Magnetoelectric Hexaferrite Thin Films Growth for Next Generation Device Applications

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by

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Dedicated to:

My parents

Azar and Hadi

For their endless love and support
Abstract

The main step toward miniaturizing microwave and magnetic devices and integrating them with semiconducting elements, is to deposit thin film of hexaferrite materials. In this work, alternating target laser ablation deposition (ATLAD) is used for in-situ deposition of M-type and Y-type hexaferrites. There have been considerable reports on epitaxial growth of M-type hexaferrite but not on Y-types, since it is very difficult and challenging to produce them. One of the main problems is the need of substrate temperatures in excess of 1150°C which requires additional expensive high temperature equipment. Our developed process can be done at lower temperatures by PLD equipment and can form unique crystal structures which cannot be achieved by other techniques.

Due to excellent dielectric properties, ferrites possess the advantages of low loss and high power handling relative to semiconductors. However, parameters of magnetic materials are controlled by an external magnetic field which is generated using permanent magnets or current driven coils, leading to relatively large component size, weight, cost, and slow response time in comparison to semiconductor-based technologies. Magnetoelectric (ME) materials can be a practical solution to control the magnetic parameters of ferrites by voltage and can overcome most of the disadvantages in the use of ferrites for microwave devices. Here, the ME effect, in Z-type Sr₃Co₂Fe₂₄O₄1 and M-type SrCo₂Ti₂Fe₈O₁₉ with high ME coupling coefficient at room temperature, is studied. In addition, for the first time, the ME effect at room temperature in thin film of SrCo₂Ti₂Fe₈O₁₉ is demonstrated. The required voltage (< 2V) in order to observe the
effect was substantially smaller than the voltage required using bulk materials. This is quite promising in terms of miniaturizing future ME devices and integrating them in electronic and telecommunication components while they have the advantage of low loss and high power handling compared to semiconductors.

The complex permeability spectrum of a magnetic thin film is among the most important factors determining the suitability of a magnetic thin film for a microwave application and the performances of the devices made from the magnetic thin film. Hence, a microstrip device is also designed and fabricated to measure the permeability of thin films.

Magnetoelectric thin films are good candidates for tunable inductors since it possible to tune their magnetic properties by electric field with low power consumption. Therefore, a voltage tunable magnetoelectric thin film inductor consisting of SrCo$_2$Ti$_2$Fe$_8$O$_{19}$ thin film core, is also designed and fabricated. Potential applications include an electric field sensor when utilized in a simple LC resonator circuit analogous to sensors built from piezoelectric/magnetostrictive acoustic resonance sensors.
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Chapter 1. Introduction

1.1. Motivation

Hexagonal ferrites are an important family of ferrite materials and are classified in several groups: M-type, Y-type, Z-type, etc. The hexagonal crystal structure of these materials allows various ionic substitutions which affect the magnetic properties of hexagonal ferrites, such as the uniaxial magnetic anisotropy field, the coercive field, the saturation magnetization and finally extends the range of possible applications for these materials. In addition, due to their excellent dielectric properties, ferrites possess the advantages of low loss and high power handling relative to semiconductors. However, parameters of magnetic materials are controlled by an external magnetic field which is usually generated using permanent magnets or current driven coils, leading to relatively large component size, weight, and cost, as well as slow response time in comparison to semiconductor-based technologies. Magnetoelectric materials can be a practical solution to control the magnetic parameters of ferrites by electric field and/or voltage and would eliminate permanent magnets and tuning coils to overcome most of the disadvantages in the use of ferrites for microwave devices.

Leading scientific journals have reported on magnetoelectric effects at room temperature on single phase of hexaferrite materials. The magnetoelectric coupling in these single phase ferrites is comparable to the most efficient ME multiferroic composites. However, all of the research activities on single phase magnetoelectric
Hexaferrites have been concentrated on bulk materials.

Thin films of the ME hexaferrites can contribute much to the understanding of physics and to societal needs of the future, such as: medical and field sensors, computers, wireless communication systems, magnetic recording, IC electronic circuits, green energy sources, etc. In this regard, the transition to modern technologies is facilitated with the use of thin film planar configurations, especially when required voltages to induce magnetoelectric effects in films are in the millivolts range rather than 100 volts and higher in bulk materials.

The unique feature of the hexaferrites is that the unit cell consists of spinel blocks stacked on top of each other. These spinel blocks are referred to as S (TMFe$_2$O$_4$), R (BaFe$_4$O$_7$) and T (2BaFe$_4$O$_7$) blocks, where TM implies a transition metal ion and Ba substitution may be replaced by Sr or Pb ions. The chemical formula of a typical M-type hexaferrite is BaFe$_{12}$O$_{19}$, for Y-type as Ba$_2$Fe$_{12}$TM$_2$O$_{22}$ and Z-type as Ba$_3$Fe$_{24}$TM$_2$O$_{41}$. The lattice constants along the c-axis are, respectively, 22, 43 and 52 Å. Clearly, the Z-type hexaferrite contains the largest unit cell along the c-axis and, therefore, the most spinel blocks (SRSTS*R*S*T*), where the * imply 120, 240 and 180 degrees rotation with respect to the unmarked block [1]. As a general experimental rule the more stacking of the spinel blocks required, the more difficult it is to prepare the hexaferrite in question, since other hexaferrite phases may readily admix with the intended phase. For example, the Z-Type requires the most stacking of the above set of spinel blocks and indeed it is the most difficult to prepare, as it readily admixes with M-
and U-type hexaferrites \[2\] at high temperatures (~1200°C).

There have been considerable reports on epitaxial growth of M-type hexaferrite but not on Y-types and Z-type. Ideally, the growth of Y- and Z-type hexaferrites requires temperatures of ~1200°C. These elevated temperatures in a deposition chamber raises havoc in terms of maintaining such high temperatures of a substrate during deposition. This explains why Y and Z-type hexaferrites have never been deposited before. Here, an alternative technique is developed and studied to produce hexaferrite thin film. It is also used to produce single crystal films of M-type hexaferrite and extended the developed method to Y-type hexaferrite thin film deposition. The technique is called alternative target laser ablation deposition and was first introduced by Karim and Vitcoria in 1997 \[3\]. The ATLAD technique allows for deposition of ferrite films at the atomic scale – one oxide layer at a time. For fundamental studies it is extremely important to be able to make ionic substitutions at any site within the unit cell, since local anisotropic spin interactions within a unit cell are responsible for magnetoelectricity. Conventional growth techniques are not able to select a particular site for substitution. Thus, the ATLAD technique is a powerful tool to understand magnetoelectricity at the fundamental level as well as learning to design the next generation of “artificial” ME ferrites. Equally important the ATLAD technique allows for deposition at much lower temperatures (800-900°C) rather than at 1200°C.
1.2. Magnetoelectric Hexaferrites for Microwave Applications

In the past 2-3 years a new family of magnetoelectric (ME) materials have been discovered [4-7]. Whereas previous [8] single phase ME materials were operational at low temperatures and the linear ME coupling parameter, $\alpha$, was measured to be in the order of $10^{-4}$ (CGS), the new [4-7] ME materials are operational at room temperature with low magnetic and/or electric fields and the measured $\alpha$ was 50-60 times greater than the low temperature ME materials [8]. These values of $\alpha$ are comparable with composite ME materials [9] consisting of layers of magnetostriction and piezoelectric materials. Interestingly, only bulk ME materials or composites have been reported on so far. Example of low temperature single phase ME materials are rhombohedral BiFeO$_3$ and the family of hexagonal manganites [8]. Both of these multiferroic materials consist of two or more primary ferroic properties in a single phase material. These new single phase ME materials which are operational at room temperature are identified as hexaferrites of the M, Y and Z-types.

According to refs [4-7] the mechanism that gives rise to magnetoelectricity (ME) is due to local distortions or strains induced by replacing Ba with a smaller Sr ion. The local distortion, located in the T block for Z-type and Y-type hexaferrites, implies that the bonding angle in Fe-O-Fe combination near the Sr substitution is changed from 116 degrees (with Ba) to 123 degrees (with Sr). This has great ramifications in terms of the super-exchange interaction between the two Fe ions, where both are located in tetrahedral sites. This implies that two of the three exchange parameters are comparable giving rise
to a localized anisotropic exchange situation. As such, a spin spiral configuration may be possible [10,11] as described by the Dzyaloshinski-Moriya [1] interaction model. Thus, any change in the cone angle of the spin spiral configuration is reflected in a change in the local strain and vice versa. The change in the strain manifests itself as a change in electric polarization, since these hexaferrites are also piezoelectric. For example, a change in magnetization means the cone angle of the spin spiral configuration must necessarily change and induce a local strain or electric polarization. This is the essence of the magnetoelectric effect.

However, a spin spiral configuration alone is not sufficient to induce the ME effect in hexaferrites. For example, we prepared single phase bulk of BaFe$_{10.2}$Sc$_{1.8}$O$_{19}$ which is characterized by a spin spiral configuration [12], and we did not measure any ME effect in the material. Also, we did not measure any ME effect, when we replaced Ba with Sr in order to induce local strains as in previous work [1-4]. It appears that substitutions of TM ions in either the S or T blocks together with the spin spiral and local strain settings are important in being able to produce ME hexaferrites at room temperature. We surmise that the role of TM ion substitutions is to mitigate multi-block interactions between spins and strains as in magnetoelastic coupling mechanisms. Understanding the physics of ME hexaferrites is important, because it provides guidance to experimental efforts in producing ME hexaferrite films.
1.3. Dissertation Overview

Chapter 2 discuss the deposition of single crystal films of M-Type by ATLAD technique using targets of Fe$_2$O$_3$ (S block) and BaFe$_4$O$_7$ (R block). Previous deposition of barium ferrite, BaFe$_{12}$O$_{19}$, by the ATLAD technique utilized targets of BaFe$_2$O$_4$ and Fe$_2$O$_3$ [13]. The results in this chapter show that using BaFe$_4$O$_7$ as R block provide more controllable magnetic and electrical properties of the thin film material and proves to be a promising target in epitaxial growth of M-type, Y-type and Z-type hexaferrites films by ATLAD.

In chapter 3, we discuss the process to produce thin films of single phase Y-type hexaferrites. Hexagonal Y-type ferrites are closely related to the M-type. The M-type barium ferrite unit cell is obtained by combining spinel S blocks with hexagonally stacked R blocks containing the barium ion, for example. Similarly, the Y-type barium ferrite unit cell is obtained by combining spinel S blocks with hexagonal T-blocks. Y-type ferrites are different from M-types with regard to the nature of the magnetocrystalline anisotropy fields in these structures. In M-type ferrites, the axis of easy magnetization is parallel to the crystallographic c-axis. In Y-type ferrites, there is no easy axis of magnetization, but there is an easy plane of magnetization perpendicular to the c-axis. Because of this property, Y-type ferrites are also referred to as ferrox planar-type, or planar ferrites. There exists an additional, weaker anisotropy field $H_\Phi$ in the easy plane of magnetization that possesses a six-fold symmetry. The fact that the easy plane of magnetization in Y-type ferrites lies in the basal plane creates unique
opportunities in magnetic device design. The magnetic softness of this material in the basal plane means that weak magnetic fields are required to saturate the material.

In chapter 4, an overview of magnetoelastic effect and ME effect is presented. The physical concepts of single phase ferroically ordered materials and multi-ferroic composite structures and magnetoelastic coupling are discussed. Combining various ferroics, potentially can be used in different applications such as sensors and communication devices and circuits. Understanding of magnetic and electrical properties of ferroic materials helps us to take advantage of special coupling phenomena in ferroics to push current technology toward smaller, cheaper, more compact and more efficient devices.

Chapter 5 represents the M-type magnetoelastic thin film deposition and ME effect measurements on these films. The measurements imply a stronger ME effect in SrCo$_2$Ti$_2$Fe$_8$O$_{19}$ films compared to the bulk materials of the same composition, due to the improved quality of the films. We performed two different configurations for ME measurements: (i) in plane and (ii) out-of plane applied electric field to the thin films. The in-plane configuration with increased number of microstrips can provide bigger electric fields along the film surface and consequently show bigger changes in remanence magnetization versus electric field. We also employed a conductive ITO buffer layer which could eliminate the need for high voltage power supply and we could perform the experiments at significantly lower voltages. Clearly, the small thickness of ME ferrite
makes it possible to observe ME effects by applying even much lower voltages. This achievement is promising in future ME based sensors and microwave devices.

