CHAPTER - III

Synthesis of $\text{Ba}_{0.7}\text{Ca}_{0.3}\text{TiO}_3$ (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)

3.1 Introduction

This chapter describes types of synthesis methods which can be found useful for production of materials, as per the application. Whereas the methods used for synthesis of ferroelectric and ferromagnetic phases, in bulk as well as thin film heterostructures are discussed in details. Followed by the discussion on synthesis techniques, this chapter reports on synthesis of lead free ferroelectric material $\text{Ba}_{0.7}\text{Ca}_{0.3}\text{TiO}_3$, $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ and its composition as $x[\text{Ba}_{0.7}\text{Ca}_{0.3}\text{TiO}_3]-(1-x)[\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3]$ at various $x$ composition. Here we have employed hydroxide coprecipitation method followed by microwave sintering.

Further the most studied and used material for the magnetostrictive part in the ME materials is $\text{CoFe}_2\text{O}_4$ as the magnetic phase due to its large magnetostriction. Cobalt ferrite is a well-known hard magnetic material with relatively high coercivity and saturation magnetization while nickel ferrite is a soft material with low coercivity and saturation magnetization. But due to the poor ME coupling between the two phases the ME voltage coefficient was extremely smaller than the predicted value. Substitution of Ni in $\text{CoFe}_2\text{O}_4$ causes reduction in magnetic anisotropy, leads to high permeability and magnetostriction, strengthening of low-field piezomagnetic coupling and, therefore, a strong magneto-mechanical effect in the ferrite. This feature has been attributed to large anisotropy energy of the $\text{CoFe}_2\text{O}_4$ [12-13]. Here $\text{Co}_{0.9}\text{Ni}_{0.1}\text{Fe}_2\text{O}_4$ (CNFO) ferrite is selected to be a magnetostrictive phase considering its high value of coefficient of magnetostriction [14]. The synthesis of CNFO is also discussed in detail.

Also the formation of MD compositions, including BCT-BZT as ferroelectric phase and CNFO as ferromagnetic phase is reported in this chapter. Synthesis of thin film heterostructures of $0.5[(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3]-0.5[\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3]$ and its MD composite formation with $\text{Co}_{0.9}\text{Ni}_{0.1}\text{Fe}_2\text{O}_4$ prepared by sol-gel method followed by spin coating technique is also discussed in brief. Some important characterization techniques used for analysis of different properties, are discussed briefly at the end of this chapter.
3.2 Synthesis methods

Synthesis of material in a proper way and optimization of its physical properties that it can satisfy the condition of to be used for specific multifunctional device is the most important part in the field materials science [1]. Literatures suggest that there are many more methods which can be used for synthesis ultra fine material powders with high purity and homogeneity. Materials with multifunctional properties or ferroelectric properties can be synthesized in different forms like single crystals polycrystals or in the form of thin/thick film coatings on different types of substrates [2]. Ceramic materials with polycrystalline nature (where the group of small signal crystals oriented with respect to each other in more or less completely random way) are the most interesting materials due to its advantages over single crystal materials and thin film heterostructures. More sophisticated infrastructure and high cost synthesis methods are requires developing the materials with single crystal and thin films on the other hand polycrystalline materials can be prepared easily with low cost methods [2]. Polycrystalline materials has an advantages over the single crystal material like easy fabrication with different shapes and sizes, improvement in the structural and microstructural properties which will results in improved electric and mechanical properties [1-2]. In general two methods are founds more useful for synthesis of multifunctional materials as: a) mechanical method (top-down) and b) chemical method (bottom up) [4].

3.2.1 Mechanical methods

Various synthesis process as like solid state method, turbo milling, high energy ball milling, fluid energy milling, attrition milling, roll crushing and mixed oxide process vibratory milling, hammer milling, are some methods comes under the category of mechanical method. The solid state reaction method is most used and is a very successful method for development of multifunctional materials in large quantity. Though this method is able to produce materials in bulk quantities it has several limitations which hinder its use in synthesis of multifunctional materials. For preparation of materials with solid state reaction requires high cost carbonates or oxides as minerals. The prepared material needs a ball milling for longer time and also high temperature for more time is required for complete phase formation in material. This prolonged heating at higher temperature makes the particles coarse of the material under process. Different parameters like particle size, homogeneity of the mixture, heating schedule and atmosphere at the time of heating process plays an important role in the formation of product [3-4].
3.2.2 Chemical methods

Use of the chemical methods provides the preparation of materials with scale down structure in a controlled manner. Sol-gel synthesis, hydrothermal synthesis, citrate gel method, decomposition of molecular precursors and coprecipitation method are some commonly used chemical methods [4]. Materials synthesized with chemical methods shows the improved physical and mechanical properties. Also the improvement in purity, homogeneity, stoichiometry, reactivity and size, shape and agglomeration behaviour can possible with the help of chemical processing’s [5]. Chemical sources used for development of materials are low cost nitrates or chloride precursors which are easily soluble in water and mixed in each other. Particle size in the range of nanometre with fine grains can be achieved with the help of chemical methods as a result powder materials synthesized with these processes are more reactive and there is no need to procure this powder particles at higher temperature. Solvents used during the reaction can be easily removed results in crushable agglomerates. Both the methods discussed above have an individual advantages and disadvantages. Many times complex techniques are required for production of material with chemical methods. As multiferroic materials synthesized with the help of one of the chemical method and studies on these materials are carried out as a part of present research work here in this section some of the chemical methods are discussed.

