![SEM image of the Co$_2$Y film surface](image1.png)

**Fig. 25** a) SEM image of the Co$_2$Y film surface; b) Hysteresis loop of thick Co$_2$Y ferrite films with in-plane and out-of-plane magnetic field applied. Inset of b) is an enlarged magnetic hysteresis loops at low field.

The microwave properties of the Co$_2$Y thick film samples were
measured by ferromagnetic resonance (FMR) as the power derivative as a function of applied magnetic field and plotted as Fig. 26 (a). FMR was measured at a frequency of 9.53 GHz with a peak-to-peak derivative line width of 280 ± 20 Oe for the case where the magnetic field was applied along the plane of the sample. In-plane angular variation was studied and the results indicate the FMR resonance field experiences six-fold symmetry with a period of 60°. By plotting the magnetic resonant field, $H_r$, versus the in-plane angle of the external field, $\phi$, (see Fig. 26 (b)), it is clear that $H_r$ behaves as a cosine function of $\phi$. Here, $H_r = H_A^\phi \cos 6\phi$, were we deduced the in plane anisotropy field $H_A^\phi$ to be 55 ± 2 Oe. As expected for the Y type hexaferrite, the out of plane anisotropy field $H_A^\theta$ was found to be substantially larger than $H_A^\phi$. The theoretical resonance condition is given by:

$$f = \gamma' \sqrt{(H + H_A^\phi)(H + H_A^\phi + H_A^\theta + 4\pi M_s)}.$$

Here, $\gamma'$ refers to the effective electron gyromagnetic ratio and its value is $2.8 \times 10^6$ Hz/Oe. Substituting the FMR driving frequency and the saturation magnetization into the FMR condition, the out of plane magnetocrystalline anisotropy, $H_A^\theta$, value was determined to be 32 ± 3 kOe. This value is in good agreement with published results.\textsuperscript{92}
3.2.5 Magnetization of the thick single crystal Co$_2$Y ferrite film dependence on temperature

The study of magnetoelectric multiferroics in which both magnetic and ferroelectric orders coexist attracted considerable interest in the 1960s and 1970s. In magnetoelectric multiferroics, one can realize complex phenomena such as the magnetoelectric (ME) effect, i.e. the generation of electric polarization by a magnetic field or magnetization by an electric field. However, in most of the early multiferroics, the temperature scale for ferroelectric order is much larger than for magnetic order. In other words, the origins of these orders have no relation to each other. This leads to only weak coupling between magnetism and ferroelectricity in these systems. About five years ago, ferroelectric order accompanied by a magnetic phase transition has been found for...
perovskite-type rare-earth manganites, TbMnO$_3$ and DyMnO$_3$, which show antiferromagnetic orders with long wavelengths and remarkable ME effects driven by metamagnetic transitions. The discovery of the spin-driven ferroelectricity triggered rapid developments in the exploration of new multiferroics (e.g. Ni$_3$V$_2$O$_8$ and CoCr$_2$O$_4$) and motivated an extensive study to understand the origin of ferroelectricity in known multiferroics such as RMn$_2$O$_5$ (R = rare-earth or Bi). A characteristic property of these multiferroics is the simultaneous occurrence of a ferroelectric phase transition and a noncollinear spiral magnetic order. Thus, the spiral magnetism is the key to understanding the ferroelectric and magnetoelectric properties in these multiferroics. Because spiral magnetic order often arises from the competition between nearest-neighbor and further-neighbor magnetic interactions, systems containing competing magnetic interactions (spin frustration) are promising candidates for this class of multiferroics. On the basis of this strategy several new multiferroics related to spiral magnetic orders have been found in the past few years. This means the emergence of a new class of ferroelectrics in which the origin of ferroelectricity is driven by spiral magnetism and is completely different from that in conventional ferroelectrics. There are several types of spiral magnetic structures. The classification of the spiral type is critical for understanding the spiral-spin-driven ferroelectricity. In fig. 8, we schematically depict various noncollinear spiral magnetic structures on a one-dimensional array of magnetic moments $S(r)$. Here, the direction of $(r_{i+1} - r_i)$ is along the magnetic modulation wavevector $q$ of the spiral structure, and $[S(r_i) \times S(r_{i+1})]$ gives the spin rotation axis. If the spin rotation axis is parallel to the modulation wavevector, the arrangement gives a
screw spiral structure (fig. 27 (a)). If the spin rotation axis is perpendicular to the propagation vector of the spiral, the resulting arrangement is termed a cycloidal spiral structure (fig. 27 (b)). A rather more complicated system is a conical spiral in which a ferromagnetic component coexists with a screw or cycloidal component for longitudinal (fig.27 (c)) or transverse (fig.27 (d)) conical structure, respectively. These conical structures are generally obtained by applying weak magnetic fields to screw or cycloidal spiral structures. However, in some compounds such as CoCr$_2$O$_4$, the conical structure can be stabilized even at zero magnetic field.

