CHAPTER - VII

Summary and Conclusions

Materials which are possesses two or more properties like ferroelectric, ferromagnetic, ferroelasticity etc in the same phase, and can be tuned on application of either one of these effect, these materials are called as multiferroic materials and are the most interesting materials in the today’s technological world. With their potential application in the devices like, transducers, phase shifters, magnetic field sensors, current sensors, filters, resonators and memory devices etc, these materials are one of the most emerging materials which have trapped the scientific community among the globe. Magnetoelectric (ME) or magneto-dielectric (MD) materials are among the multiferroic materials which show very interesting properties and research on these materials is growing tremendously from last few decades. In ME materials cross-linking dependence of ferroelectricity and ferromagnetism is observed, where the magnetization (M) or polarization (P) can be induced in the material on application of electric (E) or magnetic field (H) respectively. Further these multiferroics are divided in to two groups single phase multiferroics and two phase multiferroic materials. Single phase multiferroics are found rare and usually this material shows large magnetoelectric coupling coefficient but below room temperature and as the temperature reaches towards room temperature ME coefficient gets very low value. To overrule this problem of single phase ME material, two phase materials constituting ferroelectricity and ferromagnetism was introduced.

For development of ME composite material out of two materials one should have posses spontaneous polarization and the material have to satisfy the criteria of linear magnetoelectric coupling. But there are some composite materials, which possess neither spontaneous polarization nor satisfy the symmetry criteria for the linear magnetoelectric effect, but even so demonstrate some kind of coupling between dielectric properties and magnetization. This type of coupling is bilinear i.e. coupling occurs in both electric as well as magnetic field region, this coupling is known as magnetodielectric coupling or the magnetodielectric effect in multiferroic composite which is a scalar quantity. With the use of any insulating magnets this type of magnetodielectric coupling can be produced. This founds very useful to increase the flexibility in designing materials with enhanced properties and can be useful developing devices for multiple applications. Due to the coupling between the magnetic and ferroelectric material the magnetic properties of the
MD material can be controlled by an applied electric field, while the electric polarization can be modified by applying a magnetic field. The magnetodielectric (magnetocapacitance) effect is observed in magnetolectric materials, in view of the fact that the dielectric constant is intrinsically related to electric polarization and indirectly related to the magnetic order. Several ferrite materials such as, EuTiO$_3$, TmFeO$_3$, MnF$_2$, Mn$_3$O$_4$, Tb$_3$Fe$_5$O$_{12}$ etc are known to exhibit magnetodielectric effect at lower frequency regions. Frustrated magnets as, Dy$_2$Ti$_2$O$_7$, Tb$_2$Ti$_2$O$_7$, and ZnFe$_2$O$_4$ are also shows significant MD effect but now a day’s these frustrated magnets are replaced by composites of ferroelectric-ferromagnetic phases. The composite materials such as CoFe$_2$O$_4$-BaTiO$_3$, γFe$_2$O$_3$-BaTiO$_3$, LCMO-BaTiO$_3$ in the form of bulk as well as thin film heterostructures are known to exhibit MD effect at room temperature. Both the ME and MD effects in these systems are possible to be understood in terms of Landau thermodynamic theory. MD effect can be measured in terms of percentage and can be represented as,

$$Mc(\%) = \frac{\varepsilon(H)-\varepsilon(0)}{\varepsilon(0)} \times 100\%$$

In View of this here we have synthesized following ferroelectric, magnetic and magnetodielectric systems, 1) BCT, 2) BZT, 3) xBCT-(1-x)BZT 4) CNFO and 5) CNFO-[BCT-BZT] in bulk and thin film form. The synthesis, characterization of these individual materials and its composites is presented in the present thesis in the following manner.