3.2.2.1 Sol-gel Method

Sol-gel is the one of important chemical method used to develop thin/Thick films as well as materials in the fine powder form. It is biphasic method where the solution of chemicals gradually converted to gel like from and contains both liquid and solid phases. Formation of material at lower temperature as compared with other techniques is possible with sol-gel process. It is possible to dope the solution with organic dyes and rare earth metals in this method. Dopants used in the solution are uniformly disseminated in the final product. Though ceramics prepared with sol-gel are highly pure in a well controlled manner it competes with the ceramics processed with methods like CVD or derived from metalloorganic vapours. Also, the synthesis method will be selected depending on product of interest required size/quantity available instrumentation facility and ease of processing. In some cases sol-gel can be an economical route, provided precursors are not very expensive. This method is a unique technique which can be used for materials such as aerogel, xerogel, and porous solid structures with hybridization of organic-inorganic
materials. Production of nanoparticles, nanorods or nanotubes can be possible with sol-gel process. Nano materials derived by this method have wide applications in electronics, medicine, separation technology, and optics [6].

![Figure 3.1 a) Sol of precursor b) gel form of sol and c) sol-gel monolithic solid.](image)

Figure 3.1 a) Sol of precursor b) gel form of sol and c) sol-gel monolithic solid.

Sol means nothing but the particles which are dispersed in the liquid phase while gel is continuous chain type network of particles having pores filled with liquid phase and can be schematically represented as shown in figure 3.1. Evaporation of the containing liquid phase will results in powders, thin thick films or even monolithic solid. This method is mostly useful for synthesize ceramics or metal oxides moreover synthesis of sulphides, borides and nitrides can be possible with use of sol-gel method. In sol-gel process various steps are involved from beginning like, hydrolysis of precursors, condensation followed by polycondensation to form particles, gelation and drying process which can be shown in figure 3.2. Both alkoxides and salts of metal oxide can be used for development of final product provided that they are precursors used as starting chemicals are chosen in such a way that they have a tendency to form gels.
3.2.2.2 Co-precipitation Method

Coprecipitation method is one of the important chemical processes found useful for synthesis of nanoparticles. In this method all the starting materials are dissolved in water and for precipitation of this starting precursor base solution was added. Precipitate of required metal oxides found in the form of hydroxides, carbonates, formates or citrates [7-8]. Coprecipitation involves nucleation and crystal growth of cation solution and anion solution followed by agglomeration of precipitate. These precipitate of are calcinated at the specific temperature after filtration and drying process to remove excessive amount of water content and other impurities. Mixing of the materials at the atomic scale can be possible with the coprecipitation method due to which the calcination temperature required for final precipitate is low. Though it is the simplest and cheap process of synthesizing nano-material one has to obtain and maintain some parameters like, pH, temperature and stirring speed of the mixture control on the concentration of solution during the synthesis process to obtain the final product with desired properties.
Figure 3.3 Schematic of coprecipitation method.

In the coprecipitation method when the concentration of a solute in the solvent exceeds its equilibrium solubility, a new phase i.e. supersaturating takes place. Nucleation of the cations and anions is the important step in coprecipitation and without the supersaturating stage nucleation would not occurs. Precipitation can be also results while at the time of chemical reaction if a insoluble substance is provided in the solution and the density of the solution becomes greater. When the solution becomes super saturated precipitation gathers speedily with soluble substances. A simple schematic of stages in coprecipitation can be shown as in figure 3.3. An essential point of precipitation progression is the onset of nucleation. The formation of hypothetical solid particle consist of the construction of an edge which entail a few force based on the virtual surface energy of the solid and the solution. If this energy is not available, and no suitable nucleation surface is available, supersaturating phase occurs [9].

3.3 Synthesis of Ba$_{0.7}$Ca$_{0.3}$TiO$_3$ and BaZr$_{0.2}$Ti$_{0.8}$O$_3$

3.3.1 Synthesis of Ba$_{0.7}$Ca$_{0.3}$TiO$_3$ (BCT)

Powder samples of (Ba$_{0.7}$Ca$_{0.3}$)TiO$_3$ (BCT) were synthesized by employing hydroxide coprecipitation method. For synthesis of BCT barium nitrate Ba(NO$_3$)$_2$, calcium nitrate Ca(NO$_3$)$_2$·4H$_2$O, and potassium titanium oxalate K$_2$TiO(C$_2$O$_4$)$_3$·2H$_2$O were used as starting materials. Precursors used for synthesis are of analytical reagent grade with purity > 99.9% purchased from S-D fine chemicals and used without any
further purification. 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. KOH is used as a precipitating agent for complete precipitation of Ba(OH)₂ and TiO(OH)₂. The molar ratio of KOH to (BaTi) of 1.6 has been used, based on the earlier report [10]. It is seen that, molecules of Ba(OH)₂ and Sr(OH)₂ are fractionally soluble in water but these ions are insoluble in alkaline medium. Therefore, the precipitates are washed in dilute ammonium (NH₄OH) solution and distilled water for 5-6 times by keeping the pH > 10 in each stage of precipitation [11]. The obtained precipitates of BCT after filtration were dried and grinded for 4-5 hours to make a fine powder which is then separately calcinated at 1000 °C for 4 hours. Here in synthesis of BCT the ratio Ba/Ca chosen in such a way that it can be further found useful for formation of solid with Ba(Zr₀.₂Ti₀.₈)O₃ (BZT). Schematically synthesis of BCT is as shown in figure 3.4.