![Fig. 27 Schematic illustrations of types of spiral magnetic structures on a one-dimensional array of magnetic moments $S(r)$.](image)

Hexaferrites are iron oxides with hexagonal structures and have long been used in technological applications such as permanent magnets and microwave devices because of their room-temperature ferromagnetic and insulating properties. The hexaferrites are classified into several types depending on their chemical formulae and crystal structures.
(for example, M-type (Ba;Sr)Fe_{12}O_{19} and Y-type (Ba;Sr)_{2}Met_{2}Fe_{12}O_{22} (Met = divalent metal ion). Recently, it has been reported that some Y-type hexaferrites, such as (Ba;Sr)_{2}Zn_{2}Fe_{12}O_{22} and Ba_{2}Mg_{2}Fe_{12}O_{22}, show magnetically induced ferroelectricity and resultant magnetoelectric effects related to modifications of spiral magnetic structures by applying a magnetic field. Although the magnetic ordering temperatures of these Y-type hexaferrites are above room temperature, their magnetoelectric effects can be observed only up to 130 K. This is mainly because these hexaferrites are not sufficiently insulating to sustain a substantial macroscopic ferroelectric polarization above 130 K.

The structure of Z-type (Ba;Sr)_{3}Met_{2}Fe_{24}O_{41} can be regarded as an alternate stacking of a 1/2 unit cell of M and a 1/3 unit cell of Y. Although most of the Z-type hexaferrites have a uniaxial magnetic anisotropy parallel to the c axis, Ba_{3}Co_{2}Fe_{24}O_{41} is, exceptionally, a planar ferrimagnet at room temperature. As a result of this planar anisotropy, Ba_{3}Co_{2}Fe_{24}O_{41} is magnetically soft. In addition, it has a relatively high permeability and ferromagnetic resonance frequency. Owing to these properties, Ba_{3}Co_{2}Fe_{24}O_{41} has been studied as one of the promising inductor materials for gigahertz-range application. Early studies suggested that Ba_{3}Co_{2}Fe_{24}O_{41} undergoes a magnetic transition at around 230 K and has a cone of easy magnetization below this temperature. The magnetic properties of Ba_{3}Co_{2}Fe_{24}O_{41} are affected by replacing Ba with Sr. According to recent studies on polycrystalline samples; the room-temperature magnetization curve of Sr_{3}Co_{2}Fe_{24}O_{41} does not increase monotonically up to a saturation magnetic field, but has a graded increase, which suggests that Sr_{3}Co_{2}Fe_{24}O_{41} is not a simple ferrimagnet at room temperature. The shape of the magnetization curve is very similar to that in the magnetoelectric Y-type hexaferrite Ba_{0.5}Sr_{1.5}Zn_{2}Fe_{12}O_{22}. In the Y-
type hexaferrite, the partial replacement of Ba with Sr modifies the superexchange interaction of the Fe\_O\_Fe bonds near (Ba,Sr) and stabilizes the spiral magnetic ordered state. As the Z-type structure also contains the same structural components, we expected that the Z-type Sr\textsubscript{3}Co\textsubscript{2}Fe\textsubscript{24}O\textsubscript{41} would show a similar spiral magnetic ordered state and a resultant magnetoelectric effect at room temperature.