**Chapter-I** is the introductory remark on the basic properties of materials having the ferroelectric, ferromagnetic phase and their magnetolectric or magnetodielectric composite. From the overall discussion it could be seen that, in the application point of view, for formation of magnetodielectric composite material the ferroelectric material must possess a high dielectric constant with low dielectric loss as well good piezoelectric and ferroelectric properties whereas the ferromagnetic material should have high magnetostrictive properties. PZT is one of the most useful and intensively studied materials as ferroelectric constituent, but its toxic properties hinder its direct application in the devices. The compatible material for PZT is unknown till the introduction of Ca and Zr doped BaTiO$_3$ with interesting morphotropic phase boundary properties. Whereas, sintering of ferroelectric, ferromagnetic phases and their composites is the most necessary and important stage in the formation of these individual phase as well as composite material. Method of sintering plays an important role in formation of material as per the
particular application requirements. Here sintering at desired temperature for desired amount of time is required to meet the structural, microstructural, electrical and physical properties as per the requirement. Though conventional method is widely used technique worldwide it has various drawbacks such as, sintering at higher temperature for longer duration, where as there is more possibility of temperature gradient during the process. To avoid these problems various sintering techniques are developed and it is found that the microwave sintering technique has many advantages over conventional sintering technique and other methods. The microwave sintering provides heating from the material to the outward surface with the fast heating rate also the holding time can be minimized with the use of this method. Sintering at lower temperature can be possible with microwave sintering method whereas the whole mechanism can be done in short period of time without any temperature gradient. This technique is known to improve physical and electrical properties of the material under process.

Chapter-II deals with the literature survey which provides the details about the ferroelectric, ferromagnetic and magnetodielectric composite materials which have been searched and studied in past few years. Here the ferroelectric systems containing lead material and its comparative lead free material are mentioned with their properties. Some literatures on the materials processed with microwave sintering are discussed in this chapter whereas, some literatures on comparison of microwave and conventional sintering shows how the microwave sintering is beneficial for processing of ceramic materials. With this points the theories related to the properties of ferroelectric material such as dielectric constant ($\varepsilon_r$), dielectric loss tangent (tan$\delta$), AC and DC conductivity in ceramic samples, polarization phenomenon, impedance spectroscopy etc. On the other hand theoretical background on saturation magnetization (Ms), remanant magnetization (Mr), and coercive field (Hc) is discussed in details. Whereas chapter gives fruitful discussion about the origin of magnetoelectric (ME) and magnetodielectric (MD) / magnetocapacitance (MC) effect in the composite materials with ferromagnetic and ferroelectric phase.

Considering introductory remark and the literature part, it is noticed that to develop magnetodielectric composite one phase having good ferroelectric properties and another with high magnetostriective phase are required. In the view of this here we have selected the ferroelectric solid solution $x$[(Ba$_{0.7}$Ca$_{0.3}$)TiO$_3$]- (1-x)[(BaZr$_{0.2}$Ti$_{0.8}$)O$_3$] which has a compatible properties with lead containing systems like, PbZrTiO$_3$. This material is one of the most important lead free material which under investigation to its various
applications and found useful for many devices in replacement of PZT. Whereas it found that the substitution of Ni$^{2+}$ towards Co$^{2+}$ will results in the anisotropy and improvement in the magneto mechanical coupling of CoFe$_2$O$_4$. Considering this we have selected Co$_{0.9}$Ni$_{0.1}$Fe$_2$O$_4$ (CNFO) as magnetic system in the formation of ME/MD compositions.

It is also seen that the sintering method has a considerable role over improvement of properties in ferroelectric, ferromagnetic similarly on magnetodielectric materials. Therefore here we have employed fast microwave sintering technique. Considering this it is found interesting to the study the various electrical and physical properties of following individual systems sintered using microwave technique, a) Ba$_{0.7}$Ca$_{0.3}$TiO$_3$ (BCT), b) BaZr$_{0.2}$Ti$_{0.8}$O$_3$ (BZT), and c) magnetic Co$_{0.9}$Ni$_{0.1}$Fe$_2$O$_4$ (CNFO). These individual phases of BCT and BZT are used in the formation of solid solution as,

$$x[(Ba_{0.7}Ca_{0.3})TiO_3]-(1-x)[(BaZr_{0.2}Ti_{0.8})O_3]$$

which will mentioned as, $x$BCT-(1-x) BZT

where $x=0.15, 0.3, 0.4$ and $0.5$. These ferroelectric solid solutions are used for formation of MD composition with magnetic CNFO phase as per follows.