Figure 3.4 Flow chart of synthesis process of Ba₀.₇Ca₀.₃TiO₃.
3.3.2 Synthesis of BaZr$_{0.2}$Ti$_{0.8}$O$_3$ (BZT)

Powder particles of Ba(Zr$_{0.2}$)Ti$_{0.8}$O$_3$ (BZT) were synthesized by similar method as used for synthesis of BCT i.e. hydroxide coprecipitation method. For synthesis of BZT barium nitrate Ba(NO$_3$)$_2$, Zirconyl nitrate Zr(NO$_3$)$_2$.2H$_2$O, and potassium titanium oxalate K$_2$TiO(C$_2$O$_4$)$_4$.2H$_2$O were used as starting materials. Precursors used for synthesis are of analytical reagent grade with purity > 99.9% purchased from S-D fine chemicals and used without any further purification. 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. KOH is used as a precipitating agent for complete precipitation of Ba(OH)$_2$ and TiO(OH)$_2$. The molar ratio of KOH to (BaTi) of 1.6 has been used, based on the earlier report [10]. It has been observed that the Ba(OH)$_2$ and Zr(OH)$_2$ are fractionally soluble in water but insoluble in alkaline medium. Therefore, the precipitates are washed in dilute ammonium (NH$_4$OH) solution and distilled water for 5-6 times by keeping the pH > 10 in each stage of precipitation [11]. The obtained precipitates of BZT after filtration were dried and grinded for 4-5 hours to make a fine powder which is then separately calcinated at 1000 °C for 4 hours. Here in synthesis of BZT the ratio Zr/Ti chosen in such a way that it can be further found useful for formation of solid with BCT. Schematically synthesis of BZT is as shown in figure 3.5.

3.3.3 Sintering of Ba$_{0.7}$Ca$_{0.3}$TiO$_3$ (BCT) and BaZr$_{0.2}$Ti$_{0.8}$O$_3$ (BZT) ceramics

After being calcinated at 1000 °C for 4 hrs, petite amount of the powder sample of BCT and BZT ceramic taken out separately. Calcination process of the both ceramic sample are carried out in a programmable muffle furnace from thermo concept instruments. Small portion of the BCT and BZT powdered sample are grinded thoroughly for 4-5 hours with an agate mortar. After grinding polyvinyl alcohol (PVA) was mixed in the powder samples. PVA will work as binder to tighten the tiny particles in the powder sample. This mixed powder samples with PVA are pressed using a hydraulic press, results in the formation circular disc having 1 cm diameter and nearly 1.2 mm thickness. For this purpose die with inner circular radius 0.5 cm was used, while the pressure of the hydraulic press was maintained between 5-6 tons for while a time to form the compact disk shape pellet. This pellets of the BCT and BZT ceramic samples and the remaining powder nanoparticles where sintered at the different temperature also the holding time maintained is different. For sintering purpose of these ceramics microwave sintering technique was
adopted, microwave furnace purchased from VB ceramics Pvt Ltd Chennai India was used for sintering purpose. Microwave furnace with power 1.3 KW, frequency range of 2.45 GHz and having multimode cavity with thermally insulated chamber to prevent heat loss is used for this purpose. After final sintering various properties of ceramic samples are obtained through various characterization techniques. Calcination temperature and sintering temperature with holding time for BCT and BZT ceramic samples separately are mentioned in table 3.1.

Figure 3.5 Flow chart of synthesis process of BaZr$_{0.2}$Ti$_{0.8}$O$_3$. 
Table 3.1 Calcination and sintering temperature schedule of BCT and BZT ceramics.

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>Calcination Temperature or Pre-sintering</th>
<th>Sintering Temperature (MWS)</th>
<th>Temperature rate</th>
<th>Soaking Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba$<em>{0.7}$Ca$</em>{0.3}$TiO$_3$ (BCT)</td>
<td>1000 °C for 4 hrs</td>
<td>1100 °C, 1200 °C</td>
<td>30 °C/min, 40 °C/min</td>
<td>30 min, 20 min</td>
</tr>
<tr>
<td>BaZr$<em>{0.2}$Ti$</em>{0.8}$O$_3$ (BZT)</td>
<td>1000 °C for 4 hr.</td>
<td>1100 °C, 1200 °C</td>
<td>30 °C/min, 40 °C/min</td>
<td>30 min, 20 min</td>
</tr>
</tbody>
</table>

