CHAPTER - VI

Characterization of [0.5BCT-0.5BZT] and CNFO-[0.5BCT-0.5BZT] Thin Film Heterostructures

6.1 Introduction

This chapter basically deals with characterization of 0.5BCT-0.5BZT ferroelectric and CNFO-(0.5BCT-0.5BZT) magnetodielectric thin film heterostructures. Both the thin films are deposited on Pt/Ti/SiO$_2$/Si substrate by spin coating technique. Here again the ferroelectric composition 0.5BCT-0.5BZT is selected due to its excellent properties at morphotropic phase boundary which is confirmed in chapter-IV and V in case of bulk phase material. In synthesis of magnetodielectric thin film ferromagnetic layers are deposited on ferroelectric layers using spin coating. Instead of microwave sintering here we have used conventional sintering technique in annealing of thin both films because there is possibility that the microwaves gets reflect back from the conducting substrate in the chamber of microwave furnace. Considering this fact here the conventional sintering method is selected for thin films deposited on Pt/Ti/SiO$_2$/Si substrates. Both the films are characterized by various techniques as x-ray diffraction, FE-SEM, AFM, and Raman spectroscopy, for their structural, morphological and vibrational band analysis. Here, the dielectric properties are measured with variation of frequency at room temperature using LCR-Q meter. All the observed properties through various characterizations of these thin film heterostructures are presented and discussed in this chapter.

6.2 Characterization of 0.5BCT-0.5BZT ferroelectric thin film

Ferroelectric 0.5BCT-0.5BZT thin films were prepared by sol-gel spin coating technique. The overall process of sol-gel formation and development of thin film on Pt/Ti/SiO$_2$/Si substrate by spin coating method were discussed in details and included in chapter-III, the schematic of thin film deposition process were represented in figure 6.1.
Figure 6.1 Schematic of 0.5BCT-0.5BZT thin film on Pt/Ti/SiO$_2$/Si substrate.

6.2.1 Structural analysis of 0.5BCT-0.5BZT thin film

Figure 6.2 shows the room temperature x-ray diffraction pattern of 0.5BCT-0.5BZT thin film deposited on Pt/Ti/SiO$_2$/Si substrate by spin coating and annealed at 800 °C. X-ray diffraction pattern was measured between angle 20° to 60° with scan rate of about 1°/min. It could be seen that the deposited 0.5BCT-0.5BZT ferroelectric thin film has a polycrystalline nature with (210) diffraction dominant peak. This indicates the formation of 0.5BCT-0.5BZT ferroelectric thin film on the substrate surface. With detection of one pyrochlore diffraction pattern shows that there is very low impurity exists in the as prepared thin film annealed at 800 °C [1]. Splitting at 20 ~ 44.5° in to 002/200 diffraction peaks confirms the tetragonal crystal structure of the BCT-BZT thin film as seen in bulk powder diffraction pattern. Again, here observed values of interplanar distance (d) are well matches with calculated values which confirm the existence of polycrystalline structure in the as prepared thin film. The lattice parameters values for tetragonal crystalline system, where $a = b$ and $c$ and the average crystallite size calculated from the diffraction pattern by Scherrer’s method were listed in table 6.1.
Figure 6.2 X-ray diffraction pattern of 0.5BCT-0.5BZT thin film on Pt/Ti/SiO$_2$/Si substrate.

Table 6.1 Parameters observed and calculated from x-ray diffraction pattern of 0.5BCT-0.5BZT thin film.

<table>
<thead>
<tr>
<th>Plane (hkl)</th>
<th>d- values</th>
<th>Lattice parameters</th>
<th>Crystallite size (nm)</th>
<th>Volume of unit cell v= (a$^2$c)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Obs.</td>
<td>Cal.</td>
<td>a(Å)</td>
<td>c(Å)</td>
</tr>
<tr>
<td>100</td>
<td>3.9979</td>
<td>4.006</td>
<td>4.006</td>
<td>4.068</td>
</tr>
<tr>
<td>110</td>
<td>2.8319</td>
<td>2.8326</td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>2.0402</td>
<td>2.034</td>
<td></td>
<td></td>
</tr>
<tr>
<td>210</td>
<td>1.7936</td>
<td>1.7915</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6.1.2 Surface morphology of 0.5BCT-0.5BZT thin film