The complex permeability $\mu_r = \mu_r' - j\mu_r''$ of a magnetic thin film is among the most important factors determining the suitability of a magnetic thin film for an application and the performances of the devices made from the magnetic thin film. Hence, in chapter 6, we represent the design and results of a microstrip device to measure the permeability of the thin films. We have used a coaxial technique to measure the permeability of a ME Z-type hexaferrite and a short circited transmission line to measure permeability of a ME M-type hexaferrite thin film. The magnetic permeability of the thin film was obtained from the changes in reflection coefficient ($S_{11}$) measurements due to presence of the magnetic thin film in the designed microstrip device.

Finally, chapter 7 is a summary of the accomplished works and represents ideas for future work to impact modern technologies where size, efficiency, multi-functionality, compatibility and costs are important. For example, the tunable inductors which suffer from huge sizes of external permanent magnets, can be miniaturized by replacing ME thin films since it is possible to tune their magnetic properties by electric field with low power consumption. Hence, in this chapter we also demonstrate the preliminary results of a voltage tunable magnetoelectric thin film inductor consisting of $\text{SrCo}_2\text{Ti}_2\text{Fe}_8\text{O}_{19}$ magnetoelectric M-type hexaferrite thin film core.
References:

Chapter 2. In-situ Deposition of C-Axis Oriented Barium Ferrite Films

2.1. Introduction

Hexagonal ferrites have long been used for permanent magnets and are of great interest for microwave applications and magnetic recording media. There is a large amount of knowledge on the structure and the properties of hexaferrites from past decades [1, 2]. Hexaferrites are classified into M-, Y-, Z-, W-, U-type,..., depending on their chemical formulas and crystal structures. In addition to the bulk form processing of these materials there is significant interest on thin film growth of hexaferrites due to need for miniaturizing microwave and magnetic devices and integrate them with semiconducting elements [3-7].

In this chapter, we demonstrate an alternative approach to the deposition of epitaxial hexagonal barium ferrite thin films through a method referred to as the alternating target laser ablation deposition (ATLAD) and was first introduced by Karim and Vittoria in 1995 [8] and refined later [9], [10]. Pulsed laser deposition has been known as an effective epitaxial growth technique for complicated stoichiometries such as hexagonal ferrites [11]. For instance, barium hexaferrite films deposited by this pulsed laser deposition possess single crystal structure with acceptable magnetic and microwave properties. ATLAD method employs multiple targets with different chemical compositions with the potential to control redistribution of magnetic cations in the unit
cell which consequently affects the interaction between electron spins [10]. In fact, ATLAD forms unique crystal structures which cannot be achieved by conventional ferrite thin film deposition techniques. In this paper, we expand this ATLAD method to include an alternative target of barium diferrite (BaFe$_4$O$_7$) and hematite ($\alpha$-Fe$_2$O$_3$). Previous deposition of barium ferrite, BaFe$_{12}$O$_{19}$, by the ATLAD technique utilized targets of BaFe$_2$O$_4$ and Fe$_2$O$_3$ [10].

Barium diferrite, BaFe$_4$O$_7$, is hexagonal with lattice dimensions of $a=5.16$ Å and $c=13.811$ Å. The unit cell consists of six layers of large ions. The third layer contains one oxygen and one barium ion which creates an open space. The ferrite ions are distributed equally into surrounded tetrahedrally and octahedrally sites by oxygen ions [12]. The structure of BaFe$_4$O$_7$ makes it a good candidate for hexaferrites deposition from M to Y and Z-type. We demonstrate the capability of this composition to control the magnetic properties of the deposited films by changing the impinged pulses from BaFe$_4$O$_7$ target.

![Figure 2.1: Schematic of a part of BaFe$_4$O$_7$ unit cell structure. [12]](image)
As it is shown in figure 2.2, the unit cell structure of a hexagonal M-type ferrite consists of stacking basic S (spinel) and R blocks with sequence of RSR*S*, where * indicates the structure rotated by 180° around the c-axis, resulting in the height of c =23.17 Å [2]. We used Fe₂O₃ and BaFe₄O₇ to simulate this structure and repeated it to specific times until the resultant film is thick enough to be evaluated by various characterization measurements.

![Diagram of M-type hexaferrite unit cell structure]

**Figure 2.2:** Schematic of a part of the M-type hexaferrite unit cell structure.

The results of the barium ferrite thin film deposited from monoferrite BaFe₂O₄ and Hematite α-Fe₂O₃ targets is given in the next section and the same film deposited from barium di-ferrite BaFe₂O₄ and Hematite α-Fe₂O₃ is reported in the next sections.
2.2. ATLAD Deposition of BaFe\textsubscript{12}O\textsubscript{19} from Barium Monoferrite BaFe\textsubscript{2}O\textsubscript{4} and Hematite α-Fe\textsubscript{2}O\textsubscript{3}

Thin films of BaFe\textsubscript{12}O\textsubscript{19} were deposited by the ATLAD technique with adapted recipe from Ref. [10]. The base pressure in the deposition chamber was controlled at 8×10\textsuperscript{-6} Torr. During the deposition high purity oxygen of 200 mTorr was introduced in the chamber and the sapphire (0001) substrates were heated to 900°C. Laser pulses from a KrF excimer laser with a wavelength of 248 nm, energy of 410 mJ/pulse, and pulse width of 25 ns full width at half maximum were optically focused on the target surface to an energy density of 10 J/cm\textsuperscript{2}. The distance between the target and the substrate was approximately 5 cm. Targets utilized in the deposition were prepared by conventional ceramics processing techniques. The BaFe\textsubscript{12}O\textsubscript{19} thin films were deposited by sequential ablation of BaFe\textsubscript{2}O\textsubscript{4} and Fe\textsubscript{2}O\textsubscript{3} targets. The targets were mounted on a carrousel synchronized with the laser trigger signal via a computer. To maximize surface usage all three targets were rastered and rotated throughout the deposition. The deposition routine consisted of 3 pulses on the BaFe\textsubscript{2}O\textsubscript{4} and 33 pulses on the Fe\textsubscript{2}O\textsubscript{3} target. The growth rates from the BaFe\textsubscript{2}O\textsubscript{4} and the Fe\textsubscript{2}O\textsubscript{3} targets were estimated by depositing films from each target on the sapphire substrate under the above conditions to be approximately 1.4 and 0.6 Å/shot, respectively [10]. The repetition rate of laser was gradually increased from 1 Hz to 10 Hz. It was set to 1 Hz for the first 10 repetitions of the deposition routine, 5 Hz for the subsequent 10 repetitions, and finally 10 Hz for the remaining 230 repetitions. Upon completion of the deposition process the films were flash annealed in flowing oxygen in a preheated tube furnace at 1050°C for 20 min and
were quickly removed from the furnace and cooled in air. The structural and magnetic properties of these films were in close agreement with the reference values. The XRD measurements of the films show high degree of c-axis orientation. However, surface morphology of the film as it is shown in figure 2.3, shows this films suffer from some deficiencies such as cracks and non uniform grain sizes.

![Image](image_url)

**Figure 2.3:** SEM image of the barium M-type hexaferrite deposited from BaFe$_2$O$_4$ and Fe$_2$O$_3$ targets.

In the next sections we will show the results of the barium hexaferrite thin films deposited from Fe$_2$O$_3$ and BaFe$_4$O$_{7}$ target instead of BaFe$_2$O$_4$ and study the structural and magnetic properties of the resulted films.

**2.3. ATLAD Deposition of BaFe$_{12}$O$_{19}$ from Barium diferrite BaFe$_4$O$_{7}$ and Hematite $\alpha$-Fe$_2$O$_3$**

Polycrystalline samples of Fe$_2$O$_3$ and BaFe$_4$O$_7$ were prepared by conventional solid state reaction processing for two targets used in the ATLAD sequential deposition. For
BaFe$_4$O$_7$, high purity powders of BaCO$_3$ and Fe$_2$O$_3$ were mixed stoichiometrically and sintered at 1200°C in air for 10 hours and then pulverized. Resulting powder was mixed with polyvinyl alcohol (PVA) and sintered again at 1200°C in air for 10 hours. The chemical compositions of both targets were verified by θ-2θ x-ray diffraction (XRD), using a Cu Kα source, and energy dispersive x-ray spectroscopy (EDXS) and determined to be single phase. BaFe$_{12}$O$_{19}$ films were deposited on sapphire (0001) substrates which provide the optimum lattice match between the substrate and deposited film [10]. Substrates were cleaned and baked before deposition. The substrates were heated to 910°C during deposition. The base pressure in the deposition chamber was controlled at 8×10$^{-6}$ Torr. The films were deposited in a high purity oxygen environment of 300 mTorr. A KrF excimer laser with a wavelength of 248 nm, energy of 400 mJ/pulse, and 25 ns full width at half maximum pulse width was focused to an energy density of 10 J/cm$^2$ on the target surface. The two targets were mounted on the carrousel in 0° and 180° positions. The distance between the target and the substrate was set to 5 cm. The rotation of the target carrousel was synchronized with the laser trigger signal to allow the targets to be alternated during film growth and the laser beam to be rastered to maximize target surface usage. The two step deposition routine consisted of 27 laser pulse shots on the Fe$_2$O$_3$ and 6~14 shots on the BaFe$_4$O$_7$ targets. The number of shots had significant effect on structure and magnetic properties of the films. The results of each performed experiment were evaluated by XRD and EDXS to check the atomic weight of each element in the BaFe$_{12}$O$_{19}$ composition. The growth under the above conditions was approximately 22~25 Å/cycle. The repetition rate
of laser was gradually increased from 1 Hz to 10 Hz during deposition to improve the film quality. After deposition the films were cooled to room temperature in the oxygen pressure of 300 mTorr. The whole deposition was repeated 420 times and resulted in an average film thickness of 0.7-1 µm. The film thickness was measured by masking a small part of the substrate during deposition and measured by a scanning surface profilometer.

### 2.3.1. Results and Discussions

The composition and structure of these films were determined by the X-ray diffractometer and energy dispersive x-ray spectroscopy. The XRD patterns of the films are illustrated in figure 2.4. Strong and sharp diffraction peaks at \((002n)\) \([n=1,2,3,…]\) show a c-axis oriented \(\text{BaFe}_{12}\text{O}_{19}\). The result was consistent with XRD measurements of barium ferrite. Surface morphology of these films was performed by scanning electron microscopy (SEM). Crystalline structures with individual hexagonal grains grown perpendicular to the c-axis can be seen in figure 2.5. Despite the surface morphology of the films deposited using \(\text{BaFe}_2\text{O}_4\) target, this films show a uniform grain structures with no cracks and as we will show later, they have more controllable magnetic properties.
Figure 2.4: XRD pattern of M-type BaFe₁₂O₁₉ thin films deposited by ATLAD from Fe₂O₃ and BaFe₄O₇ targets.

![XRD pattern](image)

Figure 2.5: SEM image of M-type BaFe₁₂O₁₉ thin films deposited by ATLAD from Fe₂O₃ and BaFe₄O₇ targets resulted in uniform hexagonal crystalline structures.

![SEM image](image)

The static magnetic properties of the films were studied by vibrating sample magnetometry (VSM) with the magnetic field applied perpendicular and parallel to the film plane. In figure 2.6 typical hysteresis loops of the films are shown for the films deposited with 27 shots of Fe₂O₃ and 7 shots of BaFe₄O₇ without annealing. This result is in agreement with XRD and SEM results and confirms an easy axis perpendicular to the
film plane. The anisotropy field and coercive field were estimated to be 16.2 kOe and 1000 kOe, respectively. These parameters improved with an annealing process which is beyond the purpose of this paper. The ferromagnetic resonance (FMR) measurements were performed with the static magnetic field applied parallel to the film plane. By considering $H_A = 16.2$ kOe, the $g$-factor was calculated to be 2.04 and $4\pi M_S = 2900$G from FMR result, which is consistent with VSM result. The FMR linewidth is rather broad which could be improved by annealing [10]. Figure 2.7 and 2.8 show the effect of number of pulses impinging on BaFe$_4$O$_7$ target on VSM and FMR results while the number of pulses on Fe$_2$O$_3$ target is fixed to 27. It shows that as the number of shots increased the coercive field decreased and the anisotropy field increased. This is an interesting control of magnetic properties by a small change in deposition process. As, it is shown in figure 2.8, the FMR linewidth was reasonably constant and there was a constant shift in FMR field with number of pulses. This shift reflects the idea that the anisotropy field changed. The optimum growth condition was 7 shots of BaFe$_4$O$_7$, since the anisotropy field was maximized.
Figure 2.6: Hysteresis loop of M-type BaFe\textsubscript{12}O\textsubscript{19} thin films with 0.7 µm thickness deposited from 27 shots of Fe\textsubscript{2}O\textsubscript{3} and 7 shots of BaFe\textsubscript{4}O\textsubscript{7} targets on 5mm×5mm sapphire substrates.