3.4 Ferroelectric composite of x[(Ba$_{0.7}$Ca$_{0.3}$)TiO$_3$]-(1-x)[Ba(Zr$_{0.2}$Ti$_{0.8}$)O$_3$] (BCT-BZT)

After being separately calcinated nanopowders of Ba$_{0.7}$Ca$_{0.3}$TiO$_3$ and BaZr$_{0.2}$Ti$_{0.8}$O$_3$, the individual powders are mixed in the stoichiometric proportions, as x[(Ba$_{0.7}$Ca$_{0.3}$)TiO$_3$]-(1-x)[Ba(Zr$_{0.2}$Ti$_{0.8}$)O$_3$] to develop the solid solution of BCT-BZT ferroelectric ceramics with variation in x as x= 0.15, 0.3, 0.4 and 0.5. This mixture of BCT-BZT ceramics was grinded for 3-4 hours in an agate mortar for well mixing and results in the ferroelectric composition. PVA (polyvinyl alcohol) was added to the ferroelectric composition, PVA will act as a binder. After being mixed with PVA powder samples are pressed by using hydraulic press. The pressure applied is about 5-6 tons to get the material in a disk shape of 1 cm diameter and about 2 mm thickness. The pellets are subjected to microwave sintering at different temperatures with different soaking time. The detailed about the sintering temperature and holding time of proportion-wise ceramic samples are mentioned in table 3.2. After being sintered at different temperature pellet and powder samples are used for further characterizations. To understand importance of microwave sintering over the conventional sintering method 0.5[(Ba$_{0.7}$Ca$_{0.3}$)TiO$_3$]-0.5[Ba(Zr$_{0.2}$Ti$_{0.8}$)O$_3$] ceramic samples are sintered with microwave sintering as well as conventional sintering technique. While sintering with both the techniques the temperature was maintained at 1200 °C while the temperature rate and holding time for both the methods are different which was listed in table 3.2. After being sintered with two different techniques the ceramic samples are characterized by various techniques and the obtained results are compared and mentioned.
Table 3.2 Sintering parameters for x(BCT)-(1-x)BZT at various x values.

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>Sintering Temperature</th>
<th>Temperature rate</th>
<th>Soaking Time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Microwave Sintering</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.15[(Ba_{0.7}Ca_{0.3})TiO_3]-0.85[Ba(Zr_{0.2}Ti_{0.8})O_3] or 15BCT-85BZT</td>
<td>1200 °C</td>
<td>40 °C/min</td>
<td>20 min</td>
</tr>
<tr>
<td>0.3[(Ba_{0.7}Ca_{0.3})TiO_3]-0.7[Ba(Zr_{0.2}Ti_{0.8})O_3] or 30BCT-70BZT</td>
<td>1200 °C</td>
<td>40 °C/min</td>
<td>20 min</td>
</tr>
<tr>
<td>0.4[(Ba_{0.7}Ca_{0.3})TiO_3]-0.6[Ba(Zr_{0.2}Ti_{0.8})O_3] or (40BCT-60BZT)</td>
<td>1100 °C</td>
<td>30 °C/min</td>
<td>80 min</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1200 °C</td>
<td>40 °C/min</td>
</tr>
<tr>
<td>0.5[(Ba_{0.7}Ca_{0.3})TiO_3]-0.5[Ba(Zr_{0.2}Ti_{0.8})O_3] or 50BCT-50BZT</td>
<td>1100 °C</td>
<td>30 °C/min</td>
<td>80 min</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1200 °C</td>
<td>40 °C/min</td>
</tr>
<tr>
<td>0.5[(Ba_{0.7}Ca_{0.3})TiO_3]-0.5[Ba(Zr_{0.2}Ti_{0.8})O_3] or 50BCT-50BZT</td>
<td>Conventional Sintering</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1200 °C</td>
<td>5 °C/min</td>
</tr>
</tbody>
</table>

3.5 Synthesis of Co_{0.9}Ni_{0.1}Fe_{2}O_{4} (CNFO)

The powder particles of CNFO were also synthesized by employing the hydroxide co-precipitation route. Nitrate precursors of a analytical reagent (AR) grade Co(NO_3)_2·6H_2O, Fe(NO_3)_3·9H_2O, and Ni(NO_3)_2·6H_2O are used as the starting materials for synthesis of ferromagnetic CNFO. The precursors as mentioned are dissolved in double distilled water to form nearly 40mM solutions of the constituents. A mixture of NH_4OH and KOH is used as precipitants. It has been observed that Ni(OH)_2 is fractionally soluble in distilled water but insoluble in alkaline medium and therefore the precipitates are
thoroughly washed in distilled water 5-6 times keeping alkaline medium using NH₄OH (pH~ 10) [14]. The obtained precipitate were filtered and dried under infra red (temp~150 °C) light for 5-6 hours. The dried powder was grounded and calcinated at 1000 ºC for 4 hours to achieve the ferrite phase formation.