The temperature dependence of the zero-field cooled magnetization curve was measured between 5 K and 900 K at an applied field strength of 100 Oe along the c-axis of the sample,\textsuperscript{93} as depicted in Fig. 28 (a). It is observed that the magnetization exhibits four pronounced changes with temperature at 162 K, 456 K, 680 K and 759 K for the particular ferrite heterostructure studied. It is noticed that the magnetization drops precipitously at \(\sim\) 680 K presumably corresponding to the Curie temperature \(T_{c1}\) for the Y type ferrite. It represents a magnetic phase transition from ferrimagnetic (\textit{i.e.} collinear spins structure) to paramagnetic structure, as the temperature increases beyond \(T_{c1}\). The paramagnetic phase gives rise to very small moments (usually close to zero). However, interestingly, what we observed is that the ferrite heterostructure is still of high magnetization (half the magnetization of Y-type) at \(T>T_{c1}\), followed by another precipitous drop in magnetization to near zero as the temperature rises to \(\sim\) 759 K. The following phase transition is attributed to the Curie temperature, \(T_{c2}\), for the M-type ferrite buffer film in this heterostructure.\textsuperscript{22} The M vs T plot of BaM ferrite was also measured and is shown as the inset to Fig. 28 (a). These data clearly indicate a phase transition (\textit{i.e.}, ferrimagnetism- paramagnetism) at \(\sim\) 730 K (\textit{i.e.}, Curie temperature of
BaM). This is evidence that the phase transition of \( \sim 759 \text{ K} \) observed for a Co\(_2\)Y/BaM heterostructure stems from the BaM buffer layer. The increase in Curie temperature of the BaM film in a Co\(_2\)Y/BaM heterostructure likely results from an internal interfacial strain as the BaM thin layer is sandwiched between the substrate and the Co\(_2\)Y crystal. Thus, it’s reasonable that the magnetization between \( T_{c_1} \) and \( T_{c_2} \) originates from the ferrimagnetism of the M-type hexaferrite with collinear spin structure. The magnetic signature of the BaM in the M-T curve is evidence that the thin seed layer of BaM between MgO and Y-type ferrite crystal is well formed without extensive diffusion during growth of the Y-type heterostructure by the nanoparticle-assisted growth technique.
Fig. 28 a) Temperature dependence of magnetization for the Co$_2$Y crystal at applied magnetic fields along $c$-axis and over a temperature range from 5-1000 K. a) Applied magnetic field of 100 Oe, and b) applied magnetic fields of 0.1, 0.5, 1.0, 5.0 and 10 kOe.

Furthermore, two peaks observed in the M vs. T curve of Fig. 28 (a)
appear at low temperatures. Previous investigations of Y-type ferrites indicate that ferrimagnetic spin structure may transfer into a proper screw, \cite{94,95} and even conical spin structure, at temperatures much lower than its Curie temperature. In the present work, it is assumed that the phase transition at 456 K corresponds to a spin transition to a screw spin state, in which alternating stacks of magnetic blocks develop a screw rotation with the spin rotation axis parallel to the modulation wave vector $\vec{q}$ (parallel to $c$-axis), whereas the moment $\vec{S}$ in each of the magnetic blocks prefers to lie within the $a$-$b$ plane, which was verified by neutron diffraction studies.\cite{21,22} More importantly, as the temperature drops further, the screw phase transforms to a transverse conical structure. The anomaly at 162 K from Fig. 28 (a) is likely to reflect a transition from screw to transverse conical spin configurations (named a transverse conical spin temperature $T_{\text{con}}$). The transverse conical structure is of great importance and may result in the observation of a magnetoelectric effect.

Below $T_{\text{con}}$ an increase or decrease in net magnetization with decreasing temperature may be observed as the materials remain in a conical spin state. Actually, the temperature dependence of magnetization in conical spin structures is complicated and depends upon both the strength and orientation of the applied magnetic field. Previous work includes a systematic investigation of the dependence of magnetization with temperature under different applied magnetic field strengths.\cite{27} Either enhanced or suppressed, the magnetization can be measured as the strength of the applied field changes. Only when the temperature is below $T_{\text{con}}$ does a nonzero solution to the above
equation can be derived from the transverse conical structure. It ultimately may lead to the induced electrical polarization so as to lay the foundation of future ME-based applications. Based on previously reports on magnetolectric effect and conical spin structure, it is predictable that the Co$_2$Y ferrite crystal demonstrate a magnetolectric effect at T< T$_{con}$=162 K, which is a remarkable increase in conical temperature among those Y-type ferrites reported (T$_{con}$=5~10 K). This increased temperature is associated with introduction of cobalt ion into Y-type ferrite, enhancing magnetocrystalline anisotropy field up to H$_A$ =30 kOe, compared to those Zn or Mg doped Y-type ferrites with H$_A$ =10 kOe. The enhanced temperature of conical structure may lead to the realization of magnetolectric tuning of real microwave devices. However, it should be pointed out that all of the magnetic phase transitions presented are sensitive to applied magnetic field, as shown in Fig. 28(b). Screw and conical structure temperature shift to low temperature as a magnetic field is increased, whereas Curie temperatures for Y- and M-type ferrites increase with increasing field. In particular, a high magnetic field (>1 kOe) may destroy the conical structure leading to the disappearance of the magnetization peak at around 162 K. These new results provide potential to manipulate spin structures in Y-type ferrites having a high temperature of magnetolectric coupling.

