Summary and Conclusions

In recent years, the magnetodielectric materials have been attracting attention of microwave researchers for their possible use in miniaturized circuits as well as in radar absorbing materials as it exhibit both magnetic as well as dielectric properties at the same time. Several classes of natural materials exhibit only magnetic or dielectric properties. Ferrites are the class of materials which exhibits permanent magnetization as well as good dielectric properties. M type hexaferrites are the materials with electromagnetic conductivity, significantly high permittivity and permeability suitable for electromagnetic interference suppression and radar absorbing material coatings from centimeter to sub millimeter wavelengths of the electromagnetic spectrum. The technological application of these ferrites at high frequencies needs pure material in planar form. Thick film technology is of interest because it has been proved to be cost effective and highly conducive to planarization, and also meets the requirements of high reproducibility, flexibility and compatibility.

The composite of magnetic phases and dielectric phases have been used in order to achieve magnetodielectric properties but impedance mismatch between the boundaries of two different phases takes place which results in increase in reflection. To avoid this ambiguity in the internal impedance, a material such as hexaferrite which itself exhibit both high permittivity and permeability needs to be synthesized. Different synthesis techniques are available for the preparation of hexaferrites powder.

In the present work, nanosized, granular M type barium hexaferrite and strontium hexaferrite powders were synthesized by chemical coprecipitation technique at different synthesis conditions. For planarization, thick films of barium hexaferrite and strontium hexaferrite were formulated on alumina substrate by screen printing technique. The structural properties of both hexaferrites bulk and thick films were studied by X ray diffraction, Fourier transform Infrared absorption, Fourier transform Raman absorption
and scanning electron microscopy. The electrical properties such as dc resistivity, AC dielectric properties were studied. DC magnetic properties like saturation magnetization, coercivity, remanence, magnetocrystalline anisotropy of hexaferrites bulk and thick films were measured from hysteresis curve. To study the possible use of hexaferrites bulk and thick films as magnetodielectric material in microwave 8-18 GHz frequencies, their intrinsic properties such as conductivity, complex permittivity and complex permeability by different microwave measurement techniques were investigated. The transmittance and absorbance of hexaferrites was measured by waveguide reflectometer technique and complex permittivity by voltage standing wave ratio technique. The complex permeability was calculated by reflectance obtained by waveguide method and using values of complex permittivity obtained by VSWR method. The microwave properties of hexaferrites were also measured by in touch overlay on microstrip components technique. For this purpose four different types of Ag thick film microstrip circuits were used. The Ag thick film microstrip components studied were microstripline, microstrip straight (or line) resonator, annular ring antenna and electromagnetically coupled microstrip patch antenna. For the first time the permeability of thick film hexaferrite has been reported using overlay on Ag thick film microstrip component. Though the present work emphasize on studies of thick film barium hexaferrite and strontium hexaferrite, for the formulation of hexaferrite thick films paste, the hexaferrite powder has to be synthesized and characterized, hence, characterization and microwave studies of bulk hexaferrites was also done.

The subject matter of the thesis is presented in five chapters. Chapter-I, “Introduction” deals with the brief introduction of magnetodielectric materials and their need in microwaves for electromagnetic interference suppression for radar absorbing material coatings and hexaferrites being exhibiting significant $\varepsilon^*$ and $\mu^*$, a possible candidate for magnetodielectric materials. Various aspects of hexaferrites such as types of hexaferrites,
crystal structure, electrical properties, magnetic properties, synthesis techniques are discussed in chapter-I. The advantages of coprecipitation method over other methods have been mentioned. Being simple, cost effective and environment friendly, coprecipitation technique was used for the synthesis of hexaferrite powder. Distribution of metal ions and oxygen in the M type hexagonal crystal system have been elaborated in chapter-I. The theory of magnetism and magnetization process in ferrites by applying external dc magnetic field has been illustrated. The electrical polarization and dielectric behavior of ferrites have been discussed. The measurement techniques for microwave properties as resonant, non resonant and overlay techniques have been discussed. The brief information on MIC’s, synthesis techniques especially thick film technology for their fabrication and microstrip circuits used for the present study have been discussed in brief. The relevant literature survey for magnetodielectric materials, synthesis techniques of hexaferrites, electrical and magnetic properties and microwave properties of hexaferrites are also included in it.