For studying various properties of ferromagnetic Co₀.⁹Ni₀.¹Fe₂O₄ by different characterization tools, small quantity of calcinated magnetic nanoparticles were taken and grounded for 3-4 hours. PVA was added to the magnetic nanoparticles and pressed by using hydraulic press. The was maintained between 5-6 tons to produce a disk shape pellet of material, has an diameter of about 1 cm while the thickness is about 2 mm. This disk shaped magnetic phase and powder samples are sintered with microwave sintering technique. The temperature was maintained at 1100 ºC for 30 minutes, while the rate of increasing temperature was maintained at 30 ºC/min. Flow chart of synthesis process of CNFO is as shown in figure 3.6.
3.6 Synthesis of magnetodielectric composites

Based on the discussion of literature survey here for formation of magnetodielectric composites BCT-BZT and CNFO are selected as ferroelectric and ferromagnetic phases as constituents in the composite. The calcinated powders were used to form the CNFO-(BCT-BZT) composite after rigorous grinding for 4-5 hours through in agate mortar and pestle. The MD composites are formed by the formula as,

\[ y[Co_{0.9}Ni_{0.1}Fe_2O_4] + (1-y) [x[Ba_{0.7}Ca_{0.3}TiO_3] - (1-x)[BaZr_{0.2}Ti_{0.8}O_3]] \]

Where \( y = 0.1, 0.2, 0.3, \) and \( 0.4 \) and \( x = 0.15, 0.3, 0.4 \) and \( 0.5 \). In the present thesis three compositions of \( y \) are selected as \( 0.15\text{BCT}-0.85\text{BZT}, 0.3\text{BCT}-0.7\text{BZT} \) and \( 0.5\text{BCT}-0.5\text{BZT} \) and included. These composite powder samples are pressed by applying uniaxial pressure of about 5 tons using hydraulic press to get the compound in a disk shape of 1 cm diameter and 2 mm thickness pellets. PVA is used as binder which is further removed on heating. Pellet samples of MD composites are sintered with microwave sintering. The details of sintering schedule and various maintained parameters for during heating process are mentioned in table 3.3. Sintered pellet samples are further characterized by various techniques to obtain their properties. Further out of three MD compositions reported two compositions are studied for the temperature dependent properties.

Table 3.3 Sintering parameters for \( x[\text{CNFO}]- (1-x)[y(\text{BCT})-(1-y)\text{BZT}] \) at various \( x \) and \( y \) values.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Sintering Temperature</th>
<th>Holding Time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Microwave Sintering</td>
<td>Rate</td>
</tr>
<tr>
<td>( x[\text{CNFO}]- (1-x) ) [0.15\text{BCT}-0.85\text{BZT}] Where ( x= 0.1, 0.2, 0.3 ) and 0.4</td>
<td>1200 °C</td>
<td>40 °C/min</td>
</tr>
<tr>
<td>( x[\text{CNFO}]- (1-x) ) [0.3\text{BCT}-0.7\text{BZT}], Where ( x= 0.1, 0.2, 0.3 ) and 0.4</td>
<td>1100 °C</td>
<td>30 °C/min</td>
</tr>
<tr>
<td></td>
<td>1200 °C</td>
<td>40 °C/min</td>
</tr>
<tr>
<td>( x[\text{CNFO}]- (1-x) ) [0.5\text{BCT}-0.5\text{BZT}], Where ( x= 0.1, 0.2, 0.3 ) and 0.4</td>
<td>1100 °C</td>
<td>30 °C/min</td>
</tr>
<tr>
<td></td>
<td>1200 °C</td>
<td>40 °C/min</td>
</tr>
</tbody>
</table>
3.7 Synthesis of thin film heterostructures

Here thin films of ferroelectric composition 0.5BCT-0.5BZT and magnetodielectric composition CNFO-(0.5BCT-0.5BZT) were synthesized using sol-gel technique. To develop thin films Pt/Ti/SiO2/Si is used as a substrate and gels of the ferroelectric and ferromagnetic phase were deposited on this substrate layer by layer.

3.7.1 Synthesis of 0.5(Ba0.7Ca0.3TiO3)-0.5(BaZr0.2Ti0.8O3) thin film

Ferroelectric thin films of 0.5(Ba0.7Ca0.3TiO3)-0.5(BaZr0.2Ti0.8O3) 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. Initially stoichiometric amount of barium acetate was dissolved in acetic acid; meanwhile a stoichiometric amount of calcium acetate was added in the solution. This solution stirred using magnetic stirrer with temperature at 60°C for 2 hours which removes water content from acetates. Then, 2-methoxyetahanol was added to the solution results in the formation of Ba/Ca sol. On the other hand titanium isopropoxide solution was dissolved in 2-methoxyethanol, after stirring for ½ hour stoichimetric amount of zirconium isopropoxide solution was added to the solution with continuous stirring and the temperature was maintained at 50 °C for 1 hour results in the Ti/Zr sol. The procedure is followed as the literatures [15-16]. Sol of Ba/Ca was added to the sol of Ti/Zr results in formation of BCT-BZT system. Small amount of 2-methoxyethanol added, and the final sol concentration was adjusted to 0.2 molar solution. This sol was stirred continuously for 12 hours without heating for proper mixing results in the viscous gel. This gel of 0.5BCT-0.5BZT deposited layer by layer on Pt/Si/SiO2 substrate using spin coater. RPM of spinning was adjusted at 600-700 rpm for initial 5 seconds, while at 3000 rpm for next 30 seconds. After deposition of each layer thin film, was pyrolyzed at 400 °C for 10 min. Subsequently four layers of the ceramic was deposited on the substrate to obtain the desired thickness and after final layer the film was annealed at 800 °C for 40 min using a conventional furnace. This film was further characterized for their properties by various techniques. The whole process of the thin film formation can be represented as flow chart shown in figure 3.7.
3.7.2 Synthesis of $\text{Co}_{0.9}\text{Ni}_{0.1}\text{Fe}_2\text{O}_4$ by Sol-gel