In summary, we have demonstrated a technique for the low temperature crystal growth of ferrites and other ceramics. Nanoparticles are used to achieve high quality ferrite crystals grown at temperatures ~ 30% lower than conventional growth temperatures without the need for flux. More
importantly, this work has demonstrated a unique hexaferrite heterostructure featuring an integration of a magnetoelectric microwave ferrite and wideband semiconductor. The ferrite heterostructure with five layers: Co$_2$Y hexaferrite/BaM hexaferrite/MgO/GaN/sapphire, was constructed by nanoscale-driven crystal growth technique combined with the pulsed laser deposition technique. These experiments indicate that high quality Y-type ferrite crystals with thicknesses greater than 500 $\mu$m was grown on a wideband semiconductor GaN, showing high crystallographic texture and low ferromagnetic resonance linewidth at X-band. More importantly, the Co-doped Y-type ferrite crystals reveal a conical spin structure at a relatively high temperature of 162 K, and have potential to be further modified in temperature. These demonstrations allow the realization of the integration of high performance E-field tunable ferrite microwave passive devices with active circuit elements on a common semiconductor substrate: A necessary step in creating “systems-on-a-wafer” architectures.
Chapter 4 Theoretical Analysis of nano-scale driven crystal growth of ferrites

4.1. Calculation of melting temperature with particles size of Y type hexaferrite
4.2. Prediction of the relation between size and temperature of other hexaferrites
4.1 Calculation of melting temperature with particles size of Y type hexaferrite

The physical properties of small particles are a subject of intense contemporary interest. As the size decreases to the nanometer scale, many of the electronic, as well as the thermodynamic, properties are significantly altered from those of either the bulk or the single molecule. Depression of the melting point of small particles below that of the bulk, when the dimensions approach a few nanometers, has been known for a long time. This dependence of melting on size is not restricted to any particular material; rather, it encompasses a wide variety of materials from metals to semiconductors and to molecular organic crystals. A recent rare observation of melting point of tin clusters above the melting of the bulk is taken to indicate a structure different for the clusters from the bulk. Theoretical phenomenological considerations, based on the classical Kelvin equation, led Pawlow nearly a century ago to develop a quantitative relationship between the melting temperature, $T_m$, and the particle size. Whereas this correlation is not quantitatively accurate, it still is often utilized to estimate the size dependence of $T_m$. For a particle of diameter $d$ and molar heat of fusion $L$, the Pawlow relation is given in eq (1):

$$\frac{T_m(r)}{T_m(\infty)} = 1 - \frac{4}{\rho_s L} \left[ \gamma_s - \gamma_t \left( \frac{\rho_s}{\rho_t} \right)^2 \right] \frac{1}{d}$$  

(1)

Here, $T_m$, $d$ and $L$ are melting temperature, particle diameter, and molar heat of fusion,
respectively. \( \gamma \) is the specific surface free energy of the solid (s) or liquid (l). \( \propto \) signifies the bulk material and \( \rho \) is density.

For \( \rho_s \), it could be obtained from eq. (2) and eq. (3).\(^97\)

\[
V_{cell} = \frac{\sqrt{3}}{2} a^2 c \quad (2)
\]

\[
\rho_s = \frac{ZM}{N_A V_{cell}} \quad (3)
\]

The lattice constants \( a \) and \( c \) are 5.88 Å and 43.62 Å, respectively, derived from XRD analysis, and \( V_{cell} \) is the cell volume, \( M \) is the molar mass, \( N_A \) is Avogadro’s number, \( Z \) is the number of molecules per unit cell (\( Z = 6 \) for Y-type hexaferrite). The calculated \( \rho_s \) for our sample is \( \sim 5.3 \text{ g/cm}^3 \), which is close to the reported value.