The methods used for the synthesis of barium and strontium hexaferrite powder, formulation of thick films, structural characterization and microwave properties measurement are discussed in chapter-II. The advantages of coprecipitation techniques are:

1. Co-precipitation technique is an easy, cost effective, simple and environment friendly method.
2. This method requires low sintering temperature and it provides particle size control through various synthesis parameters since, this method enables the synthesis on a molecular level.

The theory of co-precipitation is included in this chapter which includes nucleation and crystal growth. Barium hexaferrite was synthesized using chloride precursors for two different Fe/Ba molar ratios 11:1 and 14:1 whereas strontium hexaferrite was synthesized for only 11:1 Fe/Sr molar ratio since; the results of dc magnetic properties of barium hexaferrite thick
films of 14:1 Fe/Ba ratio were not satisfactory. The hexaferrites were synthesized for pH11, pH12 and pH13 during precipitate formation. The sintered powder was pelletized into 1 cm and 2.3 cm diameter and 0.15 cm thickness. The pellets were sintered at 750ºC, 850ºC and 950ºC. Thick film hexaferrites were fabricated by screen printing technique using sintered powders for thicknesses 15µm, 30µm and 48µm. The detailed screen printing technique was elaborated. The crystal structure of hexaferrite powder and thick films were studied by X ray diffraction Cu-Kα and Cr-Kα radiations (Philips diffractometer PW 3710). The powder synthesized was mixed with KBr, pelletized and FTIR spectra were recorded using Perkin Elmer-USA FTIR spectrometer. FTRaman spectra of hexaferrites were studied for vibrational modes present in the material using MutiRAM Vortex 270. The surface morphology of the hexaferrite in both bulk and thick film forms was studied by scanning electron microscope Model JEOL-JSM 6360 and JEOL-JSM-7001F FESEM. The saturation magnetization, coercivity and remanent magnetization of hexaferrite powder and thick films were measured from hysteresis curves obtained by vibrating sample magnetometer (VSM Lakeshore 7307). The hysteresis measurement of typical powder and thick film samples was studied with maximum field strength of 12K Gauss at room temperature. DC electrical properties such as resistivity, activation energy and Curie temperature of hexaferrite bulk and thick films were studied by two probe method. AC capacitance, dissipation factor and resistance as a function of frequency (from 20 Hz to 1 MHz) were studied using precision LCR Meter Bridge (model HP 4284 A). AC Dielectric constant was calculated from capacitance. The AC conductivity was calculated using room-temperature dielectric data. The microwave properties such as transmittance, reflectance and absorbance of barium hexaferrite and strontium hexaferrite bulk and thick films were measured by waveguide reflectometer technique; VSWR slotted section method and overlay technique.
Chapter-III, “Results and discussions of structural and electrical properties of hexaferrite” deals with the results of structural properties, DC and AC electrical properties and DC magnetic properties of barium and strontium hexaferrite bulk and thick films. XRD pattern of hexaferrite reveals the formation of polycrystalline magnetoplumbite structure with preferred texture along (114) and (107). Nanocrystalline hexagonal crystals of size lies between 23.14nm to 45.41nm were formed for both barium hexaferrite and strontium hexaferrites. Comparatively higher crystallite size was obtained for barium hexaferrite than strontium hexaferrite but the crystallite size obtained for both hexaferrites from Debye Scherer’s formula was much smaller than the values reported. Thick films show higher crystallite size than that of bulk which is a double sintering effect. Standard JCPDS data (84-0757) and JCPDS (84-1531) were used for indexing XRD pattern. The FTIR spectra of barium and strontium hexaferrite powders show three signature absorption peaks of hexaferrite at ~ 436 cm\(^{-1}\), 546cm\(^{-1}\) and 584cm\(^{-1}\). The FTRaman spectra reveal the vibrational modes of Fe-O bonding. The SEM image of sintered hexaferrites bulk shows various shaped grains as hexagonal plates, nanorods and nano-needles of size lying between ~50 nm to 150nm. Nanorod and nanoneedle like morphology of 11:1pH11(750), 11:1pH11(950) and 14:1pH11 BaM was obtained but the growth of nanorods and needles are not over the whole surface. For other synthesis conditions, such type of morphology was not obtained. Thick films of barium as well as strontium hexaferrite show slightly larger hexagonal platelet like grains. Synthesis conditions dependant variations in surface morphology was obtained. Increase in grain size for increase in Fe/Ba molar ratio, pptR pH was obtained. The electrical resistance of hexaferrite pellets decreased from \(10^{10}\) to \(10^{7}\) ohms with increase in temperature due to hopping of electrons. Strontium hexaferrite bulk exhibits higher resistance than barium hexaferrite bulk. Thick film hexaferrites show higher resistance as compared to bulk and decreased from \(10^{12}\) to \(10^{9}\) ohms. The activation
energy of these hexaferrites calculated by Nernst Einstein relation lies in 7.13-12.1 ×10\(^{-5}\) eV. Barium hexaferrite show much higher initial permittivity than that of strontium hexaferrite. The decrease in dielectric constant with frequency reveals normal ferrite dielectric behavior. The 11:1 barium hexaferrite show higher magnetization than that of 14:1. Strontium hexaferrite powder show higher magnetization than barium hexaferrite. The remanent magnetic field in bulk hexaferrite was ~60% of their saturation magnetization.