1) $x$[CNFO]-(1-x)[0.5BCT-0.5BZT] where $x=0.1, 0.2, 0.3$ and $0.4$

2) $x$[CNFO]-(1-x)[0.3BCT-0.7BZT] where $x=0.1, 0.2, 0.3$ and $0.4$

3) $x$[CNFO]-(1-x)[0.15BCT-0.85BZT] where $x=0.1, 0.2, 0.3$ and $0.4$

Again it is seen that the variation in the temperature affect on the properties of these individual ferroelectric systems and their solid solutions and MD composites, here we have sintered above individual phases of ferroelectric systems with their solid solutions and magnetodielectric systems at 1100 °C and 1200 °C by keeping very short holding time i.e. 30 min and 20 min respectively. Though above three magnetodielectric systems are characterized for their various properties, this thesis includes only one series of MD composite i.e. $x$[CNFO]-(1-x)[0.5BCT-0.5BZT] this system was studied in both forms, the bulk phase form and as a thin film heterostructures.

Chapter-III gives the details of synthesis procedure for all materials under investigation in the present work. Here the individual phases of ferroelectric material (BCT and BZT) were synthesized by using hydroxide co-precipitation method. The magnetic phase CNFO also synthesized by using this method. Here for thin film heterostructures gels of ferroelectric material (0.5BCT-0.5BZT) and magnetic (CNFO) material was synthesized by using sol-gel method. In synthesis of nanopowders of particular individual
phase of ferroelectric material, barium nitrate Ba(NO$_3$)$_2$, calcium nitrate Ca(NO$_3$)$_2$·4H$_2$O, zirconyl nitrate Zr(NO$_3$)$_2$·2H$_2$O and potassium titanium oxalate K$_2$TiO(C$_2$O$_4$)$_2$·2H$_2$O of analytical grade (AR) were used as starting materials. On the other magnetic phase is synthesized by using nitrate precursors of a analytical reagent (AR) grade cobaltous nitrate Co(NO$_3$)$_2$·6H$_2$O, ferric nitrate Fe(NO$_3$)$_3$·9H$_2$O, and nickel nitrate Ni(NO$_3$)$_2$·6H$_2$O. All the reagents were dissolved in double distilled water separately in a beaker the final solution of each constituent was adjusted to 40 mM solution. A mixture of NH$_4$OH and KOH is used as precipitants. For complete solution of particular phase each precipitates were washed with mixture of NH$_4$OH and distilled water and the pH~10 mentioned during each stage. Finally the powders of BCT, BZT and CNFO are calcinated at 1000 °C and each individual ferroelectric phase was sintered at 1100 °C and 1200 °C and magnetic phase at 1100 °C using microwave sintering technique. On the other hand calcinated nanopowders are used for formation of ferroelectric solid solution. These ferroelectric solid solutions are also sintered at similar temperature range. Mixture of ferroelectric solid solution was combined with magnetic phase in the formation of MD composites. Ferroelectric thin films of 0.5(Ba$_{0.7}$Ca$_{0.3}$TiO$_3$)-0.5(BaZr$_{0.2}$Ti$_{0.8}$O$_3$) were fabricated by using sol-gel technique. Calcium acetate, barium acetate, titanium isopropoxide and zirconium isopropoxide were used as starting precursors. Whereas glacial acetic acid and 2-methoxyethanol are used as solvents. Ferromagnetic phase was synthesized using sol-gel method as reported above. For synthesis of CNFO the nitrate precursors cobalt nitrate Co(NO$_3$)$_2$·6H$_2$O, nickel nitrate Ni(NO$_3$)$_2$·6H$_2$O, and ferric nitrate Fe(NO$_3$)$_3$·6H$_2$O are used as starting materials and 2-methoxyethanol as a solvent. Here spin coating was used for deposition of this gel on substrate. This chapter ends with brief information on selected instruments used for characterization purpose to find out various properties.