Ferromagnetic phase was synthesized using sol-gel method as reported above. For synthesis of CNFO the nitrate precursors cobalt nitrate $\text{Co(NO}_3\text{)}_2\cdot 6\text{H}_2\text{O}$, nickel nitrate $\text{Ni(NO}_3\text{)}_2\cdot 6\text{H}_2\text{O}$, and ferric nitrate $\text{Fe(NO}_3\text{)}_3\cdot 6\text{H}_2\text{O}$ are used as starting materials and 2-methoxyethanol as a solvent. As nitrates are easily soluble in 2-MOE, all the starting materials are separately dissolved in the 2-MOE after weighed in their stoichiometric proportions and stirred for $\frac{1}{2}$ hour results in formation of sol of each compound. Completely dissolved separate materials are mixed together for formation of magnetic CNFO sol. Final solution was adjusted to 0.2 molar with addition of 2-MOE. This so, was stirred at room temperature for 12 hours results in thick brownish colour gel. Flow chart of the complete synthesis process of CNFO is as shown in figure 3.8
Figure 3.8 Flow chart of synthesis of Co$_{0.9}$Ni$_{0.1}$Fe$_2$O$_4$.

### 3.7.3 Synthesis of magnetodielectric (MD) thin film heterostructures

Two phases, 0.5Ba$_{0.7}$Ca$_{0.3}$TiO$_3$-0.5BaZr$_{0.2}$Ti$_{0.8}$O$_3$ ferroelectric phase and Co$_{0.9}$Ni$_{0.1}$Fe$_2$O$_4$ ferromagnetic phase synthesized using sol-gel method are used for formation MD thin film heterostructures. At first, four layers of 0.5BCT-0.5BZT material are deposited on Pt/Si/SiO$_2$ substrate. Each layer of this material was pyrolyzed at 400 °C for 10 min and finally annealed at 800 °C for 40 min, which will result in complete phase formation of ferroelectric phase. Three layers of magnetic CNFO phase are deposited on the ferroelectric phase using the spin coating technique. The RPM was maintained at 500-600 rpm for 10 sec and at 3000 rpm for 40 sec. The films are pyrolyzed at 400 °C, 10 min after deposition of each layer of CNFO. After completion of three layers this films are annealed at 800 °C for 30 min results in formation of MD composite of two layers. These films are characterized to study their characteristic properties by various techniques.

### 3.8 Characterization techniques

Confirmation of various properties of the materials under study is a very important parameter in the field of research. The quality of work done depends on the techniques and standards used during the research. This section covers some important physical characterization technique used during the work. This gives the short information on instruments used for finding various parameters which are part of present investigation like, phase analysis by x-ray diffraction (XRD), morphological studies by scanning electron microscopy (SEM/FE-SEM), presence of functional groups by RAMAN spectroscopy, Magnetic Properties by Vibrating Sample Magnetometer, Dielectric
Properties by dielectric measurement system and polarization of materials with applied electric field with P-E loop measurement system. Different techniques used in the present study with their utility to find out different properties are summarized in the table 3.4.

Table 3.4 Summary of different characterization techniques used in the present study to find out the properties of the material

<table>
<thead>
<tr>
<th>Sr. no</th>
<th>Characterization Techniques</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>X-ray diffraction (XRD)</td>
<td>Identification of material and crystalline size determination</td>
</tr>
<tr>
<td>2</td>
<td>Scanning electron microscopy (SEM)</td>
<td>Surface morphology</td>
</tr>
<tr>
<td>3</td>
<td>Raman Spectroscopy</td>
<td>Stretching and vibration modes</td>
</tr>
<tr>
<td>4</td>
<td>Vibrating Sample Magnetometer</td>
<td>Magnetic(M-Hysteresis) Measurement</td>
</tr>
<tr>
<td>5</td>
<td>Dielectric Measurement</td>
<td>Dielectric Properties</td>
</tr>
<tr>
<td>6</td>
<td>Ferroelectric Measurement</td>
<td>P-E hysteresis loop</td>
</tr>
</tbody>
</table>

3.8.1 X-Ray Diffractometer

X-Ray diffraction (XRD) is well known technique to obtain the information of composition, phase and crystallite orientations of material [17]. Structure identification, determination of lattice parameters and grain size are based on the x-ray diffraction pattern. The phenomena of X-Ray diffraction can be considered as reflection of X-ray from the crystallographic planes of lattice and it is governed by Bragg’s equation,

\[ 2d \sin \theta = n \lambda \]  

Where d is lattice spacing, \( \lambda \) is wavelength x-ray, n is order of diffraction and \( \theta \) is diffraction angle.