Figure 2.7: VSM hysteresis loop of barium hexaferrite films for various number of shots impinging on BaFe\textsubscript{4}O\textsubscript{7} target.
Figure 2.8: FMR as a function of parallel external magnetic field for various number of shots impinging on BaFe$_4$O$_7$ target.

The dependence of saturation magnetization and anisotropy filed is shown in figure 2.9. This significant control over magnetic properties is hard to achieve by previously used targets of BaFe$_2$O$_4$ or other methods. Also, the resistivity achieved in films deposited by BaFe$_4$O$_7$ is higher than the films deposited by BaFe$_2$O$_4$ target. Typical resistivity for the film deposited by 7 shots of BaFe$_4$O$_7$ and 27 shots of Fe$_2$O$_3$ was $7.1 \times 10^2$ Ω.cm while the resistance deposited by 3 shots of BaFe$_2$O$_4$ and 33 shots of Fe$_2$O$_3$ was $4.3 \times 10^2$ Ω.cm. Figure 2.10 shows the change in the resistivity of the films under various number of shots on BaFe$_4$O$_7$ films.
Figure 2.9: Variation of saturation magnetization and anisotropy field with various number of shots on BaFe$_4$O$_7$ target.

Magnetization was increased due to the fact that the Fe atoms are increasing with the increased number of shots impinging on BaFe$_4$O$_7$. The resistivity was also increased because of the minimized electron hopping through Fe$^{3+}$ ions. In fact, the valance state of
Fe in the BaFe$_4$O$_7$ target is 3+. The anisotropy field is determined by the local symmetry near the Ba site. According to the single ion model which has been used before to explain $H_A$ [13] and depending on the local strains near the Ba site and Fe distributions, $H_A$ can vary quite strongly. The calculation of $H_A$ requires exact determination of Fe distribution near Ba sites which is quite random.

2.4. Conclusions

Films deposited by the ATLAD technique utilizing targets of BaFe$_4$O$_7$ and Fe$_2$O$_3$ indeed exhibited magnetic and electrical properties consistent with barium ferrite. Changing BaFe$_2$O$_4$ target with BaFe$_4$O$_7$ target also gave rise to reasonable properties consistent with barium ferrite but noticeable improvement in resistivity was obtained when targets of BaFe$_4$O$_7$ were utilized. This could be an important factor for microwave applications of these M-type hexaferrite films.
References:


Chapter 3. Growth of Y-Type Hexaferrite Thin Films by Alternating Target Laser Ablation Deposition

3.1. Introduction

Hexagonal ferrites are an important family of ferrite materials and are classified in several groups: M-type, Y-type, Z-type, ... as mentioned in previous chapters [1]. There has been much attention on developing bulk samples of these materials and their application in fabricating high throughput magnetic microwave devices [2]-[4]. In fact, the hexagonal crystal structure of these materials allows various ionic substitutions which affect the magnetic properties of hexagonal ferrites, such as the uniaxial magnetic anisotropy field, the coercive field, the saturation magnetization [1], [5] and finally extends the range of possible applications for these materials. However, the major need in today’s technology is to downsize the magnetic components in electronic and telecommunication devices. The main step toward this goal is to deposit thin films of hexaferrite material. There have been considerable reports on epitaxial growth of M-type hexaferrite as discussed in previous chapter [6], [7] but not on Y-types since it is very difficult and challenging to produce single phase Y-type thin films. In fact, single crystal phase of Y-type magnetoplumbite is difficult to obtain in bulk and presumed to be even more difficult in thin films. The problem is that the basic unit consists ($a$-axis length = 5.8 Å, $c$-axis length = 43.5 Å) of 6 sublattices and requires very high substrate temperatures in
excess of 1150°C in order to stabilize growth from single target by pulsed laser deposition [8] and such high temperatures require very expensive additional equipment. In this chapter, we demonstrate a method to grow single phase Y-type thin films at substrate temperatures of 910°C which can be achieved easily by routine pulsed laser deposition (PLD). Y-type hexaferrites are soft ferrite materials for the applications of magnetic external fields, H, applied perpendicular to the c-axis. For high frequency applications they are an important class of ferrites. The unit cell structure of a hexagonal Y-type ferrite is shown in figure 3.1. The spinel S-block, has the chemical formula TM$_2$Fe$_4$O$_8$, where TM represents a transition metal ion, and the T block contains 4 oxygen layers where the Ba$^{2+}$ ion is substituted in the middle of two layers. The T block has the chemical formula Ba$2$Fe$_{8}$O$_{14}$ and the entire Y-type unit cell has the chemical formula of Ba$_2$TM$_2$Fe$_{12}$O$_{22}$, for example. The Y-type unit cell is constructed by stacking three S blocks and three T blocks in the sequence STS*T*ST, where * indicates the structure rotated by 180° around the c-axis, resulting in the height of c = 43.566 Å. The distribution of metallic ions among the various sublattices in the unit cell, along with the spin orientations is given in Table 3.1.

<table>
<thead>
<tr>
<th>Sublattice</th>
<th>Coordination</th>
<th>Block</th>
<th># Ions</th>
<th>Spin</th>
</tr>
</thead>
<tbody>
<tr>
<td>6c$_{IV}$</td>
<td>Tetrahedral</td>
<td>S</td>
<td>6</td>
<td>down</td>
</tr>
<tr>
<td>3a$_{VI}$</td>
<td>Octahedral</td>
<td>S</td>
<td>3</td>
<td>up</td>
</tr>
<tr>
<td>18h$_{VI}$</td>
<td>Octahedral</td>
<td>S-T</td>
<td>18</td>
<td>up</td>
</tr>
<tr>
<td>6c$_{VI}$</td>
<td>Octahedral</td>
<td>T</td>
<td>6</td>
<td>down</td>
</tr>
<tr>
<td>6c$_{IV}$*</td>
<td>Tetrahedral</td>
<td>T</td>
<td>6</td>
<td>down</td>
</tr>
<tr>
<td>3b$_{VI}$</td>
<td>Octahedral</td>
<td>T</td>
<td>3</td>
<td>up</td>
</tr>
</tbody>
</table>

*Same crystalline symmetry in a different block
Figure 3.1: Schematic of a part of the Y-type magnetoplumbite unit cell structure.

Pulsed laser deposition (PLD) has long been established as an effective epitaxial growth technique for the production of ferrite thin films of complicated stoichiometries such as hexagonal ferrites [9]-[11]. For Ba₂Co₂Fe₁₂O₃₂ (Co₂Y) film deposition at the atomic scale we used a technique which is referred to as the alternating target laser ablation deposition (ATLAD) and is discussed in the previous chapter. The technique was first introduced by Karim and Vittoria in 1995 [7] and refined later [12], [13]. By depositing from three different targets sequentially we grew a single phase polycrystalline Co₂Y thin film. The deposited films were determined to possess crystallographic, magnetic, and microwave properties that were comparable to bulk values of Y-type hexaferrites.
3.2. Bulk Single Crystal Y-type Hexaferrite

In order to have a reliable reference to develop a Y-type thin film, we used a sample of single crystal Ba$_2$Zn$_2$Fe$_{12}$O$_{22}$ (Zn$_2$Y), which were prepared by Dr. Soack Dae Yoon from the recipe adapted from Ref. 14. Crystals of ZnY were prepared by crystallization from molten starting materials in a platinum crucible. The starting materials with total weight of 100 gr (B$_2$O$_3$: 9.25 gr, BaCO$_3$: 51.50 gr, ZnO: 5.75 gr and Fe$_2$O$_3$: 33.50gr) were mixed in a ball mill and melted at 1250ºC for 24 hr. The materials were added gradually to the melt. And finally the flux was melted again at 1350ºC for another 24 hr. Cooling down was done in three steps: (1) very slowly to 1200ºC for at least 36 hr. (2) cooled down to 800 in 48 hr and (3) turned off the furnace. A picture and also SEM images of final crystals are shown in figure 3.2 and figure 3.3. The chemical composition of the ZnY Crystals were determined by the θ-2θ X-ray diffracometer (XRD), using a Cu $K\alpha$ source and energy dispersive x-ray spectroscopy (figure 3.4) and the static magnetic properties of the films were studied by vibrating sample magnetometry (VSM) with the magnetic field applied perpendicular and parallel to the film plane as it is shown in figure 3.5.

![Figure 3.2](image)

**Figure 3.2:** Picture of single crystals of ZnY obtained with the technique described above.
**Figure 3.3:** SEM images of single crystals of ZnY, big hexagonal structures can be seen in these images.

**Figure 3.4:** XRD pattern of the ZnY single crystal.
3.3. $\text{Ba}_2\text{Co}_2\text{Fe}_{12}\text{O}_{22}$ (Co$_2$Y) Thin Film from One Target

A 1-inch target of $\text{Ba}_2\text{Co}_2\text{Fe}_{12}\text{O}_{22}$ (Co$_2$Y) was prepared by conventional ceramics processing. The high purity powders of $\text{BaCO}_3$, $\text{Fe}_2\text{O}_3$, $\text{Co}_3\text{O}_4$, were mixed stoichiometrically by a planetary mill at 350 rpm for 4 h. The mixture was pressed at 1000 psi and sintered at 1000°C for 4 hours in the oxygen atmosphere. The resulting puck was then crushed and ground and mixed with polyvinyl alcohol (PVA) binder, pressed at 2000 psi, and sintered for second time in 1150°C for 6 hr to obtain a high density target. The XRD result of this target is shown in figure 3.6.
Figure 3.6: XRD result of bulk Ba$_2$Co$_2$Fe$_{12}$O$_{22}$ (Co$_2$Y) prepared for the PLD target. The black vertical lines represent the reference peak positions for the Y-type hexaferrite in Jade software.

Thin films of Ba$_2$Co$_2$Fe$_{12}$O$_{22}$ film were deposited on MgAl$_2$O$_4$ (111) with 2.5% lattice mismatch by pulsed laser deposition which is an effective epitaxial growth technique for the production of hexaferrite thin films. The base pressure in the deposition chamber was maintained at $8 \times 10^{-6}$ Torr and the substrates were heated to 915°C which is the maximum achievable temperature by PLD. The films were deposited in a high purity oxygen environment of 200 mTorr. A KrF excimer laser with a wavelength of 248 nm and energy of 400 mJ/pulse, was focused on the target surface. The distance between the target and the substrate was set to 5 cm and the repetition rate of the laser was gradually increased from 1 Hz to 10 Hz during deposition to improve the growth. After deposition, the films were cooled to room temperature in oxygen pressure of 200 mTorr. The deposition run was timed for 50 min. After deposition, the films were annealed in oxygen atmosphere in a tube furnace at 900°C for 30 minutes. The XRD result of this thin film is shown in figure 3.7.
Figure 3.7: XRD result of Ba$_2$Co$_2$Fe$_{12}$O$_{22}$ thin film prepared by PLD from one target. The red pattern is the single crystal Y-type pattern from previous section, used as a reference.

As it can be seen from the XRD result, the pattern is a mixture of different phases of spinel, M-type and Y-type and some unknown phases. Based on the Ref. 8, some of these phases might be from BaFe$_2$O$_4$ layer which may preferentially grow beneath the Co$_2$Y film to form a bi-layer structure of Co$_2$Y/BaFe$_2$O$_4$ on MgAl$_2$O$_4$ (111). The impurity of BaFe$_2$O$_4$ is then considered as Co deficient phase, and a CoO buffer layer was recommended to use in order to suppress the formation of BaFe$_2$O$_4$. A thickness gradient method was even suggested by same group [15] by using a motion linear mask in order to optimize the CoO buffer layer thickness, as it is shown in figure 3.8. It is noticeable that these experiments is done at 1140°C by a PLD equipped with the substrate heating system by Nd:YAG laser which is expensive.
We also employed the same method and used a CoO buffer layer which was deposited from a CoO target. The CoO target was prepared by solid state method from CoO powder mixed with PVA and pressed in 1500 psi and sintered in vacumm in a tube furnace. After CoO buffer layer deposition, the Y-type thin film was deposited same as the routine described earlier. The XRD result of this film is shown in figure 3.9. The result is improved compared to the result in figure 3.7, but still suffers from mixed and unknown phases. A SEM image is also shown in figure 3.10 which does not show any hexagonal structures.

**Figure 3.8:** (a) Thickness gradient thin film method by using the linear motion mask. (b) The resulted XRD pattern [15].