Chapter-IV deals with characterization of Ba$_{0.7}$Ca$_{0.3}$TiO$_3$ (BCT), BaZr$_{0.2}$Ti$_{0.8}$O$_3$ (BZT), Co$_{0.9}$Ni$_{0.1}$Fe$_2$O$_4$ (CNFO) and ferroelectric solid solution of xBCT-(1-x)BZT sintered at different temperatures using microwave technique. This chapter includes structural, microstructural, dielectric, ferroelectric and magnetic properties. BCT is a perovskite ceramic, which is a solid solution of BaTiO$_3$ and CaTiO$_3$. It could be seen that the, at room temperature BaTiO$_3$ exhibits a tetragonal crystal structure while CaTiO$_3$ reveal orthorhombic structure. From diffraction pattern it could be seen that the perovskite ferroelectric (BZT) phase crystallizes into the single phase crystal with a cubic structure. Random distribution of BTO and BZO phases results in formation of solid solution of
BZT. Solid solution of these two ferroelectric materials xBCT- (1-x)BZT crystallites in to pure perovskite phase with coexistence of tetragonal and rhombohedral crystal structures. Existence of the polycrystalline perovskite structure without any secondary is in good agreement with the diffusion of Ca\(^{2+}\) and Zr\(^{4+}\) ions in to BaTiO\(_3\) lattice and confirms formation of stable solid solution. All samples sintered with microwave technique for shorter exhibits dense microstructures. The Tc pure BCT shifts towards higher temperature value (~ 155 °C) with moderate dielectric constant. In case of BZT transition is near room temperature and posse’s high dielectric constant. Solid solution of BCT-BZT at 50/50 composition shows morphotropic phase boundary (MPB) with coexistence of two dielectric spectra, here also the transition temperature was shifted towards higher temperature. Dielectric spectra reveals the existence of triple point in BCT-BZT composition, as there founds two transition temperatures one is around room temperature corresponding to rhombohedral to tetragonal and other at higher temperature corresponding to tetragonal to cubic transition. This ferroelectric solid solution exhibits relaxor type of characteristic with existence of diffuse phase transition behaviour (DPT). These properties of BCT-BZT lead free piezoelectric ceramic are comparable with lead containing piezoelectric material like PbZrTiO\(_3\). Room temperature x-ray diffraction pattern for CNFO ferromagnetic material shows that as prepared CNFO powder crystallize into a single phase face centered cubic spinel structure with Fd3m space group. The magnetic parameters such as saturation magnetisation (Ms), coercive magnetic field (Hc), remanance magnetisation (Mr) observed are show characteristics of good magnetic material. This chapter also includes Raman spectroscopy of individual ferroelectric and ferroelectric properties.

**Chapter-V** deals with characterization of x[Co\(_{0.1}\)Ni\(_{0.9}\)Fe\(_2\)O\(_4\)]-(1-x)[0.5BCT-0.5BZT] particulate composites. The comparative study on 0.5BCT-0.5BZT ferroelectric ceramic sintered with microwave and conventionally sintered ceramics also included in this chapter. For comparative study temperature was maintained at 1200 °C. This comparative study implies how the microwave sintering is important technique over the conventional sintering method. The microstructural properties of microwave sintered material are improved as compared to the conventionally sintered material. This result in the improvement in the dielectric and ferroelectric properties, dielectric spectra shows that the transition of conventionally sintered ferroelectric material has lower value (~ 95 °C). On the other hand transition temperature of the microwave sintered 0.5BCT-0.5BZT is
higher (~ 140 °C). This features shows that microwave sintering not only improves microstructural properties but also, improves the electrical properties; this feature found very useful for developing materials for above room temperature applications.

Here, considering the morphotropic phase boundary properties and ferroelectric properties, 0.5BCT-0.5BZT is selected as a ferroelectric phase and this MPB composition was mixed with magnetoresentive, Co$_{0.9}$Ni$_{0.1}$Fe$_2$O$_4$ (CNFO) in formation of particulate magnetodielectric composite. Again this MD composite are sintered at 1100 °C and 1200 °C for 30 and 20 min respectively. All the planes related with the ferroelectric 0.5BCT-0.5BCT and the ferrite CNFO are observed in the composites formed for MD properties. The major peak corresponding to ferrite (311) as well as the other peaks like (220), (440) becomes more intense as the concentration of CNFO increase from $x = 0.1$ to $x = 0.4$. It could be seen that the crystallite size increases with increase in CNFO concentration. Microstructural images show the presence of both ferroelectric and ferromagnetic phases in the MD composition. Similar kind of properties as observed in x-ray diffraction pattern are observed in microstructural analysis, here grain size increases with increase in CNFO content. Temperature and frequency dependant dielectric properties are studied with variation of CNFO concentration. The dielectric constant ($\varepsilon_r$) increases with and loss tangent also increases with increase in CNFO concentration. MD composites have two dielectric anomalies lower temperature corresponding to ferroelectric transition and higher temperature dielectric anomaly represents magnetic transition. Higher ME and MD values are observed for 0.4CNFO-0.6[0.5BCT-0.5BZT] composition sintered at both temperatures. ME coefficient increases with increase in temperature whereas, MD (%) decreases. P-E hysteresis loop becomes more circular with magnetic concentration and ferroelectric loss increases. Magnetic properties are studied for MD compositions sintered at both temperatures, and found values of magnetic characteristic increases with increases in CNFO concentration. Raman analysis of MD composition sintered at 1200 °C is also included in this chapter. Raman analysis confirms formation of MD composition with existence of vibrational modes corresponding to ferroelectric and ferromagnetic phase.

**Chapter-VI** deals with characterization of 0.5BCT-0.5BZT ferroelectric thin film and CNFO-[0.5BCT-0.5BZT] MD thin film deposited on Pt/Ti/Si/SiO$_2$ substrate using spin coating technique. The deposited ferroelectric thin film after annealing at 800 °C, shows perovskite structure with tetragonal crystal structure having lattice parameters $a = b = 4.006$ and $c = 4.068$. On the other hand CNFO-[0.5BCT-0.5BZT] magnetodielectric thin
film exhibits both crystal structures, i.e. cubic spinel structure corresponding to ferrite material and perovskite tetragonal crystal structure of ferroelectric phase. Real part ($\varepsilon_r$) and imaginary part ($\varepsilon'$) of dielectric constant were measured at room temperature and plotted against frequency. Dielectric behaviour of thin has similar kind of nature as observed for bulk ferroelectric and magnetodielectric composites. Here the loss tangent and imaginary part ($\varepsilon'$) of dielectric constant are calculated as per the formula given as,

$$\varepsilon' = \varepsilon_r \tan \delta$$

The calculated and observed values of loss tangent almost coincide with each other. The both thin films are analyzed by Raman spectroscopy for their vibrational modes.

The overall conclusions derived from the obtained results are summarized as follows

1) The compositions $\text{Ba}_{0.7}\text{Ca}_{0.3}\text{TiO}_3$ (BCT), $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ (BZT) and $\text{Co}_{0.9}\text{Ni}_{0.1}\text{Fe}_2\text{O}_4$ (CNFO) are studied in the bulk phase form. On the other hand ferroelectric solid solution of BCT-BZT and the magnetodielectric composition of CNFO-[BCT-BZT] are studied in the bulk as well as in thin film form. All observed results with detailed analysis have been interpreted in the thesis.

2) Microwave sintering method is successfully employed for processing of above ferroelectric, magnetic and magnetodielectric systems. Microwave sintering technique plays an important role in the phase formation, densification of material, grain growth of the material under process. Improvement in the microstructure and crystallinity results in the enhancement of $T_c$ as compared to materials processed by the conventional sintering.

3) It is observed that the, dielectric permittivity or Curie temperature of $\text{BaTiO}_3$ could be altered by either substitution of Ca or Zr ions on Ba or Ti sublattices. The DPT behaviour observed in case of BCT-BZT microwave sintered samples confirms the shifting of transition temperature ($T_c$) towards higher values. The diffuse phase transition shows that BCT-BZT solid solutions are neither normal ferroelectrics nor the relaxor type of ferroelectrics.