Figure 6.3 (a) shows the surface FE-SEM image of the 0.5BCT-0.5BZT thin film developed on Pt/Ti/SiO$_2$/Si substrate through spin coating, annealed at 800 °C. FE-SEM image shows that as annealed 0.5BCT-0.5BZT thin film exhibits very dense microstructure with small circular grains which are connected to each other like a dumbbell, the average grain size is about ~ 80 nm. Again here the difference observed between average grain size
from microstructural analysis and average crystallite from structural analysis confirms that the grains are formed with no of crystallites.

Measurement of thickness of all deposited layers is necessary for the purpose of calculation of dielectric constant of the ferroelectric/dielectric thin film material. Now here figure 6.3 (b) shows the cross sectional view of the deposited 0.5BCT-0.5BZT thin film. It could be seen that each pyrolyzed layer of ferroelectric material well situated on one another, whereas the first layer adhere well to the surface of the substrate without any lattice imperfection which leads to formation of dielectric phase on metallic plate. Here each deposited layer of the 0.5BCT-0.5BZT thin film exhibits thickness of ~100 nm after pyrolyzation at 400 °C, and here we have deposited 5 layers of the ferroelectric 0.5BCT-0.5BZT on the substrate leads a final thin film with overall thickness of ~ 0.5 μm after 5 cycles of spin coating on Pt/Ti/SiO\textsubscript{2}/Si substrate.

![Figure 6.3 FE-SEM images of 0.5BCT-0.5BZT thin film on Pt/Ti/SiO\textsubscript{2}/Si substrate](image)

(a) Surface morphology, (b) Cross sectional view.

### 6.2.3 Atomic force micrographs of 0.5BCT-0.5BZT thin films

Figure 6.4 represents the AFM topography image of ferroelectric 0.5BCT-0.5BZT thin film in 2 dimensional and 3 dimensional views. Image confirms the spin coated thin film annealed at 800 °C has a homogeneous and denser microstructure. The observed root mean square (RMS) surface roughness value ~ 2.22 nm and the average grain size is about 60 nm, low value of surface roughness factor implies that the surface of thin film is very smooth, while the grain size measured from the AFM is a statistical average value [1]. WSxM [2], scanning probe microscopy software based on MS-Windows was used for develop AFM microstructural image and calculate other parameters. The roughness (RMS)
factor was calculated based on the height distribution of image and then assuming that the height follows a Gaussian distribution [2].

![AFM image of 0.5BCT-0.5BZT thin film on Pt/Ti/SiO$_2$/Si substrate]

Figure 6.4 AFM images of 0.5BCT-0.5BZT thin film on Pt/Ti/SiO$_2$/Si substrate.

6.2.4 Frequency dependent room temperature dielectric properties of 0.5BCT-0.5BZT thin film

Dielectric measurements of thin films were carried out using the Wayne-Kerr 6500B impedance analyzer as mentioned in chapter-III. For measurement of dielectric constant substrate surface (Pt/Ti/SiO$_2$/Si) is considered as bottom electrode and silver point having diameter of about 1 mm where made on the ferroelectric layer and this silver point is considered as an top electrode. Frequency dependent real part of permittivity ($\varepsilon_r$), was calculated using equation as,

$$\varepsilon_r = \frac{cd}{\varepsilon_0 A} \quad ----- 6.1$$

Where $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m, c- value of capacitance, d thickness of the overall layers of thin film, A is area of the small point on thin film surface, on that point value of capacitance were measured. Now here the imaginary part of the permittivity is calculated by using equation as,