Surface energy, defined as the excess energy of a free surface compared to that of the bulk, is an important parameter of a ceramic material. It controls many chemical and physical processes, such as sintering, mass loss, adhesion, crack nucleation and growth, colloid dispersion, diffusion bonding, etc. A precise knowledge of this quantity would be very useful in estimating and optimizing processing and properties of ceramic materials. Unfortunately, for most materials, due to various theoretical and experimental difficulties, a precise value for this parameter is not easily obtained. While it has been measured for a very limited number of materials, theoretical calculations have been restricted to solids with simple structures. Extension of the calculations to complex ionic solids has been lacking due to insufficient knowledge about the repulsive potential functions, although such calculations may be of practical interest since a number of complex technological materials are ionic in nature, e. g., ferrites.

An estimation of the surface energy can be done\(^4\) by estimating the amount of
work necessary to separate two internal surfaces. Let the attractive stress between the surfaces be approximated by a sine function. The stress is zero when the surfaces have their normal spacing \( d \). As the interplanar spacing increases due to an applied stress normal to these planes, the stress rises to a maximum value \( \sigma_0 \) and then drops to zero when the separation of the planes exceeds the range \( h \) of the attractive forces. If \( y \) denotes the increase in the spacing, the strain between the planes is \( y/d \) and for small strains, by Hooke's law, \( a = E(y/d) \). \( E \) is the elastic modulus normal to the plane under consideration.

From the above consideration, \( \sigma = \sigma_0 \sin(\pi y/h) \), \( h > y > 0 \), and for small \( y \), \( \sigma = \sigma_0 (\pi y/h) = E y/d \), \( \sigma_0 = E h/\pi d \), or \( \sigma = (E h/\pi d) \sin(\pi y/h) \). The work done in moving the surfaces from \( y = 0 \) to \( y = h \), where they are no longer attracted, is

\[
W = \int_0^h \sigma \, dy = \left( E h/\pi d \right) \int_0^h \sin(\pi y/h) \, dy = 2E h^2/\pi^2 d \text{ per unit area.}
\]

This energy appears as the surface energies of the two newly created surfaces. Hence, the surface energy of solid ferrite can be estimated from eq. (4).98

\[
\gamma_s = \frac{E h^2}{\pi^2 d} \quad (4)
\]

\( E \) refers here to the elastic constant normal to the \((hkl)\) plane of the crystal structure, which can be estimated by the elastic wave velocity and strain matrix.99 For the particular case of a hexagonal structure, \(^{100}\) the expression of \( E \) can be obtained from the elastic wave in the longitudinal direction of \((001)\) plane, \( i.e. \), \( E_{(001)} = C_{33} \), whereas \( C_{33} = C_{11} \) if considering an elastically isotropic hexagonal crystal.\(^{101}\) Taking a value of \( C_{11} \sim 2.825 \times 10^{12} \text{dyn/cm}^2 \) for a typical ferrite, an elastic constant \( E_{(001)} \) for the Y-type hexaferrite exhibits the same order of magnitude as the reported elastic constant for
hexagonal ferrites.$^{102}$

Next, $h$ as the smallest possible interlayer spacing that could be obtained from the Y-type crystal structure,$^{103}$ as illustrated in Fig. 1. Along the $<001>$ directions, the Y-type hexaferrite can be considered to consist of a 18-layer stacking of cations and anions with an interlayer spacing of $h\ (001)=c/18$. The periodicity $d$ as the separation between two successive stoichiometric blocks is $d\ (001)=c$. Thus, the surface energy is derived $\gamma_s\sim 379\ \text{erg/cm}^2$ from eq. (5), which is comparable to other ferrites.$^{22}$
Finally, we estimate a melting temperature of 1050-1150 °C for the Y-type hexaferrite nanoparticles by taking the parameters: $\gamma_l=311.6$ erg/cm$^2$ based on a ratio (1.15~1.2) of $\gamma_s$ to $\gamma_l$, $^{104} \rho_s/\rho_l\sim 1.1-1.2$, $^{105} T_m(\infty)\sim 1550$ °C for bulk Co$_2$Y$_6$L $\sim 1594.6$ cal/mol, $^{106}$ and the particle size, $d=20-30$ nm for the nanopowders used in this
experiment. The predicted melting temperature for the studied hexaferrite nanoparticle is fully consistent with the experimental observation, as depicted in Fig. 2. It should be pointed out that the nanoscale-driven crystal growth technique is of universal significance in lowering the temperature crystal growth for other ceramics or alloys.