Chapter-IV, “Microwave properties of hexaferrites: Results and discussions” deals with results and discussions of the microwave properties such as transmittance, absorbance, complex permittivity and complex permeability of barium and strontium hexaferrite bulk and thick films. Low transmittance and high absorbance was observed due to hexaferrite thick films than that of bulk. In X band ~ 85% whereas in Ku band ~90% absorbance was obtained by barium hexaferrite thick films (of 14:1pH11 and 11:1pH12) and strontium hexaferrite thick films (of pH11(15µm) and pH11(30µm)) respectively. Also a high ~93% and ~90% absorption was obtained by bulk strontium hexaferrite of pH11 (sintered at 750ºC and 950ºC) and pH12 respectively. Complex permittivity of hexaferrites measured by VSWR technique shows dielectric as well as magnetic resonance at 9 GHz by barium hexaferrite bulk. The permittivity of barium hexaferrite bulk measured by VSWR technique was ~17.07 and permittivity loss lies ~0.79. Multiple dispersions in complex permittivity and permeability of barium hexaferrite thick films were obtained in 9.5 to 10.5 GHz where, absorption also shows dispersive behavior. The permittivity of barium hexaferrite thick film was ~17.81 and loss was ~2.16. Strontium hexaferrite thick films show resonance behavior at 9.3 GHz and 14.5 GHz.

The transmittance of microstripline was decreased by ~30% due to both hexaferrites bulk and thick films as fringing fields of microstripline were absorbed upto ~40% by them which revealed the highly absorbing
behavior of hexaferrites synthesized. The effective permittivity and permeability was calculated by microstripline overlay. The obtained effective values of permittivity and permeability shows good agreement with the measured transmittance and absorbance properties of microstripline overlaid with hexaferrites.

The overlay of Hexaferrites does not show any further shift than alumina overlay over direct fed microstrip circuits such as straight resonator and ring antenna since, coupling of electric field takes place in these circuits therefore permittivity of the overlaid material plays an important role in this case. As permittivity of the hexaferrites are nearer to alumina, the effective permittivity due to overlay of either alumina or hexaferrite are almost same and hence, the shift in frequency due to overlay of hexaferrite in both bulk and thick film form show no further shift in resonant frequency than due to alumina overlay.