**Figure 3.9:** XRD result of Ba$_2$Co$_2$Fe$_{12}$O$_{22}$ thin film with CoO buffer layer.
3.4. ATLAD deposition of Ba$_2$Co$_2$Fe$_{12}$O$_{22}$ (Co$_2$Y) Thin Film (Multi Targets)

Three targets were used for the ATLAD sequential deposition to simulate S and T blocks of the unit cell in the deposition of Ba$_2$Co$_2$Fe$_{12}$O$_{22}$ films. We studied several targets for T block of the unit cell of Ba$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$, BaFe$_2$O$_4$ and BaFe$_4$O$_7$. The final three targets included CoFe$_2$O$_4$, BaFe$_4$O$_7$ and Fe$_2$O$_3$ and were prepared by the conventional ceramics processing and their chemical compositions were verified by θ-2θ x-ray diffraction (XRD), using a Cu Kα source, and energy dispersive x-ray spectroscopy (EDXS) and determined to be single phase. Co$_2$Y films were deposited on basal plane oriented rhombohedral sapphire (Al$_2$O$_3$) substrates which were cleaned and baked before deposition. The base pressure in the deposition chamber was controlled at 8×10$^{-6}$ Torr. The substrates were heated to 910°C, well below the natural sintering temperatures of bulk materials. The films were deposited in a high purity oxygen environment of 200 mTorr. A KrF excimer laser with a wavelength of 248 nm, energy of 400 mJ/pulse, and 25 ns full
width at half maximum pulse width was focused to an energy density of 10 J/cm² on the target surface. The distance between the target and the substrate was set to 5 cm. The rotation of the target carrousel was synchronized with the laser trigger signal to allow the targets to be alternated during film growth and the laser beam to be rastered to maximize target surface usage. The three targets were mounted on the carrousel in a way to keep the equal distance between each other. The number of shots had significant effect on crystal structure of the films. Several calibration experiments were performed with different number of shots and the results were evaluated by XRD and EDXS to determine the atomic weight of each element in the Ba₃Co₂Fe₁₂O₂₂ composition. Also, the order of the targets during sequential ablation was crucial since other ablation orders resulted in Co deficiency and created spinel or monoferrite phases in the deposited film. A schematic picture of the used ATLAD set up is shown in figure 3.11.

**Figure 3.11:** Alternating Target Laser Deposition set up.
After several experiments we employed a four step deposition routine with more number of shots on CoFe$_2$O$_4$ target compare to BaFe$_4$O$_7$, in order to minimize the Co deficiency. The EDXS result of a 12 laser pulse shots on the Fe$_2$O$_3$, 17 shots on the CoFe$_2$O$_4$, 12 shots on the Fe$_2$O$_3$ and finally 7 shots on BaFe$_4$O$_7$ targets is shown in figure 3.12. As the calculations in table 3.2 shows, the actual atomic weight results are different from expected values and it suffers from Ba deficiency. So we recalculated the results and increased the number of shots on BaFe$_4$O$_7$ target and decreased the number of shots on CoFe$_2$O$_4$.

**Figure 3.12:** The EDXS result of the film deposited from 12 shots on the Fe$_2$O$_3$, 17 shots on the CoFe$_2$O$_4$, 12 shots on the Fe$_2$O$_3$ and 7 shots on BaFe$_4$O$_7$ targets.
Table 3.2: The atomic weight results versus the number of shots.

<table>
<thead>
<tr>
<th>Applied number of shots</th>
<th>Expected ratio</th>
<th>Actual ratio</th>
<th>New modified ratio</th>
<th>New number of shots</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃; 24</td>
<td>Fe/Co = 6.47</td>
<td>Fe/Co = 6.08</td>
<td>Co' = 0.94Co</td>
<td>Ba' = 7.99  →  8</td>
</tr>
<tr>
<td>CoFe₂O₄; 17</td>
<td>Fe/Ba = 15.71</td>
<td>Fe/Ba = 17.94</td>
<td>Ba' = 1.142Ba</td>
<td>Co' = 15.98 → 16</td>
</tr>
<tr>
<td>BaFe₄O₇; 7</td>
<td>Co/Ba = 2.42</td>
<td>Co/Ba = 2.95</td>
<td>Fe' = Fe</td>
<td>Fe' = 110  → 112</td>
</tr>
</tbody>
</table>

Based on the analyzed results the best four step deposition routine consisted of 12 laser pulse shots on the Fe₂O₃, 16 shots on the CoFe₂O₄, 12 shots on the Fe₂O₃ and finally 8 shots on BaFe₄O₇ targets. The growth under the above conditions was approximately 43.8 Å/cycle. The repetition rate of laser was gradually increased from 1 Hz to 10 Hz during deposition to force the ions to localize at the designated sites and create the 43.566 Å unit cell of magnetoplumbite Co₂Y structure.

After deposition, the films were cooled to room temperature in the oxygen pressure of 200 mTorr. The whole deposition was repeated 180 times and resulted in an average film thickness of 0.8 μm. The film thickness was measured by masking a small part of the substrate during deposition and measured by a scanning surface profilometer. The films were annealed in flowing oxygen in a tube furnace at 1050 °C for 30 minutes. Leaving the films in the furnace during temperature ramping, will change the ions localization and affect crystal structure due to diffusion at the film-substrate interface. To prevent this problem the films were rapidly inserted into the preheated furnace, annealed for 30 minutes and rapidly removed from the furnace (flash annealed). Annealing of the films beyond the 30 min interval resulted effectively lowering the film thickness and rapid reduction of the
magnetic moment, which was interpreted as evidence of interfacial diffusion. The deposition process parameters are summarized in table 3.3 and table 3.4.

**Table 3.3:** Final sequence and number of shots in Ba₂Co₂Fe₁₂O₂₂ deposition.

<table>
<thead>
<tr>
<th>Targets</th>
<th>Number of Shots</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>12</td>
</tr>
<tr>
<td>CoFe₂O₄</td>
<td>16</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>12</td>
</tr>
<tr>
<td>BaFe₂O₇</td>
<td>8</td>
</tr>
</tbody>
</table>

**Table 3.4:** Parameters of the Ba₂Co₂Fe₁₂O₂₂ thin film deposition process.

<table>
<thead>
<tr>
<th>Base Pressure</th>
<th>Deposition Settings</th>
<th>Annealing</th>
</tr>
</thead>
<tbody>
<tr>
<td>8×10⁻⁶ Torr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxygen Pressure</td>
<td>Substrate Temperature</td>
<td>Number of Cycles</td>
</tr>
<tr>
<td>200 mT</td>
<td>910°C</td>
<td>180</td>
</tr>
</tbody>
</table>

**3.5. Structural and Magnetic Characterization**

The composition and structure of these films were determined by the X-ray diffractometer and energy dispersive x-ray spectroscopy. The XRD patterns are illustrated in figure 3.13 for films before and after annealing. It approves that before annealing there are unknown diffraction peaks and phases. In addition, some of the Y-type phases are not exactly at the desired 2θ angles. Annealing improved the structure and the quality of the films in a way that single phase of Y-type hexaferrite was achieved. For instance, (0012) and (0015) diffraction peaks were improved with sharper amplified intensities. The rocking curves for four diffraction peaks in figure 3.14 show that on the average c-axis alignment falls within 0.625° of the normal to the film plane. Thus, the films are reasonably well ordered, but not of single crystal quality. This means that the number of laser pulse
shots to implement the ATLAD technique has not been perfectly optimized. However, the ATLAD technique does yield for the first time Y-type hexaferrite films grown at relatively low temperatures ~ 900°C by pulsed laser deposition. It also implies that the ATLAD technique is the correct technique to yield single crystal films of the Y-type hexaferrites in the future. Surface morphology of these films was studied by scanning electron microscopy (SEM) as shown in figure 3.15. Polycrystalline hexagonal structures were clearly visible in the SEM image which was consistent with XRD measurements. The inset of Fig. 4 shows a grown hexagonal grain in the film surface.

**Figure 3.13:** XRD pattern of Y-type Ba$_2$Co$_2$Fe$_{12}$O$_{22}$ thin films, (a) before annealing and (b) after annealing. The green and red symbols represent the peak positions for single crystals of Y-type and M-type hexaferrites, respectively.
Figure 3.14: Rocking curve measurements of (0 0 12), (0 0 15), (0 0 27) and (0 0 36) diffraction peaks on the annealed film which show $\Delta \omega = 1.25$ on the average.

Figure 3.15: SEM image of Y-type Ba$_2$Co$_2$Fe$_{12}$O$_{22}$ thin film.

The static magnetic properties of the films were studied by vibrating sample magnetometry (VSM) with the magnetic field applied perpendicular and parallel to the
film plane. In figure 3.16 typical hysteresis loops of the films are shown for the films before and after annealing. The coercive field of the hysteresis loop is improved after annealing and with the field applied parallel to the film plane was measured to be 1.2 kOe. With the field applied perpendicular to the film plane the uniaxial magnetic anisotropy field of 13.2 kOe was deduced. These magnetic parameters are in agreement with reference bulk values found in the literature [1], [5].

![Hysteresis Loops](image)

**Figure 3.16:** VSM hysteresis loop of the Y-type Ba$_2$Co$_2$Fe$_{12}$O$_{22}$ thin film (a) before annealing, (b) after annealing.
The ferromagnetic resonance (FMR) measurements were performed with the static magnetic field applied both parallel and perpendicular to the film plane. The resonance condition in each configuration is given by

Parallel: \[ f = \gamma' \sqrt{H_\parallel + H_A + 4\pi M_s} \] (3.1)

Perpendicular: \[ f = \gamma' (H_\perp - H_A - 4\pi M_s) \] (3.2)

Where \( H_\parallel, H_\perp \) is the externally applied magnetic field parallel (\( \parallel \)) and perpendicular (\( \perp \)) to the film plane, \( H_A \) is the uniaxial magnetic anisotropy field, \( 4\pi M_s \) is the saturation magnetization, \( \gamma' \)is the gyromagnetic ratio over \( 2\pi \), and \( f \) is the FMR frequency [16].

Typical FMR plot of derivative absorption versus external field (\( \parallel \)) is shown in Fig. 6. Utilizing measured \( H_\parallel \) and \( H_\perp \) in (3.1) and (3.2), the \( g \)-factor was calculated to be 1.52 and \( 4\pi M_s = 2520 \) G which are in agreement with the reference value of bulk Y-type single crystals [1]. In this calculation we assumed \( H_A = 13.2 \) kOe as measured in VSM. Calculated \( 4\pi M_s \) is in close agreement with the value measured from VSM (2463 G). The FMR linewidth was measured to be 1400 Oe which is rather broad when compared to single crystal value of 2 Oe. The broadening in linewidth may be due to inhomogeneous magnetic distributions as, for example, in polycrystalline samples.
Figure 3.17: FMR as a function of parallel external magnetic field of the Ba$_2$Co$_2$Fe$_{12}$O$_{22}$ thin film.

3.6. Bulk Single Crystal Z-type Hexaferrite

We also characterized a single crystal of Z-type hexaferrite for future Z-type thin film deposition using ATLAD technique. Z-type has even more complicated unit structure than Y-type. The unit cell structure of part of a Z-type hexaferrite is shown in figure 3.18.

Figure 3.18: Crystal structure of a part of the Z-type hexagonal unit cell.
SEM images of this single crystals are shown in figure 3.19, crystalline structures are clearly visible in the micrographs. The XRD result is shown in figure 3.20 which shows narrow and sharp diffraction peaks at \((0 \ 0 \ 2n)\). The static magnetic properties were studied by VSM with the magnetic field applied perpendicular and parallel to the sample as it is shown in figure 3.21. FMR (Ferromagnetic Resonance) measurements are shown in Figures 3.22. From VSM measurements we measured \(4\pi M_s\approx3100\ G\) and \(H_c=14\ Oe\). From FMR measurements, we deduced the following parameters: \(g=2, \Delta H=750\ Oe\ (9.53\ GHz), H_0=12\ kOe,\) and \(H_\phi=60\ Oe,\) where \(4\pi M_s, H_c, \Delta H, H_0,\) and \(H_\phi\) are the saturation magnetization, coercive field, the FMR linewidth, the uniaxial magnetic anisotropy field, and the azimuth anisotropy field (six fold symmetry), respectively.

\[ \text{Figure 3.19: SEM images of Z-type single crystals.} \]
Figure 3.20: XRD pattern of Z-type single crystal.

Figure 3.21: VSM hysteresis loop of Z-type single crystal.
3.7. Conclusions

We have demonstrated that the ATLAD technique is a very viable procedure by which Y-type hexaferrite films can be deposited at temperatures near 900°C. These films are of improved quality in terms of magnetic and crystal structure properties when compared to films deposited from a single target at much higher PLD temperatures [8]. Indeed the ATLAD technique allowed the deposition to occur sequentially and, therefore, localized the ions in the proper crystal structure. That is the essence of the deposition technique. It is very important to control the conditions during deposition to avoid formation of other phases. Annealing simply reinforced single phase of the film and improved the magnetic properties. The magnetic and structural properties are consistent with the bulk Y-type hexaferrite material. The next phase of research is to improve the crystalline quality of the film by continually adjusting the number of pulses impinging the targets sequentially. And also to deposit Z-type hexaferrite thin films by this ATLAD technique.