4) BCT-BZT ceramic exhibits excellent electrical and physical properties at the morphotrophic phase boundary composition i.e. 0.5BCT-0.5BZT. MPB composition of BCT-BZT could be found alternative ferroelectric to replace lead based ferroelectric materials like PZT. Enhanced electrical properties are found for 0.5BCT-0.5BZT sintered with microwave technique as compared with conventional technique.
5) The dielectric dispersion behaviour can be explained on the basis of Maxwell-Wagner theory and interfacial polarization in accordance with Koop’s model.

6) An observation from the structural, microstructural confirms the presence of both ferroelectric and ferromagnetic phases in the CNFO-[BCT-BZT] composite. Presence of two dielectric anomalies, one at lower temperature and another at higher temperature indicates the formation of ME/MD coupling in CNFO-[BCT-BZT] composite.

7) Introduction of ferrite phase with increasing concentration in ferroelectric phase results in shifting of dielectric anomalies towards higher temperature.

8) Raman analysis of ferroelectric, magnetic and magnetodielectric compounds confirms the formation of respective phase.

9) Here it could be seen that the MD composites sintered at lower temperature (1100 °C) posses positive magnetocapacitance and the numerical value of magnetocapacitance at maximum applied magnetic field at x=0.2 and 0.4 are high (6-7%).

10) All the properties like mechanical, physical and electrical for example, dielectric properties in case of ferroelectric composition are enhanced with increase in temperature. Also the overall like microstructural, dielectric, magnetic and magnetoelectric properties of magnetodielectric composition excepting MD tunability are enhanced with the increase in temperature from 1100 °C to 1200 °C.

11) Increasing sintering temperature results in enhancement of linear magnetoelectric coupling coefficient (α). Here the 0.4CNFO-0.6(0.5BCT-0.5BZT) MD composite sintered at 1200 °C shows a ME value (~ 21 mV/Oe.cm).

12) With increasing concentration of the ferrite CNFO values of saturation polarization decreases continuously, this may resulted as increase in ferrite concentration reduces the ferroelectric nature of BCT-BZT and ferroelectric hysteresis loop becomes more circular. This may be result as, the of mixed valance states of Fe³⁺ and Fe²⁺ has a higher leakage current density than the ferrite materials consisting ferroelectric phase.

13) The Saturation magnetisation, magnetic moment and coercive field of the composites increase with increase in CNFO content. Increase in the Hc value with increase in ferrite concentration indicates that the magnetization becomes harder.

14) The thin film heterostructures of ferroelectric BCT-BZT and CNFO-[0.5BCT-0.5BZT] presented here has the similar kind of behaviour to their counterparts which are synthesized in bulk phase form.

15) Overall this synthesized ferroelectric, ferromagnetic phases and multiferroic composites synthesized with microwave sintering technique are founds very useful
materials and can be applicable for many devices and components depending on their properties.

16) Microwave sintering method found very useful sintering technique for development of materials at comparatively lower (\(\sim 100 \text{ – } 150 \,^\circ C\)) and in a very short time. Here it is proved that not only ceramic materials can be processed with microwave sintering but one can also process magnetic material and multiferroic composite of ferroelectric and ferromagnetic phase by using this technique.

**Future Directions:**

This thesis reports an extensive study on ferroelectric phase \((xBCT-(1-x)BZT)\), ferrite phase \((CNFO)\) material and its particulate composite \(CNFO-[BCT-BZT]\). Here we have standardized the process of synthesis of these materials. The microwave sintering technique for heating of multiferroic composite is introduced and the structural, morphological, dielectric and magnetic study is presented in this thesis. Considering this as a future plan we have decided to attempt the synthesis of these materials and its thin film heterostructures using the MW sintering technique. For synthesis of MD thin films using MW sintering technique, the search for suitable substrate is under study. It interesting to understand the consequences of structural phase coexistence of ferroelectric and ferrite phase in these MD materials. Also the detailed investigation on MD properties at lower temperature value is required. The growth of these materials on different substrates using PLD will also be interesting. The formation of these materials in new form may allow more surface area for better interfacial interactions of different phases.