Fig. 2 The predictions of melting temperatures varying with particle size for Y type hexaferrites
4.2 Prediction of the relation between size and temperature of other hexaferrites

As mentioned earlier, such low temperature crystal growth driven by nanoparticles is not restricted to Y-type hexaferrites or other ferrites. This new technique is available for a wide range of ceramics. M-, Y-, U- and Z-type hexaferrites with different numbers of the oxygen ion layers along the <001> direction in a unit cell, were illustrated in the inset to Fig. 3. As we can see in the plot, M, Z and U type ferrite have 10, 28 and 38 oxygen layers within a cell along <001> direction, respectively.
The relationship between melting temperature and particle size is predicted by using the equation (1)-(4) for M, Z and U type ferrites. Fig. 4 presents the predictions of melting temperatures varying with particle size for four types of hexaferrites that show the magnetoelectric effect, and potential for applications in ME-based microwave or other electronic devices.

![Graph showing predictions of melting temperatures varying with particle size for four types of hexaferrites](image-url)
It is promising that Z-type hexaferrites can be grown at a relatively low temperature, *i.e.*, 1100-1200 °C, for the case when the enhancing nanoparticle size is less than 15 nm. This could overcome a longstanding limitation in Z-type ferrite crystals that must be grown at extremely high temperatures. As a result, crystal growth temperatures are anticipated to be lowered 20-30% if nanoparticle size is controlled below 20 nm for most ferrites.
Chapter 5 Summary and prospect of the project
In summary, we have demonstrated a technique for the low temperature crystal growth of ferrites and other ceramics. Nanoparticles are used to achieve high quality ferrite crystals grown at temperatures ~ 30% lower than conventional growth temperatures without the need for flux. More importantly, this work has demonstrated a unique hexaferrite heterostructure featuring an integration of a magnetoelectric microwave ferrite and wideband semiconductor. The ferrite heterostructure with five layers: $Co_2Y$ hexaferrite/BaM hexaferrite/MgO/GaN/sapphire, was constructed by nanoscale-driven crystal growth technique combined with the pulsed laser deposition technique. These experiments indicate that high quality Y-type ferrite crystals with thicknesses greater than 500 μm was grown on a wideband semiconductor GaN, showing high crystallographic texture and low ferromagnetic resonance linewidth at X-band. More importantly, the Co-doped Y-type ferrite crystals reveal a conical spin structure at a relatively high temperature of 162 K, and have potential to be further modified in temperature. These demonstrations allow the realization of the integration of high performance E-field tunable ferrite microwave passive devices with active circuit elements on a common semiconductor substrate: A necessary step in creating “systems-on-a-wafer” architectures.

Next step, we are planning to fabricate a notch filter integrated on semiconductor GaN. In signal processing, a band-stop filter or band-rejection filter is a filter that passes most frequencies unaltered, but attenuates those in a specific range to very low levels. It is the opposite of a band-pass filter. A
A notch filter is a band-stop filter with a narrow stopband (high Q factor). Narrow notch filters are used in Raman spectroscopy, live sound reproduction (public address systems, or PA systems) and in instrument amplifiers (especially amplifiers or preamplifiers for acoustic instruments such as acoustic guitar, mandolin, bass instrument amplifier, etc.) to reduce or prevent audio feedback, while having little noticeable effect on the rest of the frequency spectrum (electronic or software filters). Other names include 'band limit filter', 'T-notch filter', 'band-elimination filter', and 'band-reject filter'. Typically, the width of the stopband is 1 to 2 decades (that is, the highest frequency attenuated is 10 to 100 times the lowest frequency attenuated). However, in the audio band, a notch filter has high and low frequencies that may be only semitones apart.

We used high frequency structural simulator (HFSS) to design the notch filter, shown in Fig. 1. The stripe line width was 0.4 mm, and the Y type ferrite sample size was 10*10*0.5 mm. The size of CPW is 20*20*0.01 mm (thickness of coper). The bias field was H= 3400 Oe which is along Y axis and the driving frequency ranges from 1-20 GHz with step size of 0.01 GHz.
In Fig.2, the simulation result was shown. The return loss $S_{11}$ is below -10 dB, and the insertion loss $S_{12}$ showed a sharp absorption peak around 12.5 GHz, indicating a successful design for the notch filter.

For the next step, we are planning to fabricate the designed notch filter on GaN. All the results showed in the thesis proved the efficacy of our technique in producing epitaxial growth of thick crystal ferrite films, and lay the foundation for a pathway to realizing thick film based devices that operate at low frequencies (X band to $K_u$ band), and possess the potential to advance microwave device applications.
References