Figure 3.22: FMR Figure as a function of external magnetic field of Z-type single crystal.
References:


Chapter 4. Magnetoelectric Overview

4.1. Introduction

In this chapter, the physical concepts of single phase ferroically ordered materials and multi-ferroic composite structures are presented. A ferroic material may be magnetically or electrically ordered without the application of external magnetic or electric fields. Combining various ferroics, potentially can be used in different applications such as sensors and communication devices and circuits. Understanding of magnetic and electrical properties of ferroic materials helps us to take advantage of special coupling phenomena in ferroics to push current technology toward smaller, cheaper, more compact and more efficient devices [1].

4.1.1. Ferroics

Ferroics is the area to the study of ferromagnets, ferroelectrics, ferroelastics and ferrotoroidicity. The basis of this study is to understand the changes in physical characteristics that occur around critical temperature ($T_c$). Above this critical temperature, the crystal is in a nonferroic state and does not exhibit the physical characteristic of interest and below $T_c$ it undergoes a spontaneous phase transition. This phase transition results in a deviation from the nonferroic state and alternates the shape of the unit cell and changes the symmetry. In fact, the breaking of symmetry is physically what allows the
formation of the ferroic phase. The four basic primary ferroic orders are defined as follow and is illustrated in figure 4.1.

1) Ferromagnetic: possesses spontaneous magnetization. Most ferromagnets tend to be metallic.

2) Ferroelectric: below the T_c temperature a spontaneous dipole moment is induced along an axis of the unit cell.

3) Ferroelastic: going from the nonferroic to the ferroic phase when a spontaneous strain is induced.

4) Ferrotoroidicity: phase transition to spontaneous long range order of microscopic magnetic toroidal moments.

**Figure 4.1:** Definition of four primary ferroic orders. [2]
4.1.2. Multiferroics

These multiferroics exhibit more than one ferroic property simultaneously in a single phase.

1) Magnetoelectric coupling: represents a change in magnetization or polarization of a multiferroic material upon application of a magnetic or electric field.

2) Piezoelectricity: describes the influence of an applied linear electric field on strain, or a change in polarization as a linear function of applied stress.

3) Piezomagnetism: represents a change in strain as a linear function of applied magnetic field, or a change in magnetization as a linear function of applied stress.

4) Electrostriction: describes a change in strain as a quadratic function of applied electric field.

5) Magnetostriction: describes a change in strain as a quadratic function of applied magnetic field.

6) Single Phase Multiferroic: a material possessing at least two of ferroic properties: ferroelectricity, ferromagnetism and ferroelasticity [2].
4.2. Symmetry in Ferroics

In Ferroelectric material the electric dipole moment \( \mathbf{p} \) is represented by a positive point charge that lies asymmetrically within a crystallographic unit cell that has no net charge, \( \mathbf{p} = qr \), where \( \mathbf{p} \) is polarization, \( q \) is electric charge and \( r \) is the charges distance. There is no net time dependence, but spatial inversion \((r \rightarrow -r)\) reverses \( \mathbf{p} \), shown in Figure 4.4. In Ferromagnets the magnetic moment \( \mathbf{m} \) is represented classically by a charge tracing dynamically an orbit, \( m = \pi r^2 \frac{dq}{dt} \), where \( ds = \pi r^2 \) and \( t \) is time. A spatial inversion produces no change, since \((r^2) \rightarrow (-r)^2\), but time reversal switches the orbit and thus \( \mathbf{m} \). In summary, \( \mathbf{p} \) obeys time symmetry but not parity.
However, $m$ obeys parity but not time symmetry. Multiferroics that are both ferromagnetic and ferroelectric break time reversal and parity symmetries.

**Figure 4.3:** Time-reversal and parity symmetry in Ferroelectric, Ferromagnetic and Multiferroic materials. [3]

### 4.3. Magnetoelastic Coupling

A ferromagnetic crystal exhibits a stable and switchable magnetization that arises through the quantum mechanical phenomenon of spin exchange. The relationship between multiferroic and magnetoelastic states is shown in Figure 4.3. A multiferroic material is not necessarily magnetoelastic. There are few multiferroic materials that
exhibit both ferroelectric and ferromagnetic properties without coupling between the two.

Magnetoelectric coupling can exist wherever magnetic and electrical polarizations occur in the same temperature range. Also magnetoelectricity may occur in paramagnetic ferroelectrics [4]. Usually, the mediator for the coupling is strain as related to crystal phases.

![Figure 4.4: Coupling order of ferroics. [3]](image)

As shown in Figure 4.3, type IV, is neither Ferroelectric nor Ferromagnetic but it is magnetoelectric. The magnetoelectric effect in single-phase crystals is traditionally described [4-9] in Landau theory as in equation 4.1, by writing the free energy $F$ of the system in terms of an applied magnetic field $H$ and an applied electric field $E$. This convention is unambiguous in free space, but $E_i$ within a material includes the resultant field that a local site would experience. In a non-ferroic material, where both the temperature dependent electrical polarization $P_i(T)$ ($\mu$Ccm$^{-2}$) and the magnetization $M_i(T)$ are zero in the absence of applied fields. $F$ may be represented in an infinite, homogeneous and stress-free medium under the Einstein summation convention as:

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\[-F(E, H) = \frac{1}{2} \varepsilon_0 \varepsilon_{ij} E_i E_j + \frac{1}{2} \mu_0 \mu_{ij} H_i H_j + \alpha_{ij} E_i H_j + \frac{\beta_{ijk}}{2} E_i H_j H_k + \frac{\gamma_{ijk}}{2} H_i E_j E_k + \cdots \] (4.1)

where the SI and CGS units of the parameters and their relations are:

The first term on the right hand side of in equation 4.1 describes the contribution resulting from the electrical response to an electric field, \( \varepsilon_0 \) is the permittivity of free space, and the relative permittivity \( \varepsilon_{ij}(T) \) is a second-rank tensor that is typically independent of \( E_i \) in non-ferroic materials. The second term is the magnetic equivalent of the first term, where \( \mu_{ij}(T) \) is the relative permeability and \( \mu_0 \) denotes the permeability of free space. The third term describes linear magnetoelectric coupling via \( \alpha_{ij}(T) \); the third-rank tensors \( \beta_{ijk}(T) \) and \( \gamma_{ijk}(T) \) represent higher-order (quadratic) magnetoelectric coefficients.

The possibility to control magnetization and/or polarization by an electric field and/or magnetic field; which is magnetoelectric effect (ME) allows additional degree of freedom in multifunctional device design. The ME effect is defined as an induced electric polarization \( (P) \) of a material with an applied magnetic field \( (H) \), which is direct effect or an induced magnetization \( (M) \) with an external electric field \( (E) \), which is converse effect.

\[ \Delta P = \alpha \Delta H \text{ or } \Delta E = \alpha_E \Delta H \quad [\text{direct ME effect}] \] (4.2)
\[ \Delta M = \alpha \Delta E \quad [\text{converse ME effect}] \] (4.3)

where \( \alpha(\alpha_E) \) is the ME voltage coefficient. This means that the electric polarization/magnetization can be modified by the application of a magnetic field/electric field of the materials via the ME coupling [10].
4.4. Magnetolectric Composite Films

Due to the great potential for device applications film type ME composites have received the significant research interests during recent years. Multiferroic ME composite films can generally be divided into three types as it is shown in figure 4.5: (a) 0-3 structure, which is a magnetoelastic material embedded in a piezoelectric matrix, (b) 2-2 structure, which is multilayer thin films of magnetostrictive and piezoelectric materials, and (b) 1-3 structure, such as monolayer self-assembled nanostructures. [10]

![Figure 4.5](image)

**Figure 4.5:** Three styles of the ME composite films: (a) 0-3 particulate composite, (b) 2-2 laminate composite, and (c) 1-3 fiber/rod composite films. [10, 11]

Table 4.1 shows the summery of the properties of each of these three structure. In addition to complicated fabrication process for some of them, they all suffer from weak ME effect and they usually need bias H fields which results in large size and avoids the use of them to be integrated with other circuit components. On the other hand, magnetolectric hexaferrite materials possess magnetolectric effect at room temperature and they do not need an external biasing magnetic field.
### Table 4.1: Advantages/disadvantages of ME composite films with different structures. [10]

<table>
<thead>
<tr>
<th>Connectivity</th>
<th>Advantage</th>
<th>Disadvantage</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-3</td>
<td>Easy processing.</td>
<td>Low resistivity (difficult to pole), Low ME property.</td>
<td>Sintering with ceramic power mixture. Ceramic/polymer composite.</td>
</tr>
<tr>
<td>1-3</td>
<td>Coherent interface in an atomic scale.</td>
<td>Low resistivity. Hard to fabricate.</td>
<td>Large in-plane strain. Thin film process.</td>
</tr>
</tbody>
</table>

#### 4.5. Magnetoelectric Coupling in Hexaferrites at Room Temperature

In this section, the magnetoelectric effect in hexa ferrite materials is presented. The measurements include change in remanence magnetization ($M_r$) versus electric field.

There have been a number of publications dealing with the magneto-electric properties of M- and Z- type hexaferrites [12-18]. These hexaferrites are special ferrite materials, because they exhibit high magnetoelectric coupling coefficient at room temperature. The ME coupling coefficient of some of the materials is shown in table 4.2. This means that the application of an electric field or DC voltage induces magnetization changes and the application of a magnetic field induces electric polarization changes. The common denominator of recent publications was that the tested materials were poly-crystalline. The application of these types of materials still is not possible along with semiconductors. And converse measurements have shown that very high voltage or electric field in the range of 1-5 kV/cm is required for high magneto-electric coupling effect [14]. But the single crystal structures in bulk or as in thin films of hexaferrite materials can be a promising solution to overcome high required voltage. Here we will present the reported results on single crystal
Z-type hexaferrite and in the next chapter we will present the results of this dissertation on ME thin films of hexaferrites.

The magnetic properties of single crystals of Z-type hexaferrites, Sr$_3$Co$_2$Fe$_{24}$O$_{41}$, exhibiting the strongest magnetoelectric effect at room temperature [18]. In a very low electric field equal to 3.75 V/cm, 14% change in $M_r$ with ME coupling of $2.32 \times 10^{-6}$ sm$^{-1}$ was reported [18]. This is quite promising in terms of being able to induce magnetization changes with as little as 15 mV compared to polycrystalline materials requiring hundreds of volts affecting the same change in magnetization.