The d values are calculated using above relation for known values of \( \theta \), \( \lambda \) and n. The X-ray diffraction data thus obtained is compared with American Standard for Testing of Materials (ASTM) or Joint Committee Powder Diffraction Standards (JCPDS) powder diffraction data to identify the unknown material. The sample used may be in the powder,
single crystal or thin film form. For measurement of crystallite size, Scherer’s formula was used which can be presented as follows [17].

\[ D = \frac{K\lambda}{\beta \cos \theta} \] ---- 3.2

Where, D is crystallite size, \( \beta \) is full width at half maxima of the peak (FWHM) in radians, \( \theta \) is Bragg's angle and K is constant. Value of K varies from 0.89 to 1.39, but for most cases it is closer to 1. In general x-ray diffractometer consists of three basic elements an X-ray tube, sample holder and an X-ray detector. The schematic of x-ray diffractometer is as shown in figure.

![Schematic of X-Ray Diffractometer](image)

Figure 3.9 Schematic of X-Ray diffractometer.

For generation of x-rays cathode ray tube is used where, electrons are generated by heating a filament and these electrons are accelerated towards target by applying voltage. These electrons with sufficient energy are bombarded on target material which dislodges inner shell electrons of the target material and finally this produces characteristic x-ray spectra of the material under process. These x-rays are collimated and directed onto the sample. As the sample and detector are rotated the intensity of the reflected x-rays is recorded. When geometry of the incident x-rays impinging on the sample satisfies the Bragg equation, constructive interference occurs. A detector records and processes this x-ray signal and covers the signal to a count rate which is then given to a device such as a printer or computer monitor.
Instrument Used for X-ray diffraction study with Specification

At IIT Bombay  
1) Make : Rigaku  
   Model : Smart Lab 3KW (HR-XRD)  
   Wavelength: CuKα₁ 1.54059 Å  
   Range of 2θ scanned: 10° to 180°  

At Institute Of Science Mumbai  
2) Make: Rigaku  
   Model: Miniflex-II  
   Wavelengths: CuKα₁ 1.54059 Å  
   Range of 2θ scanned: 10° to 180°

3.8.2 Scanning electron microscopy (SEM or FE-SEM)

FESEM is the acronym for Field Emission Scanning Electron Microscope. It was Ernest Ruska whom in his PhD thesis mentioned the potential for electrons to be used in a microscope. Field Emission scanning electron microscopy (FE-SEM) is an instrument, which is used to observe the morphology of the sample at higher magnification, higher resolution and depth of focus compared to an optical microscope [18]. The working principle of SEM or FE-SEM is same the only difference is in the type of emitter.

Under vacuum, electrons generated by a field emission source are accelerated in a field gradient. The beam passes through electromagnetic lenses, focusing onto the specimen. As result of this bombardment different types of electrons are emitted from the specimen. Detector situated inside catches secondary electrons, after comparing intensity of these secondary electrons with the scanning primary electron beam the image of sample surface is constructed. Finally the image is displayed on a monitor. The ray diagram of field emission scanning electron microscope is shown in Fig.3.10. And the ray diagram of emission of different types of electrons during scanning is shown in fig.3.11.
Fig. 3.10 Schematic of field emission scanning electron microscope.

Figure 3.11 Schematic of different types of rays emerges during scanning.
3.8.3 Energy dispersive spectroscopy (EDS)

The interactions of electron with solid as shown in fig 3.11 above leads to different signals like secondary electrons, backscattered electrons and x-rays which are characteristic to atoms of host lattice. The x-ray can be used for element detection and its qualification for compositional analysis. Here, the characteristic x-rays are identified by their energy using the solid state detectors. It consists of semiconductor Si (Li) counter and FET pre-amplifier, both cooled by liquid nitrogen and multichannel analyzer (MCA). The utility of this kind of spectrometer is based on two properties,

1) The excellent energy resolution of Si (Li) counters

2) The ability of MCA to perform rapid pulse height analysis.

Semiconductor counter produces pulses proportional to the absorbed energy with better energy resolution than any other counter. The silicon and germanium is the best detector for x-rays and γ rays respectively. The pure silicon in intrinsic semiconductor has very high electrical resistivity especially at low temperatures. It is very difficult to get pure silicon. Hence a p-type Si, lightly doped with boron, were used and to make it intrinsic this is again doped with Li. Typically the resolution of Si(Li) detector is given as 147 eV for manganese Kα radiation of 5.9 KeV energy. The energy dispersive system can analyze whole x-ray spectrum simultaneously. Due to low ionization potential of Si(Li) the count
rate is very high (>10,000 c/s/nA) and hence very low current is required. It is used in conjunction with SEM; TEM where current used is very low (of the order of pA).