The resonance of electromagnetically coupled microstrip patch antenna was shifted due to hexaferrites overlay. The shift in resonant frequency of EMC patch antenna was dependant on the synthesis conditions of overlaid hexaferrites. Hexaferrites provide frequency agility to the EMC patch antenna by overlay technique. Power output of the EMC patch antenna was enhanced by 60% due to barium hexaferrite bulk overlay except 11:1pH13 pellets whereas by SrM pH13(950) pellet overlay it was enhanced by 20%. Due to barium hexaferrite thick films overlay multiple peaks were introduced which makes the antenna usable at multiple resonance frequencies but at the same time, power output of EMC patch antenna was decreased whereas due to strontium hexaferrite thick films overlay power output was enhanced by 60%.

The permittivity and permeability of hexaferrites was calculated from the shift in resonance. The real permittivity of barium hexaferrite bulk lies in 7.77 to 10.77 and permittivity loss lies in 1.348 to 2.61 whereas permittivity of BaM thick films lies in 10.2 to 13.64 and permittivity loss lies in 4.08 to
Higher values of permeability were obtained by overlay technique. The permeability of barium hexaferrite bulk lies in 5.99 to 8.128 and permeability loss lies in 0.17 to 2.615 whereas that of thick film BaM in 7.25 to 9.50 and permeability loss lies in 0.05 to 0.30. The permeability of strontium hexaferrite bulk lies in 6.021 to 8.695 and loss lies in 0.18 to 0.359 and that of thick film lies in 28 to 2.39 and that of thick films lies in 0.31 to 3.25. As the complex permittivity and permeability values by overlay technique were obtained from the perturbation in frequency, least mechanical errors were introduced and more accurate values were obtained by this method. The aim of impedance matching was partially fulfilled as the impedance matching degree reached up to 77% considering ε* and µ* measured by overlay technique.

The comparative study of permittivity of hexaferrite thick films measured by VSWR, overlay technique and theoretical (mixed oxide method) revealed that the permittivity obtained by overlay technique and theoretical mixed oxide method show similar behavior and the values agrees quite well. The permittivity obtained by VSWR technique shows quite higher values as compared to theoretical permittivity of barium hexaferrite thick film on alumina. The complex permittivity of barium and strontium hexaferrite thick films measured by overlay technique is reported for the first time by us.

The permittivity values of Strontium hexaferrite thick films obtained by overlay technique agree quite well with the theoretical permittivity. The permittivity values of strontium hexaferrite thick films of pH 11 and pH12 obtained by VSWR and overlay techniques are comparable with the theoretical permittivity. But pH 13 strontium hexaferrite thick films show large difference between permittivity obtained by VSWR technique and theoretical permittivity.

The salient Features of EMC patch antenna overlay studies are:
1. Shift in resonant frequency along with perturbation in bandwidth and quality factor of EMC patch antenna due to hexaferrites overlay.

2. For measurement of material’s properties using EMC patch antenna overlay, there is no restriction of particular shape, size and thickness of the material.

3. Power gain of EMC patch antenna was enhanced due to barium hexaferrite bulk and pH 13 strontium hexaferrite thick films overlay.

4. Multiple resonances were obtained due to barium hexaferrite thick films overlay.

5. Synthesis conditions and thickness of overlaid hexaferrites dependant changes in perturbation of resonance of EMC patch antenna was obtained which provides frequency agility.

6. The permittivity agrees quite well with the theoretical value.

7. Higher values of permeability of hexaferrites were obtained as compared to the permeability obtained by waveguide method.

8. More accurate values of complex permittivity and permeability were obtained as the values were calculated from the shift in resonance and not by the mechanical measurements.

In chapter-V “Summary and conclusions”, all the results are summarized and conclusions are made from results.

Briefly, the major results of the work carried out are as follows:

1. The hexagonal polycrystalline barium hexaferrite and strontium hexaferrite was successfully synthesized by cost effective, low temperature, environment friendly coprecipitation technique using chloride precursors.

2. The screen printed thick films of synthesized hexaferrite powder were formulated using bismuth oxide as inorganic binder instead of glass frit. The thick film hexaferrites show hexagonal crystal system with no binder peak.

3. The surface morphological studies reveals synthesis condition dependant various shaped grains like nanorods, nanoneedles, orbicular, hexagonal platelet etc. Barium hexaferrite synthesized at 11:1 Fe/Ba molar
ratio with pH 11 and sintered at 750°C forms nanorods and that sintered at 950°C forms nanoneeds of barium hexaferrite might be due to the topochemical growth by formation of α-FeOOH at some places instead of intermediate Fe(OH)$_2$ during precipitation.

4. The grain size varying from 50nm to 120 nm was obtained for barium hexaferrite. Strontium hexaferrite show slightly larger grain size varying from 70nm to 2.5 μm. Nanosized grains of size (~50nm) formed by the agglomeration of nanogranules (~10 nm) were obtained at 11:1 Fe/Ba ratio with pH13BaM bulk sintered at 750°C.

5. Thick film hexaferrite show uniform porous surface morphology and as pH increased, bulky surface was formed. As Fe/Ba molar ratio increased, the grain size was decreased.

6. The resistance of hexaferrites decrease from $\sim 10^{10}$ to $10^6$ Ω with temperature. The room temperature resistance of barium hexaferrite and strontium hexaferrite was almost similar.

7. The AC permittivity of barium hexaferrite was higher than strontium hexaferrite.

8. pH13(750) barium hexaferrite powder show highest magnetization in all the barium hexaferrite samples. In case of strontium hexaferrite, pH11 powder show highest saturation magnetization. The highest saturation magnetization obtained for barium and strontium hexaferrite powders is almost two times higher than reported values.

9. 11:1 barium hexaferrite thick films show higher saturation magnetization than that of 14:1 BaM films due to larger grain size. BaM thick films show much lower magnetization as compared to bulk due to higher porosity in thick films.

10. High absorbance of $\sim 85\%$ was obtained by barium hexaferrite thick films in X band whereas $\sim 90\%$ absorbance was obtained by strontium hexaferrite thick films in Ku band.
11. Both dielectric and magnetic resonance was obtained at 9 GHz by barium hexaferrite bulk due to domain wall resonance.

12. Multiple dispersions in complex permittivity and permeability of thick films were obtained in 9.5 to 10.5 GHz where, absorption also shows dispersive behavior. The possible reasons behind the dispersion are spin wave resonance, domain wall resonance etc.

13. Strontium hexaferrite thick films show resonance behavior at 9.3 GHz and 14.5 GHz.

14. The properties of synthesized hexaferrites were studied by overlay technique also. For overlay studies four types of Ag thick film microstrip components viz microstripline, straight resonator, annular ring antenna and electromagnetically coupled microstrip rectangular patch antenna were used.

15. The transmittance of microstripline was decreased due to both hexaferrites bulk and thick films overlay, as fringing fields of microstripline were absorbed by them.

16. Hexaferrites does not show any further shift than alumina overlaid over direct fed microstrip circuits such as straight resonator, ring antenna but the power gain was enhanced by these overlay.

17. The resonance of electromagnetically coupled microstrip patch antenna was shifted due to hexaferrites depending on their synthesis conditions. Thus hexaferrites provide frequency agility to the EMC patch antenna by overlay technique. The frequency of the resonant structure was perturbed due to overlay because of the interference of the incident electromagnetic waves with the properties of the overlaid material so lag in phase, velocity and amplitude takes place.

18. Power output of the EMC patch antenna was enhanced by 60% due to barium hexaferrite bulk overlay except 11pH13 pellets whereas due to SrM pH13(950) pellet overlay it was enhanced by 20%.
19. Due to barium hexaferrite thick films overlay multiple peaks were introduced which makes the antenna usable at multiple resonance frequencies but at the same time, the power output was decreased whereas due to strontium hexaferrite thick films overlay power output was enhanced by 60%.

20. Higher values of permeability were obtained by overlay technique. As the complex permittivity and permeability values by overlay technique were obtained from the dispersion in frequency, least mechanical errors were introduced and more accurate values were obtained by this method.

21. The aim of impedance matching was partially fulfilled as the impedance matching degree reached up to 77% considering $\varepsilon^*$ and $\mu^*$ measured by overlay technique.

Conclusions:

The results from the structural, DC and AC electrical, DC magnetic and microwave (8-18 GHz) studies of barium and strontium hexaferrite bulk and thick films reveals that magnetodielectric material in planar form was formed which can be a potential candidate for radar absorbing material. The aim of impedance matching was fulfilled upto 77% by hexaferrite thick films. The complex permeability of hexaferrites was measured successfully by overlay technique and waveguide technique which reveals from the transmittance, reflectance and absorbance properties of them. The Ag thick film microstrip components were used for the first time to measure complex permeability of the hexaferrite thick films.

From studies of structural, DC and AC electrical and magnetic properties and microwave properties it can be concluded that,

1. Hexagonal polycrystalline pure fine grains of hexaferrites were formed in both bulk and thick films.
2. The nanorods were formed on the surface of hexagonal platelet like surface for barium hexaferrite pellets synthesized under pH 11 of 11:1 Fe/Ba ratio and sintering temperature at 750ºC.
3. The nano-needles were formed at some places over the surface of hexagonal platelets for barium hexaferrite pellets synthesized at pH11(950) of 11:1 and 14:1 Fe/Ba ratio.
4. Saturation magnetization of about two times higher than the reported values was obtained for synthesized 11:1 pH13(750) BaM and 14:1 pH13(850) barium hexaferrite bulk and pH11 strontium hexaferrite bulk. Other bulk hexaferrites having saturation magnetization similar as that of reported values. Thick films show lower magnetization as compared to that of bulk.
5. About 85% absorbance was obtained by barium hexaferrite thick films in X band and ~90% absorbance was obtained by strontium hexaferrite thick films since, impedance matching was achieved upto 77% which makes them a potential candidate of magnetodielectric broadband absorbers in that particular frequency range.
6. The reflectance measured by waveguide method and complex permittivity measured by VSWR technique was used to calculate complex permeability of hexaferrites for the first time. This method is comparatively simple and broad band dielectric and magnetic properties can be studied by this technique.
7. Microstripline can also be used for broadband dielectric and magnetic characterization of the overlaid hexaferrites.
8. Barium hexaferrite bulk and strontium hexaferrite thick films can be used to amplify power gain of EMC patch antenna.
9. Hexaferrite thick films overlay provides frequency agility to the EMC patch antenna for different synthesis conditions of the overlaid thick films.
10. A single antenna can be used at multiple resonant frequencies at the same time due to barium hexaferrite thick films overlay.

11. The complex permeability of hexaferrite thick films have been successfully measured by overlay technique was reported in this thesis for the first time.

Thus, the overlay technique is a very cost effective technique which can alter the resonance of EMC patch antenna by in touch overlay of the hexaferrites. The behavior is different for bulk and thick films overlay.

**Scope of future work:**

The effect of magnetic domain orientation in hexaferrite bulk and thick films on their microwave properties needs to be investigated. The unidentified exact phenomenon behind the strange microwave properties of thick film hexaferrites has to be sort out. The Mossbauer studies of synthesized hexaferrite bulk and thick films needs to be done.

The degree of impedance matching was achieved upto 77%. There is a need of broad band perfect impedance matched materials for 100% absorption of microwaves. It could be possible by enhancing permeability of these hexaferrite by making the magnetic domains oriented along the same direction which leads to still higher saturation magnetization and lower coercive field.

Another scope of these materials is in planar metamaterials. The metamaterials can be used for infinite amplifications of antenna, total transmitting surfaces etc. Attempts towards reduction of gyromagnetic resonant frequency of these impedance matched hexaferrite thick films for achieving –ve permittivity and permeability values are needed for metamaterial formation.