**Table 4.2:** Reported magnetoelectric coefficient in some hexaferrites.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\alpha$ [sm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z-type (Sr$<em>3$Co$<em>2$Fe$</em>{24}$O$</em>{41}$)</td>
<td>$7.6 \times 10^{-10}$</td>
</tr>
<tr>
<td>M-type (SrCo$<em>2$Ti$<em>2$Fe$</em>{8}$O$</em>{19}$ sintered in O$_2$)</td>
<td>$2.4 \times 10^{-10}$</td>
</tr>
<tr>
<td>M-type (SrCo$<em>2$Ti$<em>2$Fe$</em>{8}$O$</em>{19}$ sintered in air)</td>
<td>$1.7 \times 10^{-10}$</td>
</tr>
<tr>
<td>La$<em>{0.67}$Sr$</em>{0.33}$MnO$_3$</td>
<td>$2.3 \times 10^{-7}$</td>
</tr>
<tr>
<td>Single Crystalline Sr-Z</td>
<td>$2.32 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

4.6. Conclusions

Hexaferrite materials exhibit magnetoelectric effect at room temperature and there is no need for biasing magnetic field sources which are huge in size. As a result, magnetoelectric hexaferrites are better candidates than ME composite structures for future emerging microwave devices. Single crystal form of the hexaferrite possess larger
ME coupling coefficient in compare with polycrystalline bulk form of their equivalent compositions and they need low voltages to observe ME effect. Next chapter will cover the magnetoelectric effect in hexaferrite thin films, which not only exhibit ME effect at room temperature with noticeable ME coupling coefficient, but also make it possible to integrate ferrite components.
References:


Chapter 5. Magnetoelectric Effect in M-type Hexaferrite Thin Films

5.1. Introduction

Recently, a new class of ferrite materials have been discovered whereby the magnetoelectric linear coupling at room temperature is large, comparable to the most efficient multi-ferroic composites. The implication of this is that with the application of voltage one can induce a change in magnetization of a ferrite. Hence, the need for bias fields may be relaxed in future use of ferrites. The impact of this result to modern technologies utilizing ferrites is enormous. The new class of magnetoelectric (ME) ferrites is identified as hexaferrites of the M, Y, and Z-types and is operational at room temperature. The unique feature of these hexaferrites is that the unit cell consists of spinel blocks stacked on top of each other as discussed in previous chapters. These spinel blocks are referred to as S (TMFe$_2$O$_4$), R (BaFe$_4$O$_7$) and T (2BaFe$_4$O$_7$) blocks, where TM implies a transition metal ion and Ba substitution may be replaced by Sr or Pb ions. The chemical formula of a typical M-type hexaferrite is BaFe$_{12}$O$_{19}$, for Y-type as Ba$_2$Fe$_{12}$TM$_2$O$_{22}$ and Z-type as Ba$_3$Fe$_{24}$TM$_2$O$_{41}$. The lattice constants along the c-axis are, respectively, 22, 43 and 52 Å. Clearly, the Z-type hexaferrite contains the largest unit cell along the c-axis and, therefore, the most spinel blocks (SRSTS*R*S*T*), where the * imply 120, 240 and 180 degrees rotation with respect to the unmarked block. As a general experimental rule the more stacking of the spinel blocks is required, the more difficult it is to prepare the
hexaferrite in question. For example, the Z-Type require the most stacking of the above set
of spinel blocks and indeed it is the most difficult to prepare. Local distortions or strains
induced by replacing Ba with a smaller Sr ion gives rise to magnetoelectricity (ME). The
local distortion, located in the T block for Z-type and R block in the M-type hexaferrites,
implies that the bonding angle in Fe-O-Fe combination near the Sr substitution is changed
from 116 degrees (with Ba) to 123 degrees (with Sr [1-3]). This has great ramifications in
terms of the superexchange interaction between the two Fe ions and spins in the S block
and spins in the R or T block yielding a spin spiral cone configuration described by the
Dzyaloshinski-Moriya [4] interaction model. Thus, any change in the cone angle of the
spin spiral configuration is reflected in a change in the local strain and vice versa. The
change in the strain manifests itself as a change in electric polarization, since these
hexaferrites are also piezoelectric [5]. Thus, the application of a magnetic field $H$ changes
the cone angle of the spin spiral configuration to induce a change in the local strain and,
therefore, the induction of an internal electric field or polarization, as it is shown in figure
5.1.

A spin spiral configuration alone is not sufficient to induce the ME effect in
hexaferrites. For example, BaFe$_{10.2}$Sc$_{1.8}$O$_{19}$ is characterized by a spin spiral configuration
and no ME effect in the material has been measured. This is also applicable when Ba
replaced with Sr in order to induce a local strain. It appears that substitutions of TM ions in
either the S or T blocks together with the spin spiral and local strain settings are important
in being able to produce ME hexaferrites. This is indeed the case for Ba$_2$Fe$_{12}$Mg$_2$O$_{22}$,
SrFe$_8$Co$_2$Ti$_2$O$_{19}$, and Sr$_3$Fe$_{24}$Co$_2$O$_{41}$ [6-8]. It appears that the role of TM ion substitutions is to mitigate multi-block interactions in terms of spin interactions and strain effects and as a result inducing the ME effect in hexaferrites. Theoretically, there are no reports on the elastic and magnetic coupling between sites as related to TM substitutions and the ME effects reported.

**Figure 5.1:** Spin spiral configuration for different directions of $E$.

A spin spiral configuration alone is not sufficient to induce the ME effect in hexaferrites. For example, BaFe$_{10.2}$Sc$_{1.8}$O$_{19}$ is characterized by a spin spiral configuration and no ME effect in the material has been measured. This is also applicable when Ba replaced with Sr in order to induce a local strain. It appears that substitutions of TM ions in either the S or T blocks together with the spin spiral and local strain settings are important in being able to produce ME hexaferrites. This is indeed the case for Ba$_2$Fe$_{12}$Mg$_2$O$_{22}$,
SrFe$_8$Co$_2$Ti$_2$O$_{19}$, and Sr$_3$Fe$_{24}$Co$_2$O$_{41}$ [6-8]. It appears that the role of TM ion substitutions is to mitigate multi-block interactions in terms of spin interactions and strain effects and as a result inducing the ME effect in hexaferrites. Theoretically, there are no reports on the elastic and magnetic coupling between sites as related to TM substitutions and the ME effects reported. The ME effect in M-type or Z-type hexaferrites is due to the spiral spin configuration in which the application of electric field strains the material and modifies the physical structure of the spins in the spiral configuration and induces a change in magnetization. We referred to this phenomena as the “slinky helix” model [6].

The electric control of magnetic parameters has the potential for downsizing the microwave devices by eliminating the need for permanent magnets and reduce power consumption. The other advantage of ME ferrites is that at room temperature the saturation magnetization is substantial, ranging from 1000 to 3000 G. Other single phase ME materials characterized by the orthoferrite crystal structure exhibit relatively lower magnetization at room temperature. ME hexaferrites are reported to exhibit ME effect at low magnetic field and at room temperature. Examples are Z-type Sr$_3$Co$_2$Fe$_{24}$O$_{41}$ and M-type SrCo$_2$Ti$_2$Fe$_8$O$_{19}$ [1, 9]. These hexaferrites exhibit high ME coupling coefficient at room temperature which means that by applying an electric field or DC voltage there will be changes in magnetization. In a converse experiment, where changes in magnetization induced by DC voltage, bulk samples of these materials require relatively high voltage or electric field to exhibit considerable ME coupling due to their polycrystalline bulk structure. These hexaferrites are notoriously structurally complex and difficult to prepare.
If we are to impact modern technologies where size, efficiency, multi-functionality, compatibility and costs are important, we need to transition to thin film production.

Here for the first time, we report the ME effect at room temperature in thin film of SrCo$_2$Ti$_2$Fe$_8$O$_{19}$ deposited by laser ablation. Specifically, we measured changes in magnetization with the application of a DC voltage. Furthermore, the required voltage in order to observe the effect was substantially smaller than the voltage required using bulk materials. The structural and magnetic properties of these films were evaluated and the magnetoelectric properties were observed by converse measurements with the application of 1 V$_{dc}$. This is quite promising in terms of miniaturizing future magnetoelectric devices and integrating them in electronic and telecommunication applications while they have the advantage of low loss and high power handling compared to semiconductors.

5.2. SrCo$_2$Ti$_2$Fe$_8$O$_{19}$ Preparation and ME Effect

The M-type hexaferrite of SrCo$_2$Ti$_2$Fe$_8$O$_{19}$ was prepared by conventional ceramics processing. The high purity powders of SrCO$_3$, Fe$_2$O$_3$, Co$_2$O$_3$, and TiO$_2$ were mixed stoichiometrically by a planetary mill at 350 rpm for 4 h. The mixture was pressed at 1000 psi and sintered at 1,200°C for 10 hours in the oxygen atmosphere. The resulting puck was then crushed and grinded and mixed with polyvinyl alcohol (PVA) binder, pressed at 2000 psi, and sintered for second time in 1200°C for 10 h to obtain a high density target. The chemical compositions of the sample were verified by θ-2θ x-ray diffraction
(XRD), using a Cu Kα source, as it is shown in figure 5.2 and energy dispersive x-ray spectroscopy (EDXS) and it was determined to be single phase material.

![Figure 5.2: X-ray diffraction pattern of the polycrystalline SrCo$_2$Ti$_2$Fe$_8$O$_{19}$ at room temperature.](image)

In general, the linear magnetoelectric (ME) effect implies the following: the application of a magnetic field, $\mathbf{H}$, induces a change in electric polarization, $\mathbf{P}$, and the application of an electric field, $\mathbf{E}$, induces a change in magnetization, $\mathbf{M}$. The latter, which is used in our experiments is called the "indirect converse ME effect". To measure changes in remanence magnetization versus electric field a Vibrating Sample Magnetometer (VSM) instrument was used. A slab of SrCo$_2$Ti$_2$Fe$_8$O$_{19}$ was cut and polished to final dimensions of $1\text{mm} \times 1\text{mm} \times 1\text{mm}$ and a voltage from a power supply was applied across while the sample is in a magnetic field, the electric field was applied in parallel and also perpendicular to the magnetic field as it is shown in figure 5.3.
Figure 5.3: Static electric and magnetic fields bias conditions of the hexaferrite slab in (a) $E$ perpendicular to $M_r$ and in (b) $E$ parallel to $M_r$.

We observed the remanence magnetization (for $H=0$) was affected by voltage. The change in remanence magnetization was 4% and 3% with the application of an electric field of 12 kV/cm perpendicular and parallel to the magnetic field, respectively. In Figure 5.4, the percentage change in remanence versus the applied electric field is shown. Clearly, as it is shown in figure 5.5, changes in remanence magnetization scale with polarity changes of the electric field or applied voltage. Thus, heating effects will be eliminated as a source of the remanence magnetization changes since heating effects induce changes in remanence in one polarity sense only.
Figure 5.4: Static Polycrystalline SrCo$_2$Ti$_2$Fe$_8$O$_{19}$ slab remanent magnetization change vs electric field at room temperature with \( E \) parallel and perpendicular to \( M_r \).

![Graph showing remanent magnetization change vs electric field](image)

Figure 5.5: Static remanent magnetization change vs electric field at room temperature while \( E \) parallel to \( M_r \) with both - and + polarities.

![Graph showing remanent magnetization change vs electric field](image)

As it was shown in the slinky model in figure 5.1, the application of an electric field induces a change in the spin spiral configuration of the hexaferrite via electrostriction. This spin reconfiguration manifests itself as a change in the remanence magnetization \( M_r \).
and, therefore, as a change in the permeability. With the application of \( E \) the angle \( \theta \) or the angle of the spin within the cone is affected by the direction of \( E \). As the angle \( \theta \) is varied with \( E \), the size of the “slink” changes, as well as the “net” internal magnetization along \( E \) and, therefore, \( M_r \). From practical considerations this simplifies the design of ferrite devices and applications, since \( \mu \) is the principal quantity that governs the performance of a microwave ferrite device, for example. Hence there would be less need for permanent magnets in microwave device applications, since only \( E \) is applied.

5.3. Thin Film Growth

The target of \( \text{SrCo}_2\text{Ti}_2\text{Fe}_8\text{O}_{19} \) was prepared by conventional ceramics processing as it was described in previous section. \( \text{SrCo}_2\text{Ti}_2\text{Fe}_8\text{O}_{19} \) films were deposited on sapphire (0001) by pulsed laser deposition which is an effective epitaxial growth technique for the production of hexaferrite thin films. The base pressure in the deposition chamber was maintained at \( 8 \times 10^{-6} \) Torr and the substrates were heated to 600°C. The films were deposited in a high purity oxygen environment of 200 mTorr. A KrF excimer laser with a wavelength of 248 nm and energy of 400 mJ/pulse, was focused on the target surface. The distance between the target and the substrate was set to 4.8 cm and the repetition rate of the laser was gradually increased from 1 Hz to 10 Hz during deposition to improve the growth. After deposition, the films were cooled to room temperature in oxygen pressure of 200 mTorr. The deposition run was timed for 50 min and resulted in an amorphous film structure. After deposition, the films were annealed in oxygen atmosphere in a tube furnace at 1050°C for 40 minutes. The film thickness of 0.7 \( \mu \text{m} \) was measured by masking a small
part of the substrate during deposition and measured by a scanning surface profilometer. Leaving the films in the furnace during temperature ramping appeared to affect crystal structure due to diffusion at the film-substrate interface. To prevent this problem the films were rapidly inserted into the preheated furnace of 1050°C, annealed for 40 minutes and rapidly removed from the furnace. The thin films were evaluated by XRD and EDXS to determine the atomic weight of each element in the composition of SrCo$_2$Ti$_2$Fe$_8$O$_{19}$ thin films.

5.4. Structure and Magnetic Properties

The composition and structure of the ME SrCo$_2$Ti$_2$Fe$_8$O$_{19}$ films were determined by the 0-2θ X-ray diffractometer (XRD), using a Cu $K\alpha$ source and energy dispersive x-ray spectroscopy. The XRD patterns are illustrated in figure 5.6. Annealing has localized the ions in a single phase M-type hexaferrite. It shows that the film has a polycrystalline structure but has strong and sharp diffraction peaks at some (0 0 2$n$) [$n$=1,2,3,…].