3.8.4 Raman spectroscopy

Raman spectroscopy named after C. V. Raman, this is a spectroscopic technology which can be used to study the vibrational and rotational modes of the system after low frequency modes. This technique is based on inelastic scattering or the Raman scattering of monochromatic light. Usually a laser is used in the visible region, near IR or other excitation in the system, results in the energy laser photons being shifted up or down. This up or down shifting in energy will gives the information of about the phonon modes in system. Typically, lenses are used for collection of laser beam light spot illuminated from sample, these spot where sent through a monochromator having wavelength close to the laser line. These monochromatic lines are filtered out while the remaining collected light is dispersed on detector due to elastic Rayleigh scattering.

Principle of Raman Spectroscopy

The Raman Effect occurs when light impinges up on a molecule and interacts with the electron cloud and the molecule. For the spontaneous Raman effect, photon excites the molecule from the ground state to a virtual energy state. When the molecule excites and relaxes again with emission of photon it will creates a difference in energy of the energy between the original state and new state results in change of emitted photons frequency away from the excitation wavelength. If the molecule has more energy in the final vibrational state than the initial state, then the emitted photon will shift to a lower value of frequency due to which the total energy of the system remains balanced. This type of shift in emitted photons frequency is known to be as stokes shift. On the other hand if the molecule has less energy in final vibrational state than energy at initial state, then the emitted photon will shift to a higher frequency and this shift is known as anti-stokes shift. Due to the energy shifting between the photons and molecule during their interaction Raman scattering is known to be an example of inelastic scattering.

For exhibit an Raman effect in molecule it is necessary to coordinate the final vibrational state with respect to change in molecular polarization potential or amount of deformation of the electron cloud. Intensity of the Raman scattering can be determined using the amount of change in polarizability, whereas the pattern of shift in frequencies can be determined with the help of rotational and vibrational states of the sample. With the use
of Raman spectroscopy it is possible to study vibrational modes of solid, liquid and gaseous samples.

![Energy level diagram showing the states involved in Raman signal.](image)

**Figure 3.13 Energy level diagram showing the states involved in Raman signal.**

Typically Raman system consisted with five major components as follows,

1. Excitation source (Laser) to illuminate on sample.

2. Sample illumination system and light collection optics (lenses).

3. Wavelength selector or monochromator (Filter or Spectrophotometer).

4. Detector for detection (Photodiode array, CCD or PMT).

5. Computer Interfacing software for collection of data.

Schematic of Raman spectrometer is as shown in figure 3.14.
3.8.5 Vibrating sample magnetometer (VSM)

Vibrating sample magnetometer (VSM) is a measurement technique which allows determining the magnetic moment of a sample with very high precision. Vibrating sample magnetometer (VSM) systems are used to measure the magnetic properties of materials as a function of magnetic field, temperature, and time. The VSM was first designed by Simon Foner, in 1959 at the Lincoln laboratories [19]. A VSM is used to measure the magnetic behavior of magnetic materials. Vibrating Sample Magnetometer (VSM) is based on Faraday's law which states that an electromagnetic force is generated in a coil when there is a change in flux through the coil [20]. In the measurement setup, a magnetic sample is moving in the proximity of two pickup coils as indicated in Figure 3.15.
3.8.6 Ferroelectric hysteresis loop tracer

Measurement of polarization with the applied electric field (P-E hysteresis) was done using the instrument automatic ferroelectric hysteresis loop tracer from Marine India. The system consists of a PC, software, programmable voltage source and silicon oil bath. While doing the hysteresis measurement the sample was kept in the chamber of silicon oil bath, and a high voltage was supplied to the sample the polarization were recorded at room temperature. From the hysteresis loop measurement the parameters like $P_s$, $P_r$ and $E_c$ were calculated from the hysteresis loop. The measurement of the P-E hysteresis loop is based on the modified Sawyer Tower circuit as shown in chapter-I. P-E hysteresis measurements of all samples are done at Department of Physics, Savitribai Phule Pune University.

3.8.7 Dielectric measurement setup

The frequency and temperature dependent dielectric properties of all ferroelectric, magnetic and magnetodielectric samples were measured by using Wayne Kerr 6500B Precision Impedance Analyzer. For analysis of temperature dependent dielectric properties a custom made programmable furnace was used. The sample was immersed in the furnace like parallel plate capacitor, with sample holder and the corresponding values of capacitance and figure of merit ($Q$) were noted manually. Using these values the relative dielectric constant and loss tangent values are calculated as per formulas given earlier. The room temperature dielectric properties are measured with the variation of frequency.
Dielectric properties of all samples are measured at Department of Physics, The Institute of Science, Mumbai and K.B.P Mahavidyalaya Pandharpur. Some of the specifications are listed below.

1) Frequency range: 20 Hz to 50 MHz, 2) 0.05% basic measurement accuracy, 3) Comprehensive measurement functions, 4) Easy to use with large colour TFT touch screen, 5) Traditional LCR meter can be used for single and repetitive measurements. It is possible to measure following parameters using this instrument.

Capacitance (C), Inductance (L), Resistance (R), Reactance (X), Conductance (G), Susceptance (B), Dissipation Factor (D), Quality Factor (Q), Impedance (Z) Admittance (Y), Phase Angle (Ø).

![Figure 3.16 Photograph of dielectric measurement setup.](image)
Figure 3.17 Photograph of microwave furnace.
References