$$\varepsilon'_r = \varepsilon_r \tan \delta \quad ----- 6.2$$

Real and imaginary part of dielectric constant and dielectric loss tangent (tan$\delta$) was measured at room temperature from 20 Hz to 1 MHz frequency range. Figure 6.5 shows
the room temperature frequency dependant variation of real \((\epsilon_r)\) and imaginary part \((\epsilon' \_r)\) of dielectric constant for 0.5BCT-0.5BZT thin film. It is seen that the real part of dielectric spectra exhibits similar kind of dispersion behaviour as seen in case of 0.5BCT-0.5BZT bulk phase material which is a ideal behaviour seen in case of ferroelectric/ dielectric material. Both dielectric constant values real as well as imaginary part has higher values at lower frequency range, decreases as the frequency increases from 20 Hz and at higher frequency the magnitude of dielectric constant remains unchanged. Here the magnitude of imaginary part has higher value at lower range of frequency than the real part of dielectric constant. This may due to high values of dielectric loss at lower frequency. It could be seen that the dielectric constant passes through two mild and broad relaxation peak one is near to the 2 KHz magnitude of frequency, while another nearer to the 1 MHz frequency range. Similar kind of nature is observed for imaginary part of dielectric constant. In general relaxation peaks in the dielectric constant occurs, when the frequency of observation is equal to the reciprocal of the relaxation time of the corresponding parallel RC equivalent circuit. Dielectric relaxation process at lower frequency may result from grain boundary where as relaxation process in the bulk of the grains ascribes to the dielectric dispersion at higher magnitude of frequency. Lower frequency high values of dielectric constant in thin films may be due to both effect of electrode and the interfacial polarization. This type of interfacial polarization can be explained on the basis of charge accumulation at the grain boundaries and at the interfaces between the sample and the electrode, called as space charge polarization [3]. Now here it could be seen that the dielectric dispersion of imaginary part is more at higher frequency and its value reaches to very lower magnitude. In lower frequency region, electric dipoles orient in parallel direction to the applied field which results in high values of capacitance and hence dielectric properties. On the other hand at higher frequency region \(\epsilon_r\) and \(\epsilon' \_r\) becomes constant as the electric dipoles stop to follow applied field. This region may be called as frequency independent region. Dielectric dispersion at higher frequency can be explained on the basis of Maxwell-Wagner model or Koop’s phenomenological theory of dielectrics [4-5].

Loss tangent \((\tan \delta)\) behaviour of 0.5BCT-0.5BZT thin film exhibits analogous behaviour to the dielectric constant. The calculated and observed values of loss tangent are coincides each other as seen from figure 6.5 (b). At lower frequency loss tangent has higher values and decreases with increase in frequency. Moreover loss tangent also exhibits the dispersion phenomenon as seen in case of real and imaginary part of dielectric
constant. At higher frequency range magnitude of imaginary permittivity has nearly equal to the loss tangent value.

Figure 6.5 (a) Room temperature frequency dependent variation of real part ($\varepsilon_r$) and imaginary part ($\varepsilon'_r$) of dielectric constant for 0.5BCT-0.5BZT thin film.

Figure 6.5 (b) Room temperature frequency dependent variation of dielectric loss tangent ($\tan\delta$ - cal. and obs.) of 0.5BCT-0.5BZT thin film.
6.2.5 Raman spectroscopy of 0.5BCT-0.5BZT thin film

Raman spectrum is the most important technique and found useful in detection of molecular vibrations directly, also provides information regarding the non-uniform distortions of the crystal lattice in short-range ordering [6]. Figure 6.6 shows Raman spectra of 0.5BCT-0.5BZT thin film on Pt/Ti/SiO$_2$/Si substrate. Raman vibrational modes are recorded at room temperature using the 532 nm exciting line of a He-Ne laser. Presence of Raman vibrational peaks confirms the formation of unit cell in the perovskite system. Here the observed Raman spectra confirm Ca$^{2+}$ and Zr$^{4+}$ ions are well situated in the BaTiO$_3$ lattice to form BCT-BZT perovskite structure [6]. Those Raman modes observed for 0.5BCT-0.5BZT powder sample are repeated in the ferroelectric thin film. All the peaks are assigned to their vibrational modes at corresponding Raman shift. It could be seen that the there are three broad vibrational spectra’s observed in 0.5BCT-0.5BZT thin film, among which two are observed at relatively high frequency value and one broad peak at lower frequency range having some shoulder peaks. Lower frequency broad peak centered at 194, 259 and 298 cm$^{-1}$ originates from A1(To) and [B1, E(TO+LO)] mode respectively, and the broad peaks at 525 and 724 cm$^{-1}$ are originate from [A1,E(TO)] and [A1,E(LO)] mode respectively. With this modes small peak exists at 816 cm$^{-1}$ results from A1 (g) mode. This observed vibrational modes are closely relates to the pure BaTiO$_3$ structure [6-7]. Here the peaks at lower region to lower frequency while, higher region peaks shifts towards higher frequency as compared to the Raman modes of the perovskite BT [6, 8]. Difference in the ionic radius of Ba$^{2+}$ and Ca$^{2+}$ as well as Zr$^{4+}$ and Ti$^{4+}$ ions may result in shifting of vibrational modes towards as this difference in ionic radius leads to distortion and disorder of lattice and results in widening of energy band [9].
6.3 Characterization of CNFO-(0.5BCT-0.5BZT) magnetodielectric thin film

Thin film of magnetodielectric composite was synthesized by sol-gel spin coating technique. Here Pt/Ti/SiO$_2$/Si was used as substrate, on which first four layers of ferroelectric (0.5BCT-0.5BZT) was deposited and annealed at 800 °C. After preparation of ferroelectric phase three layers of ferromagnetic (CNFO) phase was deposited on ferroelectric layer, here each layer was pyrolyzed at 400 °C while the final composition was annealed at 800 °C again. This annealed thin film was then characterized by many techniques and the obtained results are summarized in this section. The process of MD thin film formation was discussed in detail in chapter the schematic shown in figure 6.7 clears the thin film formation in detail.

6.3.1 Structural analysis of (0.5BCT-0.5BZT)-(CNFO) MD thin film

Figure 6.8 represents the x-ray diffraction pattern of CNFO-(0.5BCT-0.5BZT) magnetodielectric thin film deposited on Pt/Ti/SiO$_2$/Si substrate measured between the 2θ ranges from 20°-80°. All the observed diffraction peaks are represents the perovskite phase of 0.5BCT-0.5BZT and spinel structure of CNFO. Ferroelectric phase exhibits tetragonal crystal structure whereas ferrite phase has cubic crystal structure. The most prominent peak of ferroelectric phase is (110) while the (311) is the most intense peak corresponding to...
ferromagnetic CNFO phase, with these there are some other low intense peaks are observed which may be resulted from the substrate. Here the crystallite size was calculated from the Scherrer’s formula are 10.91 nm and 11.77 nm for ferroelectric and ferromagnetic phase respectively. Calculated lattice parameter from x-ray diffraction pattern and the volume of unit cell of ferroelectric and ferromagnetic phase are listed in table 6.2.

Figure 6.7 Schematic of CNFO-(0.5BCT-0.5BZT) magnetodielectric composite thin film on Pt/Ti/SiO\textsubscript{2}/Si substrate.

Figure 6.8 X-ray diffraction of CNFO-(0.5BCT-0.5BZT) thin film deposited on Pt/Ti/SiO\textsubscript{2}/Si substrate.
Table 6.2 Parameters calculated from the room temperature x-ray diffraction pattern of CNFO-(0.5BCT-0.5BZT) magnetodielectric thin film.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Lattice Parameters</th>
<th>Unit cell Volume</th>
<th>Crystallite Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNFO-(0.5BCT-0.5BZT)</td>
<td>a=b=c (Å)</td>
<td>a(Å)</td>
<td>c(Å)</td>
</tr>
<tr>
<td></td>
<td>8.39</td>
<td>4.025</td>
<td>4.031</td>
</tr>
</tbody>
</table>

6.3.2 Surface morphology and cross sectional view of CNFO-(0.5BCT-0.5BZT) MD thin film

Figure 6.9 (a) shows the surface morphological image (FE-SEM) of CNFO-(0.5BCT-0.5BZT) magnetodielectric thin film deposited on Pt/Ti/SiO₂/Si substrate. Here it could be seen that the as annealed thin film exhibits very dense microstructure. The circular small particles represent the ferroelectric phase whereas rectangular particles with larger grain size are of ferrite phase. As the magnetic layer was deposited on the ferroelectric layer it feels all the pour surface structures and combination exhibits a good microstructural image of magnetodielectric thin film and can be confirmed from the FE-SEM image. The overall grain size observed from the FE-SEM image is ~ 80 nm which confirms the numbers of crystallites are combined together in the formation of grains. The formation of magnetodielectric heterostructures can be confirmed from the morphological image of CNFO-(0.5BCT-0.5BZT) as the magnetic particles are grown in the ferroelectric rich region and occupy the surface throughout which confirms formation of grain-grain boundary interfacing of ferroelectric-ferromagnetic phase on the Pt/Ti/SiO₂/Si substrate.

Figure 6.9 (b) shows the cross sectional view of the similar magnetodielectric thin film heterostructures. From cross sectional view it could be seen that the overall thickness of this deposited thin film is ~ 0.6 μm, where the four layers of 0.5BCT-0.5BZT has thickness ~ 0.45 μm whereas the three layers of CNFO are deposited on ferroelectric phase has ~ 0.15 μm thickness. Cross sectional view of as annealed film exhibits three different
shades i.e. of Pt/Ti/SiO\textsubscript{2}/Si substrate on which layers of 0.5BCT-0.5BZT and the third is layers of CNFO material.

Figure 6.9 FE-SEM images of CNFO-(0.5BCT-0.5BZT) magnetodielectric thin film on Pt/Ti/SiO\textsubscript{2}/Si substrate (a) Surface morphology, (b) Cross sectional view.

6.3.3 Atomic Force Micrographs of CNFO- (0.5BCT-0.5BZT) MD thin film

Figure 6.10 shows the AFM images (2D and 3D view) of CNFO-(0.5BCT-0.5BZT) magnetodielectric thin film deposited on Pt/Ti/SiO\textsubscript{2}/Si substrate through spin coating method. These images are again developed by using the similar software as used in case of AFM images of 0.5BCT-0.5BZT ferroelectric thin film. The RMS roughness factor is \(\sim 1.93\) nm while the average particle size is \(\sim 80\) nm. Images reveals dense microstructure with smooth surface.

Figure 6.10 AFM images of CNFO-(0.5BCT-0.5BZT) thin film.
6.3.4 Frequency dependent dielectric properties of CNFO-(0.5BCT-0.5BZT) MD thin film

Figure 6.11 (a) shows the real ($\varepsilon_r$) and imaginary part ($\varepsilon'_r$) of dielectric constant of synthesized CNFO-(0.5BCT-0.5BZT) magnetodielectric thin film measured between frequency range from 20 Hz to 1 MHz at room temperature. The magnitude of real and imaginary dielectric constant increases in the magnetodielectric thin film as compared to the ferroelectric thin film. Also the values of the dielectric loss tangent are higher in the composite thin film. This increase in the values of dielectric constant may due to the more hopping of the Fe$^{2+}$ or Fe$^{3+}$ electrons at lower frequency range, whereas increase in conductivity results in the increase in the value of dielectric loss tangent [10]. Similar kinds of observations are seen in the CNFO-(0.5BCT-0.5BZT) magnetodielectric bulk composite. Here the dielectric constant values decreases with increase in the frequency. The continuous decrease in the dielectric constant at higher frequency may results due to interfacial polarization between ferroelectric-ferromagnetic layers or interfacial polarization between the composite layers and bottom electrode. The real and imaginary part of dielectric constant and dielectric loss tangent were measured using the similar equations as given in earlier section 6.1.4. Now figure 6.11 (b) shows the frequency dependent variation of calculated and observed loss tangent (tan$\delta$), here the loss tangent values are increased, with introduction of ferromagnetic phase in ferroelectric phase. This may result due to more conduction at lower frequency range in the ferromagnetic phase.

![Graph showing variation of real and imaginary dielectric constant](image)

Figure 6.11 (a) Variation of real ($\varepsilon_r$) and imaginary ($\varepsilon'_r$) dielectric constant with frequency for CNFO-(0.5BCT-0.5BZT) MD thin film.
Figure 6.11 (b) Variation of dielectric loss tangent (tan δ- obs. and cal.) with frequency for CNFO-(0.5BCT-0.5BZT) MD thin film.

6.3.5 Raman spectroscopy of CNFO-(0.5BCT-0.5BZT) MD thin film

Figure 6.12 shows the Raman spectroscopy of CNFO-(0.5BCT-0.5BZT) magnetodielectric composite thin film deposited on Pt/Ti/SiO₂/Si substrate annealed at 800 °C. All the modes are assigned to the corresponding vibrational peaks. Raman analysis confirms formation of composite having ferroelectric and ferromagnetic phase. Here it could be noted that the vibrational peaks \([A_1 \text{ (g)}]\) corresponding to CNFO spinal ferrite phase are more dominant while the vibrational modes \([A_1, E \text{ (TO)}]\) of ferroelectric [0.5BCT-0.5BZT] phase are more dominant at higher frequency. Similar Raman structure has been observed for thin film heterostructures as observed in CNFO-(0.5BCT-0.5BZT) bulk phase.
Figure 6.12 Room temperature Raman spectra of CNFO-[0.5BCT-0.5BZT] magnetodielectric thin film.

### 6.3.6 Magnetodielectric properties of CNFO-(0.5BCT-0.5BZT) MD thin film

Magnetodielectric effect in CNFO-(0.5BCT-0.5BZT) thin film was studied through measurement of dielectric permittivity under the application of magnetic field. Here the magnetic field was applied parallel to the surface of thin film from 0 Oe to 7 kOe. The magnetodielectric effect was measured using the formula as, [10]

\[
MC \, (\%) = \frac{\varepsilon(H) - \varepsilon(0)}{\varepsilon(0)} \times 100\%
\]

Where, \( \varepsilon(H) \) and \( \varepsilon(0) \) are dielectric constant values with applied magnetic field and at zero field. Figure 6.13 (a) shows the variation of dielectric constant with and without magnetic field for CNFO-(0.5BCT-0.5BZT) magnetodielectric thin film with frequency from 20Hz. It could be seen that the, dielectric constant value increase under the application of magnetic field. This suggests that the magnetodielectric effect posses’ positive magnitude. In general two effects are responsible for MD effect in ferroelectric-ferromagnetic composite. One is the due to the stress induced piezoelectric effect by the magnetic phase during the magnetostrictive phase. Whereas other is magnetoresistance effect combined with Maxwell-Wagner effect can results in magnetodielectric coupling in composite material [10-12]. Figure 6.13 (b) shows the variation of loss tangent with frequency and with applied magnetic field. It could be seen that, on application of magnetic field loss tangent value decreases at lower frequency and at higher the dispersion.
of loss tangent with and without applied magnetic field has similar nature. This dispersion of loss tangent may correspond to the electromechanical resonance frequency for the radial mode of the oscillations [12]. The calculated values of magnetodielectric coupling coefficient at various frequency at applied magnetic field 1 and 7 kOe were mentioned in table 6.3

Table 6.3 Values of MD (%) coupling coefficient with variation of frequency at applied magnetic field 1 and 7 kOe respectively.

<table>
<thead>
<tr>
<th>Sr No.</th>
<th>Applied Frequency (KHz)</th>
<th>MD (%) at Magnetic field= 1 kOe</th>
<th>MD (%) at Magnetic field= 7 kOe</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>0.28</td>
<td>0.73</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>0.49</td>
<td>0.88</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>0.34</td>
<td>0.54</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>0.63</td>
<td>0.67</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>0.71</td>
<td>0.72</td>
</tr>
<tr>
<td>6</td>
<td>1000</td>
<td>0.15</td>
<td>0.14</td>
</tr>
</tbody>
</table>

Figure 6.13 (a) Frequency dependent variation of dielectric constant \( (\varepsilon_r) \) with and without magnetic field for CNFO-(0.5BCT-0.5BZT) thin film.
Figure 6.13 (b) Frequency dependent variation of dielectric loss tangent (tanδ) with and without magnetic field for CNFO-(0.5BCT-0.5BZT) thin film.
References