![XRD pattern](image)

**Figure 5.6:** XRD pattern of the deposited SrCo$_2$Ti$_2$Fe$_8$O$_{19}$ thin film.
Surface morphology of these films was studied by scanning electron microscopy (SEM). Figures 5.7 and 5.8 show SEM image of the film. Annealing in air as resulted in incomplete and unknown grains and the crystal structure could not be formed as it is shown in figure 5.7, whereas oxygen presence helped the formation of crystalline structure in films. Figure 5.8(a) shows SEM of a film which was annealed in an oxygen atmosphere while the stage was tilted at 30° and Figure 5.8(b) shows a magnified image of the surface of the same film without tilting the stage. The hexagonal polycrystalline structures are clearly visible in the image which is consistent with XRD patterns. Clearly, annealing changed the crystal structure from an amorphous structure to a crystalline structure. Several experiments have been performed to determine the optimum parameters for annealing. The 40 min annealing time was observed to be the optimum interval. Annealing the films over 60 min interval decreased the film thickness and resulted in magnetic moment reduction, which was interpreted in terms of a diffusion effect.

Figure 5.7: SEM image of SrCo<sub>2</sub>Ti<sub>2</sub>Fe<sub>8</sub>O<sub>19</sub> thin film annealed in air.
Figure 5.8: SEM image of SrCo$_2$Ti$_2$Fe$_8$O$_{19}$ thin film annealed in flowing oxygen atmosphere.

The static magnetic properties of the films were studied by vibrating sample magnetometry (VSM) with the magnetic field applied perpendicular and parallel to the film plane. In figure 5.9, typical hysteresis loops of the films are shown. The coercive field for the cases that the external field applied parallel or perpendicular to the film plane was measured to be 20 Oe.
The ferromagnetic resonance (FMR) measurements were carried out by Varian (Electron Paramagnetic Resonance) EPR spectrometer (at 9.53 GHz), with the static magnetic field applied both parallel and perpendicular to the film plane. The resonance condition in each configuration is given by

\[ f' = \gamma' \sqrt{(H_{||} + 4\pi M_s)(H_{||})} \]  

(5.1)

\[ f = \gamma' (H_{\perp} - 4\pi M_s) \]  

(5.2)

Where \( H_{||,\perp} \) is the external applied magnetic field parallel (\( || \)) and perpendicular (\( \perp \)) to the film plane, \( 4\pi M_s \) is the saturation magnetization, \( \gamma' \) is the gyromagnetic ratio (\( \gamma \)) over 2\( \pi \), and \( f \) is the FMR frequency [10]. We ignored \( H_d \), the uniaxial magnetic anisotropy field, since the film was characterized to be polycrystalline. Typical FMR plot is shown in figure 5.10 for external field in the film plane. From Eqs. (5.1) and (5.2), the g-factor was calculated to be 2.66 and \( 4\pi M_s = 1250 \text{ G} \), which is consistent with the VSM measurements.

**Figure 5.9:** VSM hysteresis loop of SrCo2Ti2Fe8O19 thin film.
The FMR linewidth was measured to be 1000 Oe which is rather broad due to inhomogeneous magnetic distribution of the polycrystalline sample.

Figure 5.10: Main FMR line of SrCo2Ti2Fe8O19 thin film.

5.5. Magnetoelectric Measurements

We performed the ME measurements by measuring the changes in magnetization with the application of a DC voltage and it shows that the required voltage in order to observe the effect was substantially smaller than voltage required for bulk materials with same composition. In figure 5.11, the magnetization is plotted as a function of magnetic field for two different electric fields at room temperature. Change in remanence magnetization was measured to be 12.8% by applying 1 V_{dc}. The change in remanence magnetization under various electric field values are shown in figure 5.12.
The deduced ME coupling coefficient, $\alpha$, for SrCo$_2$Ti$_2$Fe$_8$O$_{19}$ thin film was $6.07 \times 10^{-9}$ sm$^{-1}$. This results show that the ME effect is stronger in SrCo$_2$Ti$_2$Fe$_8$O$_{19}$ thin films than it is in bulk form. The induced change in magnetization in bulk polycrystalline materials by the application of DC voltage or electric field is the result of averaging the change in magnetization components along the direction of the electric field in each crystallite. Thus, the resultant averaging is much less than the full effect as observed in a single crystal for example, where $\alpha$ was measured to be $2.32 \times 10^{-6}$ sm$^{-1}$ for single crystal of Z-type hexaferrites [11-13]. The fact that the measurements for $\alpha$ in the films reported here was higher than bulk polycrystalline samples imply that the deposited film quality was much improved compared to bulk materials, simulating nearly single crystal results, which was also confirmed by XRD measurements.

**Figure 5.11:** Magnetization as a function of magnetic field for two different electric fields at room temperature.
Figure 5.12: The change rate of remanence magnetization versus applied electric field, where $\Delta M_r(E) = M_r(E) - M_r(0)$.

Two different capacitive device configurations for testing the ME characteristics were employed (i) in plane and (ii) out-of plane applied electric field to the thin films. The out-of plane geometry as it is shown in figure 5.13(a,c) is described earlier in this chapter. In the in plane geometry, figure 5.13(b), four conductive stripes of silver paint were patterned on the surface of the ME film as electrodes. They were connected to a resistor bank voltage divider. The change rate of remanence magnetization versus applied voltage (from power supply) is shown in figure 5.13(d). Projected ME effects from the measurements on in plane configuration shows that it is feasible to obtain operational voltages as small as few hundred of millivolts if more microstrips be patterned by optical lithography.
Figure 5.13: Thin film and electrodes configuration (a) out-of plane geometry and (b) in plane geometry. (c) and (d) The change in magnetization versus the applied voltage/electric field.

5.6. Conductive Oxide Buffer Layer

We grew and characterized thin ME SrCo$_2$Ti$_2$Fe$_8$O$_{19}$ hexaferrite films on conductive buffer layers on a sapphire substrates. Noble metals are not suitable candidates for growing high quality single phase hexaferrite films due to mismatch in crystalline structures. In addition annealing at 1050°C will cause the metals to peal off from the sapphire substrate resulting in loss of conductive buffer layer access. A buffer conductive layer should have lattice constants commensurate with the lattice constant of the ME film.
and substrate. With sapphire being the substrate very thin conductive oxides such as In$_2$O$_3$/SnO$_2$ (ITO) or ZnO/Al$_2$O$_3$, would serve as good candidates since they also can be stable and conductive at high temperatures during annealing. We deposited a 200 nm ITO buffer layer film. The ITO/ SrCo$_2$Ti$_2$Fe$_8$O$_{19}$ multilayer structure is deposited on a sapphire (0001) substrate using a KrF eximer laser with a wavelength of 248 nm, energy of 400 mJ/pulse and 10 Hz repetition rate. During ITO deposition the substrate was heated up to 400°C in an oxygen atmosphere with pressure of 10 mT for 5 min, which resulted in 200 nm thickness of ITO layer and immediately after that the substrate temperature was raised to 600°C in 200 mTorr of oxygen pressure and the laser was set to impinge on SCTFO target for 50 min which resulted in an amorphous film structure. After deposition, the films were annealed in oxygen atmosphere in a tube furnace at 1050°C for 40 min. The ferrite film thickness was measured to be 0.7 µm. These thin films were characterized by vibrating sample magnetometer (VSM), ferromagnetic resonance (FMR), X-ray diffractometer (XRD), scanning electron microscope (SEM) and energy-dispersive spectroscopy (EDS). The characterization measurements were in agreement with the results of ME film on sapphire substrate without buffer layer. The SEM image of the film is shown in the figure 5.14. In order to achieve a single crystalline ME thin film growth by epitaxial method, there needs to be lattice matching between the conductive buffer layer and the ME film that is grown. ZnO(Al$_2$O$_3$) with 6.48 Å lattice constant is close to that of the M-type hexaferrite thin film and sapphire substrate. This may be useful in future works. The thickness of conductive oxide buffer layer would be
kept below 300 nm to avoid the relaxation of its crystalline structure which in turn would affect the quality of the ME film. The magnetoelectric measurements were performed by measuring the changes in magnetization with the application of a DC voltage across the film (out-of plane configuration) as it is shown in figure 5.15(a), and it shows that the required voltage in order to observe the effect was enormously smaller than voltage required for the ME thin film without the buffer layer. In figure 5.15(b), change in remanence magnetization is plotted as a function of electric field and also voltage. Change in remanence magnetization was measured to be 14.2% by applying 2.5 $V_{dc}$ which is significantly less than the voltage needed across the whole structure including the substrate (1200V).

![Figure 5.14: SEM image of SrCo$_2$Ti$_2$Fe$_8$O$_{19}$ thin film deposited on ITO buffer layer.](image)
5.7. Conclusions

Thin films of magnetoelectric hexaferrite material, SrCo$_2$Ti$_2$Fe$_8$O$_{19}$, were deposited and characterized and showed that the ME effect was substantial in the films even at room temperature with ME coupling coefficient ($\alpha$) of $6.07 \times 10^{-9}$ sm$^{-1}$. The measurements imply a stronger ME effect in SrCo$_2$Ti$_2$Fe$_8$O$_{19}$ films compared to the bulk materials of the
same composition, due to the improved quality of the films. We observed 12.8% changes in remanence magnetization by applying few DC voltages across the film. We also performed two different configurations for ME measurements: (i) in plane and (ii) out-of-plane applied electric field to the thin films. The in-plane configuration with increased number of microstrips can provide bigger electric fields along the film surface and, consequently, show bigger changes in remanence magnetization versus electric field. We also employed a conductive ITO buffer layer which could eliminate the need for high voltage power supply and we perform experiments at significantly lower voltages. Clearly, the small thickness of ME ferrite makes it possible to observe ME effects by applying even much lower voltages. This achievement is promising in future ME based sensors and microwave devices.
References:

Chapter 6. Permeability Measurements of ME Thin Films

6.1. Introduction

Magnetic thin films can be widely used in various applications such as microwave communication devices [1], magnetic field sensors [2] and etc. Different applications require magnetic thin films with different properties, and the complex permeability $\mu_r = \mu'_r - j\mu''_r$ spectrum of a magnetic thin film is among the most important factors determining the suitability of a magnetic thin film for an application and the performances of the devices made from the magnetic thin film [3]. For example, Low value of $\mu'_r$ and high value of $\mu''_r$ are requested for integrated electromagnetic noise countermeasure [4]. Therefore, it is desirable to measure the complex permeability of magnetic thin films at microwave frequencies. There have been many reports on broadband complex permeability characterization of magnetic thin films up to GHz frequency range. The developed methods are generally classified into two types: pick-up coil and transmission-line methods [5].

6.2. Pick-up Coil Method

In a pick-up coil method which is similar to a transformer, the fixture generally consists of two parts: a driving coil and a pick-up coil. The magnetic thin film sample is placed in the pick-up coil, the presence of the magnetic thin film changes the coupling between the driving coil and the pick-up coil which is eventually used to calculate the
permeability of the thin film. In 1975, Calcagno and Thompson proposed a semiautomatic permeance tester for magnetic films with uniaxial anisotropy in 1-100 MHz frequency range using a “figure-8” coil which was based on the flux change in the sample due to an applied drive field [6]. Since the figure-8 coil type permeameter limits the measurable frequency range below 300 MHz [7], many efforts have been made in order to increase the measurement frequency ranges. For example, Grimes [8] and Yamaguchi [9] modified the designed “figure-8” coil in Ref. 6 and increased the measurement frequency up to 500 MHz and 1 GHz, respectively. Others designed and tested fixtures such as microstrip loop coil and shielded loop coil [7].

**Figure 6.1:** Structures of a microstrip pick-up coil (a) and a shielded loop coil (b). [7]

These two types of pickup coils can extend the frequency range up to a few GHz. As it is shown in figure 6.1, microstrip loop coil has a simple structure and can be easily fabricated, but the electric field around the coil may affect the result. A shielded loop coil structure is more complicated but it is not sensitive to the electric field around the coil and the obtained results can be more accurate. The driving coils often used in permeance
meters can be generally classified into three types: Helmholtz, traveling-wave and standing-wave types [3]. A Helmholtz type driving coil can provide strong and uniform magnetic field, but the working frequency is usually lower than 100 MHz. The other two types of driving coils are based on microwave transmission lines. Usually, a traveling-wave type or standing-wave type driving coil can work up to higher frequency than a Helmholtz type driving coil. However, in their designs the higher order modes that may appear in the transmission line have to be avoided. By combining various types of driving coils and pick-up coils, several kinds of pick-up coil methods can be developed to meet various measurement requirements.

6.3. Transmission-line Method

In a transmission-line perturbation method, the magnetic thin film under measurement is inserted into a segment of a transmission line, so the characteristic parameters of the transmission line are changed. From the changes in the transmission line characteristic parameters, the complex permeability of the thin film can be obtained. In this method, the propagation mode in the transmission line should not change with the insertion of the sample. Two types of transmission lines are often used in transmission-line perturbation methods for characterizing magnetic thin films: coaxial line and planar transmission line.
6.3.1. Coaxial Line

In conventional two port design coaxial line the constitutive parameters can be calculated as follow [10].

\[ \Gamma_L = -\frac{1}{2S_{11}}(1 - S_{21}^2 + S_{11}^2) + \frac{1}{2} \sqrt{\frac{1}{S_{11}^2}(1 + S_{11}^2 - S_{21}^2)^2 - 4} \]  

(6.1)

\[ \mu = \mu' + j\mu'' = \frac{1}{j\omega} \frac{2\pi}{\ln\left(\frac{a}{b}\right)} \frac{Z_0}{t} \left(1 + \Gamma_L\right) \ln\left(1 + S_{11}\Gamma_L\right) \]  

(6.2)

\[ \varepsilon = \varepsilon' + j\varepsilon'' = \frac{1}{j\omega} \frac{2\pi}{\ln\left(\frac{a}{b}\right)} \frac{1}{Z_0 t} \left(1 + \Gamma_L\right) \ln\left(1 + S_{11}\Gamma_L\right) \]  

(6.3)

where b and a are the outer and inner diameters of the coaxial line, respectively.

The advantage of this method is that the S-parameters can be collected by the network analyzer at one time in comparison with the one port measurement which is done in two steps. And the phase adjustment can be performed by providing the sample thickness and its distance from port 1. However, for magnetoelectric measurements where high DC voltage is introduced, it might be very complicated to apply external DC voltage to do the
same measurement. If a very thin wire is put in the coaxial line, see Figure 6.2(b), such that the thickness is very small in comparison with the skin depth it results in antenna radiation and so the results may not be accurate. Therefore, recently we developed a one port coaxial line, as it is shown in figure 6.3 and 6.4, which can be used in measuring the permeability of magnetoelectric ferrite materials [12].

**Figure 6.3:** One port coaxial line schematic (a) side view, (b) top view with the ME sample in and coated by silver paint, and (c) top view without the ME sample.

**Figure 6.4:** Disassembled (top) and assembled (bottom) designed coaxial line.
\[ jZ\tan(kt) = Z_0 \left( \frac{1 + S_{11}^s}{1 - S_{11}^s} \right) \] (6.4)

Here \( Z = \sqrt{\mu/\varepsilon} \), \( k = \omega\sqrt{\mu\varepsilon} \) and \( S_{11}^s \) is the reflection coefficient for the shorted port of the coaxial transmission line, \( Z \) is the coaxial line characteristic impedance of the sample, \( k \) is the propagation constant and is equal to \( 2\pi/\lambda \), and \( Z_0 \) is characteristic impedance of the coaxial line which is 50. The permeability may then be determined from:

\[ \mu \approx Z_0 \left( \frac{1}{j\omega t} \right) \left( \frac{1 + S_{11}^s}{1 - S_{11}^s} \right) \] (6.5)

\[ \varepsilon \approx \frac{1}{Z_0} \left( \frac{1}{j\omega t} \right) \left( \frac{1 - S_{11}^o}{1 + S_{11}^o} \right) \] (6.6)

\( S_{11}^o \) is the reflection coefficient for the open port of the coaxial transmission line.

In this experiment a toroidal shaped sample was inserted in a coaxial line. One side of the toroid was shorted to the coaxial line termination as well as to the DC ground voltage. The other side of the toroid was coated with a thin film of silver paint and then connected to a high DC voltage power supply, shown in Figure 6.3. Figure 6.5 shows the permeability measurement of a bulk ME sample of hexaferrite Z-type, \( \text{Sr}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41} \).
The explained method is applicable for bulk materials and has been tested for bulk hexaferrite Z-type, Sr₃Co₂Fe₂₄O₄₁ [11]. The coaxial line method can cover a wide frequency range. For a 7-mm coaxial line, it can cover a frequency range up to 18 GHz, and it may be suitable for thin films on flexible substrates. However, it is not suitable for thin films fabricated on rigid dielectric substrates or thin films which are sensitive to mechanical stresses even if flexible substrates are used.

6.3.2. Planar Transmission Line

Magnetic thin films deposited on either rigid or flexible substrates can be characterized using planar transmission line perturbation method. In this method, the magnetic thin film is inserted into part of planar transmission line and consequently changes the boundary conditions and characteristic parameters of the transmission line. These changes will be used in characterization of magnetic thin film.
There are two approaches of using planar transmission lines for the characterization of magnetic thin films: the transmission and reflection approaches [3]. Figure 6.7 shows these two different structures.

The presence of the magnetic thin film changes both the reflection coefficient $S_{11}$ and the transmission coefficient $S_{21}$. Therefore, by measuring $S_{11}$ and $S_{21}$ the permittivity and permeability of the thin film can be obtained. In the reflection approach shown in Figure 6.7 (b), the transmission line is short circuited, and the magnetic thin film is placed at a position close to the shorted end of the transmission line where magnetic field dominates. Several models have been proposed to analyze the reflection approach, such as equivalent...
RLC circuit, transmission line and effective parameter. In the equivalent RLC circuit
model and the transmission-line model the magnetic thin film permeability is obtained
from the change of the characteristic impedance (ΔZ) and in the effective parameter the
effective permeability (Δμ_{eff}) is used to find the permeability of the thin film. The two
approaches generally agree with each other and do not require complicated data
processing [3].

6.4. Microstrip Line Fixture

The shorted microstrip technique has been used by many groups to measure the
permeability. In addition, it is easy to fabricate. Therefore, we have used a shorted
microstrip setup to measure the permeability of the magnetic thin film. The fixture that
we designed and fabricated is shown in figure 6.8, 6.9 and 6.10.

![Figure 6.8: The picture of the shorted microstrip fixture.](image)
The fixture is made of Brass. One end of the fixture is shorted to the ground and the other end is connected to the pin launcher of a sub-miniature assembly (SMA) coaxial connector. Both ends of this fixture are movable so the gap between the upper line and ground plate can be adjusted, as it is shown in figure 6.10. In addition, slabs with different widths can be used along with the desired height to meet the different design requirements. The thin film is inserted in the middle of this gap. For the magnetoelectric SrCo$_2$Ti$_2$Fe$_8$O$_{19}$ thin film sample which is deposited on 0.43 mm sapphire substrate we set the gap to 0.9 mm and the length of the upper line to be 15 mm.
6.5. Characterization of Magnetolectric Thin Film

Using the described shorted microstrip line fixture, the following procedure has been performed in order to measure the complex permeability of magnetolectric thin film. The fixture is located between the poles of an electromagnet and connected to the network analyzer (HP 8510, 45 MHz - 40 GHz). One port calibration of the network analyzer with the necessary cable was performed with open, short, and load standards. Measurement of the reflection coefficient $|S_{11}|$ of the fixture with and without thin film sample was performed. An external magnetic field parallel to the thin film was applied incrementally. The data of the changes in $S_{11}$ versus applied H field was collected and converted to frequency domain.

The resonance condition of this magnetolectric thin film is given by:

$$f = \gamma' \sqrt{H_{||} + 4\pi M_s} (H_{||})$$

(6.7)

where $H_{||}$ is the external applied magnetic field parallel $||$ to the film plane, $4\pi M_s$ is the saturation magnetization, $\gamma'$ is the gyromagnetic ratio over $2\pi$, and $f$ is the FMR frequency. We ignored $H_A$, the uniaxial magnetic anisotropy field, since the film was characterized to be polycrystalline. By equation 6.7 the data of $|S_{11}|$ variation in frequency domain was obtained.

$$\chi'' \propto |S_{11}|^2 - |S_{11}^*|^2$$

(6.8)

where $S_{11}^*$ refers to measurement without the sample inside the cavity.

Once $\chi''$ was determine, Krammers- Kronig equations were applied to obtain $\chi'$. 

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\[ \chi'(\omega_0) = -\frac{2}{\pi} \int_0^\infty \frac{\omega \chi''(\omega) d\omega}{\omega^2 - \omega_0^2} \] 

(6.9)

By the method described above, the relative permeability spectra of a magnetoelectric SrCo\(_2\)Ti\(_2\)Fe\(_8\)O\(_{19}\) thin film was measured and plotted as it is shown in figure 6.11. This technique makes it simple to obtain permeability of a magnetic thin film without the need of complicated calculations for equivalent RLC circuit, for example.

Figure 6.11: Permeability spectrum of the magnetic thin film.
References:


Chapter 7. Conclusions and Future Work

Advances in ferrite materials have led to many innovative technological changes serving societal needs dating back to 2700 BC with the discovery of the compass. These times are no different. Ferrites are being used in medical instrumentations, computer IC circuits, fluxgate sensors, wireless communication instrumentations, telecommunications technology, etc. however, the burden on the use of ferrites has always been the requirement of a bias magnetic field in whatever application. In this dissertation we demonstrated the approach to eliminate the bias field entirely. In fact, if we are to impact modern technologies where size, efficiency, multi-functionality, compatibility and costs are important, we need to develop a plan to establish a knowledge basis on ME hexaferrites by which a new generation of high quality thin film production of ME hexaferrites may be possible. In this regard, successful achievements in this dissertation which are also published in peer reviewed journals are:

1) M- and Y-type hexaferrite thin film deposition in atomic scale by ATLAD [1,2].

2) Magnetoelectric M-type hexaferrite thin film deposition [3].

3) Magnetoelectric effect studies on bulk M-type and Z-type hexaferrites [4-6].

4) Multilayer deposition of ME thin films (ITO/ ME ferrite).

5) Permeability measurement of ME thin film using a microstrip [7].

6) In addition, preliminary results of a voltage tunable magnetoelectric thin film inductor will be presented in this chapter.
Future research plan and work can be: (1) to deposit high quality films of ME hexaferrites (M-, Y- and Z-type) in order to advance the science of hexaferrite films. (2) to study mechanical, electrical and magnetic properties of the films will be compared with theory. (3) to develop the theory to understand the physics of the ME effects in hexaferrites films. (4) to launch a new class or family of ME hexaferrite films whereby ionic substitutions in each spinel blocks of the hexaferrites are controlled atomically by ATLAD technique for the purpose of enhancing the knowledge base of these materials. These novel films cannot be reproduced by “natural” processes derived from bulk growth or from deposition from single targets. (5) to develop new generation of microwave devices which will impact following applications:

1. Biasing of ferrite materials via DC voltages!
2. Electrical compatibility with semiconductor IC circuitry.
3. Non-volatile memory

Ferrite materials have been traditionally being used for non-volatile memory applications as in computer memories.
4. Sensors

Voltage detection of magnetization changes or fields imply simple sensor devices
5. Four-state logic devices
6. Antennas, phasishifters, filters, modulators, powerlimiters and tuners.

The fact that both the permittivity and permeability can be tuned by magnetic and electric fields variations imply a range of microwave linear devices.
7. Electronic devices-amplifiers, mixers

At high electromagnetic power the ME effect in hexaferrite materials may be non-linear giving rise to non-linear device applications (mixers).

8. Negative index materials

9. Inductors, IC computer circuits, micro-electronic circuits, etc.

The fact that the permeability can be changed with the application of DC voltage implies that many IC circuits for wireless communication frequencies may now utilize tunable inductors.

10. Medical applications

We believe that this research will have a broad impact to the scientific community at large and technologies.

7.1. Voltage Tunable Magnetoelectric Thin Film Inductor

Inductors are one of the fundamental components in circuits. However, the tunable inductors are magnetically tuned by external permanent magnets which have huge size. Magnetoelectric thin films are good candidates for tunable inductors since it possible to tune their magnetic properties by electric field with low power consumption. Hence, we demonstrate a voltage tunable magnetoelectric thin film inductor consisting of SrCo$_2$Ti$_2$Fe$_5$O$_{19}$ magnetoelectric M-type hexaferrite thin film core. Two structures were fabricated: coil wrapped around the core and coil on the surface of the thin film. As it is shown in figure 7.1. The DC voltage is applied across the hexaferrite film in order to
induce tunable inductance. Changes of 1.2% were measured in inductance using voltages as low as 16 volts, figure 7.2. Potential applications include an electric field sensor when utilized in a simple LC resonator circuit analogous to sensors built from piezoelectric/magnetostrictive acoustic resonance sensors.

**Figure 7.1:** Schematic of inductor structure with ME thin film as the coil. (a) the coil is wrapped around and (b) the coil is on the surface of the film.

**Figure 7.2:** The change in inductance versus the applied voltage across the film.
References:


