CHAPTER - V

Characterization of Particulate Composites

5.1 Introduction

All the properties parent phases of materials under investigations in the present work as well as the properties of ferroelectric composite of $x\text{BCT} - (1-x)\text{BZT}$ characterized from different techniques are presented and discussed in earlier chapter-IV. Considering the results obtained through various characterizations of Ca and Zr substituted BaTiO$_3$ ceramic and their composition $x[(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3] - (1-x)[\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3]$ and objectives of the present work, this chapter is focused on selected particulate composites of ferroelectric phase i.e. $0.5[(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3] - 0.5[\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3]$, and magnetic phase $\text{Co}_{0.9}\text{Ni}_{0.1}\text{Fe}_2\text{O}_4$ (CNFO) to develop magnetodielectric bulk composites. Here we have selected 0.5BCT-0.5BZT composition as a ferroelectric phase, considering its comparable properties to the lead based materials like PZT, for example existence of morphotropic phase boundary (MPB) with high values of dielectric constant and low loss values (as observed) and higher value of transition temperature ($T_c$). On the other hand, $\text{Co}_{0.9}\text{Ni}_{0.1}\text{Fe}_2\text{O}_4$ is selected as a ferromagnetic constituent considering its magnetic and magnetostrictive properties. To study comparable effect of microwave sintering with conventional sintering, here the MPB composition 0.5BCT-0.5BZT was sintered with both techniques and the various physical and electrical properties are studied and compared in a beginning section of this chapter. This study implies how the microwave sintering overrules the conventional sintering technique. The properties obtained through various characterization techniques of [BCT-BZT]-CNFO magnetodielectric composite in the form of particulate composite are mentioned and discussed in the second part of the of this chapter.

5.2 Characterization of $0.5[(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3] - 0.5[\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3]$ ceramic sintered with conventional and microwave technique

The individual calcinated powder samples of BCT and BZT are mixed in stoichimetric proportion and grinded in agate mortar for 3-4 hours to prepare the ceramic composite of 0.5BCT-0.5BZT. These mixed powder samples are pressed by using hydraulic press, the pressure was maintained at about 5 tons to get the material in a disk shape of 1 cm diameter and about 2 mm thickness. Pressed disks (pellets) and remaining powder sample were sintered with two techniques fast microwave sintering and
conventional method at 1200 °C separately. In microwave sintering process the ceramic composition was held for 20 min (soaking time) at the desired temperature (1200 °C) the temperature increased at rate 40 °C/min with microwave furnace. Similar composition of ceramic sample was conventionally sintered at same temperature for 10 hours; while the heating rate was maintained at 5 °C/min. Figure 5.1 shows the detailed sintering schedule mechanism for sample sintered with both techniques. After being sintered with two different methods viz. Conventional and microwave technique, the samples were characterized by different techniques and the observed results are interpreted and compared in this section. Here after for simplification purpose lead free ferroelectric material 0.5BCT-0.5BZT sintered with microwave sintering technique will termed as MWS and on the similar way material processed with conventional sintering will termed as CS sample throughout the entire thesis.

![Figure 5.1 Schematic of detailed sintering schedule mechanism of MWS and CS.](image)

5.2.1 Structural analysis of 0.5BCT-0.5BZT MWS and CS Sample

Figure 5.2 shows the room temperature x-ray diffraction pattern for 0.5[(Ba0.7Ca0.3)TiO3]-0.5[Ba(Zr0.2Ti0.8)O3] ceramic composite sintered by a) conventional sintering (CS) and b) microwave sintering (MWS) technique at 1200 °C. X-ray diffraction pattern of 0.5BCT-0.5BZT ceramic samples measured between 20 = 20° to 80° show the pure perovskite phase with coexistence of tetragonal and rhombohedral crystal structures and no any impure phase was detected. Diffraction patterns of 0.5BCT-0.5BZT are assigned by the JCPDS card [05-626], [83-0368]. 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 [1-3]. Separation of reflection peak 002/200 around $2\theta = 45^\circ$ and peak 202/220 at $2\theta = 66^\circ$ confirms the existence tetragonal (T) and rhombohedral (R) structure respectively [3]. The splitting of peaks at the $2\theta$ angles $45^\circ$ and $66^\circ$ is shown in the inset of fig 5.1. More splitting of the peaks at the $2\theta$ is observed for the microwave sintered ceramic sample confirms maximum diffusion of Ca$^{2+}$ and Zr$^{4+}$ ions in BaTiO$_3$ lattice resulted from the fast sintering as compared to the slow conventional sintering. Also the diffraction peaks of the microwave sintered samples shifts towards higher angle. This result shows the need of higher sintering temperature for the ceramic sample processed with the conventional sintering method. Room temperature existence of rhombohedral and tetragonal crystal structure ascribes the morphotropic phase boundary nature of the 0.5BCT-0.5BZT ceramic material [2]. Crystallite size of the reflection with highest intensity was calculated by using Scherrer’s equation which is 47 nm and 57 nm for microwave sintered and conventionally sintered ceramic respectively. Lattice parameter (a, c) values, tetragonal c/a ratio and volume of cell are listed in table 5.1.

![Figure 5.2 Room temperature x-ray diffraction pattern of microwave and conventionally sintered 0.5BCT-0.5BZT.](image-url)
Table 5.1 Parameters obtained from the x-ray diffraction analysis of 0.5BCT-0.5BZT sintered with different techniques.

<table>
<thead>
<tr>
<th>Sintering Method</th>
<th>Lattice Parameters</th>
<th>Crystallite Size</th>
<th>Unit Cell Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a(Å)</td>
<td>c(Å)</td>
<td>c/a</td>
</tr>
<tr>
<td>Microwave</td>
<td>3.9878</td>
<td>4.035</td>
<td>1.011</td>
</tr>
<tr>
<td>Conventional</td>
<td>4.009</td>
<td>4.015</td>
<td>1.001</td>
</tr>
</tbody>
</table>

5.2.2 Microstructural analysis of 0.5BCT-0.5BZT MWS and CS Sample

Microwave and conventionally sintered 0.5BCT-0.5BZT ceramics were analysed for their microstructures by means of FE-SEM. Microwave and conventionally sintered 0.5BCT-0.5BZT ceramics were analysed for their microstructures by means of FE-SEM. Figure 5.3 (a) and 5.3 (b) show the FE-SEM images of microwave and conventionally sintered ceramic sample respectively. The microstructural image of sample processed with microwave technique shows denser nature where as sample processed with conventional method has less dense nature with existence of some pores in it. Formation of grains is more in the sample processed with MWS and the average grain size is about 0.87 μm where as sample processed with conventional average grain size is about 1 μm. This may resulted due the fast hybrid microwave heating from inside, which heats all the surface of sample in equal amount as compared to the conventional heating where the heating starts from outside of the sample surface. Moreover, enhancement in the density of ceramic sample processed with microwave sintering technique results in enhancement of electrical and physical properties of composition. Bulk density of 0.5BCT-0.5BZT pellet samples sintered with both techniques was determined using Archimedes principle. The measured bulk density of sample sintered with microwave sintering is 5.62 g/cc-3 and relative density 93.35 %, where as ceramic sample sintered with conventional method shows bulk density is 5.28 g/cc-3 and relative density is 87.70 %. Presence of all elements used to synthesis lead free 0.5BCT-0.5BZT composite was confirmed by energy dispersive X-ray spectroscopy (EDS) analysis. Figure 5.3 (c) and 5.3 (d) show the obtained EDS results of 0.5BCT-0.5BZT ceramic sample processed with different techniques MWS and CS.
respectively. EDX spectrum of both samples show peaks corresponding to those elements which are incorporated in the composition and no other any peak related to any impure phase were not noticed in present composition. Weight percentage and atomic percentage of elements varies with variation of sintering mechanism which as shown in tables included in the EDS spectrum of the MWS and CS sample respectively.

Figure 5.3 FE-SEM images of 0.5BCT-0.5BZT (a) Microwave sintering (b) Conventional sintering.

Figure 5.3 EDS spectrum of 0.5BCT-0.5BZT (c) Microwave sintering (d) Conventional sintering.

5.2.3 Dielectric properties of 0.5BCT-0.5BZT MWS and CS sample

Dielectric constant of 0.5BCT-0.5BZT sample was measured at the different frequencies varying from 500 Hz up to 1MHz in temperature range from -10 °C to 180 °C. The sintered pellets of ceramic samples was pasted with the silver on both sides for conducting purpose and dried at 150 °C for 2 hours and then used for dielectric measurement. The variation of dielectric constant and dielectric loss with temperature of microwave sintered ceramics is already presented in figure 4.19 (d) and 4.20 (d)
respectively, and for conventional sintered ceramic it is shown in figure 5.4 (a) and (b) respectively. Broad dielectric anomaly is observed for both ceramic samples sintered with different methods. Similar type of behaviour is observed from temperature dependent dielectric constant spectra for both the samples. Here, the dielectric constant increases with increase in temperature for every applied frequency reaches maximum and then decreases. Microwave sintered sample found to exhibit a dielectric constant ~ 2400, while the ceramic processed with conventional sintering method shows the lower dielectric constant value ~ 1200 at room temperature. Room temperature higher dielectric constant value in MWS ceramic sample as compared to CS ceramic sample resulted due to the higher densification of ceramics. As in fast microwave sintering process the grain growth is uniform, and this uniformity of grains, well crystallinity enhances the permittivity value of the ceramic material [4]. More over the ferroelectric-paraelectric transition temperature (Tc) of the microwave sintered ceramic sample shifts to higher temperature. Tc of conventionally sintered 0.5BCT-0.5BZT ceramic was below 100 °C (~ 96 °C), while ceramic sintered with microwave sintering technique has Tc nearly equals to the transition temperature of pure BaTiO₃ lattice (~ 135 °C). Shifting of Tc mainly the composition dependent phenomenon also, the well orientation of the grains results in the improved electrical properties [5]. Internal stress increases as the free energy of the ferroelectric increases and Curie temperature decreases. The internal stress in the ceramic material can be relieved by pores. In the dense ceramics with small amounts of pores, internal stress is mainly relieved by grain-boundary sliding [6]. Thus, the dense ceramics with fine grains should have higher Tc than those with coarse grains [5]. Ceramic samples of 0.5BCT-0.5BZT sintered by both methods show the smaller dielectric anomaly near room temperature (~23 °C). This anomaly can be resulted from rhombohedral-tetragonal (R-T) phase transition at room temperature [2]. Room temperature transition of R-T phase and ferroelectric-paraelectric (T-C) transition at Tc confirms existence of morphotropic phase boundary (MPB) in as synthesized 0.5BCT-0.5BZT ceramic samples processed by both methods.

Lower values of dielectric loss are observed for MWS sample, while CS sample exhibits higher values of loss tangent as compared with MWS sample. It could be seen that loss tangent spectra show a similar kind of behaviour as the dielectric constant with temperature. As like, the dielectric constant spectra the loss tangent spectra also show the two maxima associated with the R-T and T-C phase transition [7]. Presence of broad dielectric constant anomaly, confirms the diffuse phase transition behaviour in ceramics
sintered by both methods. Evaluation of the phase transition mode is done by using the empirical comprehensive power law [2].

![Graph](image)

**Figure 5.4 (a)** Temperature dependent variation of dielectric constant ($\varepsilon_r$) of 0.5BCT-0.5BZT sintered with conventional method.

![Graph](image)

**Figure 5.4 (b)** Temperature dependent variation of dielectric loss tangent ($\tan\delta$) of 0.5BCT-0.5BZT sintered with conventional method.

Diffusivity factor $\gamma$ of samples sintered by CS and MWS technique is calculated in higher temperature range at 10 KHz frequency from slope of log ($1/\varepsilon_r - 1/\varepsilon_{rm}$) versus log (T - Tm) graph as shown in the figure. 5.5. Calculated value of $\gamma$ is 1.87 and 1.93 for CS and MWS 0.5BCT-0.5BZT ceramic respectively. It shows that the as synthesized ceramic
samples sintered by both techniques are neither normal ferroelectrics nor the relaxor type of ferroelectrics. Diffusivity factor ($\gamma$) value of MWS 0.5 BCT-0.5 BZT ceramic sample is higher than that of CS ceramic sample, which clears that the microwave sintered ceramic sample show more diffuse phase transition nature and founds closer to relaxor type behaviour. This may resulted due to the fast heating phenomenon as contest between Ti$^{4+}$ and Zr$^{4+}$ ions increases to reside in the same crystallographic site B, leads to increase in composition fluctuation of different polar micro-regions and hence increase in diffuse phase transition nature [8].

![Diffusivity graph](image)

Figure 5.5 Diffusivity graph of 0.5BCT-0.5BZT sintered with conventional and microwave technique.

5.2.4 Raman spectroscopy analysis of 0.5BCT-0.5BZT MWS and CS Sample

Figure 5.6 shows the room temperature micro-Raman spectra for 0.5BCT-0.5BZT ceramic samples sintered at 1200 °C with conventional and microwave sintering technique. Ceramic sample sintered with both methods exhibits some weak modes at 142 cm$^{-1}$, 186 cm$^{-1}$, with broad peak at 242 cm$^{-1}$ are assigned to $A_1$(TO) phonon mode [2]. Whereas shoulder peak at 302 cm$^{-1}$, asymmetric peak at 519 cm$^{-1}$ and broad weak peak at 721 cm$^{-1}$ are assigned to $B_1$ and/or $E$(TO+LO), $A_1$(TO) and/or E(TO) and $A_1$(LO) and/or E(LO) respectively [2]. The modes $A_1$(TO)and E(TO) are all assigned to Ti – O bonds, and the modes $A_1$(LO) and E(LO) are contributed to Ba – O bonds [8]. Also weak Raman active asymmetric breathing mode ($A_{1g}$) was seen at 816 cm$^{-1}$ [10] this peak is clearer in MWS sample while in CS sample it was less intense. This type of high frequency peak may due
to the presence of several dissimilar atoms at A- and B-sites in BCT-BZT ceramic samples. Higher frequency peaks at 519, 721 cm\(^{-1}\) are expected due to the different ionic radius between Ba\(^{2+}\)/Ca\(^{2+}\) and Ti\(^{4+}\)/Zr\(^{4+}\) ions which results in the distortion of the lattice structure and effect in energy band widening [10]. A Raman peak at 300 and 719 cm\(^{-1}\) confirms existence of tetragonal symmetry at room temperature in 0.5BCT-0.5BZT ceramic sample [2].

![Raman spectra of 0.5BCT-0.5BZT ceramic sintered with microwave and conventional sintering method.](image)

Figure 5.6 Raman spectra of 0.5BCT-0.5BZT ceramic sintered with microwave and conventional sintering method.

5.2.5 Ferroelectric hysteresis (P-E) measurements of 0.5BCT-0.5BZT MWS and CS sample

Figure 5.7 shows the room temperature ferroelectric hysteresis of 0.5BCT-0.5BZT sample sintered with both techniques. It is seen that P-E loops of both samples are well saturated with regular shape confirms presence of typical ferroelectric behaviour in 0.5BCT-0.5 BZT. Observed ferroelectric hysteresis loops are slim with saturation polarization (Ps) 4.28 µC/cm\(^2\) for ceramic with conventional sintering and 7.62 µC/cm\(^2\) for microwave processed ceramic sample. While, nearly equal value of remanant polarization (Pr) i.e. ~ 0.50 µC/cm\(^2\) is obtained in both CS and MWS samples. Both samples have a low coercive field (Ec) value. The ceramic sample MWS shows the slim ferroelectric loop and the observed Ec value ~2.5 Kv/cm is smaller than conventionally sintered ceramic sample which is 4.6 Kv/cm. This low Ec value and high dielectric constant value of microwave sintered ceramic sample confirms that the obtained material is soft ferroelectric material
These observed ferroelectric values of 0.5BCT-0.5BZT samples are in good agreement with previously reported elsewhere [8]. Typical ferroelectric relaxor behaviour is confirmed from the slim hysteresis loops and the relaxor type nature is more in MWS sample as compared with CS sample. Due to the fine grain structure MWS sample tends more towards the relaxor phenomenon. [9]. More relaxor type behaviour of MWS sample, also confirmed from diffusivity factor (γ) value. Formation of more grain boundaries due to slow and non-uniform heating of ceramic materials processed with the conventional technique results in the lower ferroelectric properties as compared with ceramic sample processed with fast microwave sintering technique [12].

Figure 5.7 Room temperature ferroelectric hysteresis loop of 0.5BCT-0.5BZT sintered by MWS and CS method (measuring frequency 10 KHz).

5.3 Characterization of (0.5BCT-0.5BZT)-(CNFO) particulate magnetodielectric composite

Concurring with the results obtained through the various characterization techniques here we have selected 0.5[(Ba_{0.7}Ca_{0.3})TiO_{3}]-0.5[Ba(Zr_{0.2}Ti_{0.8})O_{3}] as a ferroelectric composition with morphotropic phase boundary, whereas Co_{0.9}Ni_{0.1}Fe_{2}O_{4} is selected as a magnetostrictive phase considering its magnetic and electrical and magnetostrictive properties. This magnetodielectric composite was developed in the bulk powder/pellet from as well in the form of thin film heterostructures by spin coating method. Here the bulk phase of the MD composite material was sintered with microwave sintering technique at 1100 °C and 1200 °C. The MD composites are also synthesized with
the variation in ferroelectric phase as \(x[(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3]-(1-x)[\text{Ba(Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3] \) where \(x = 0.15, 0.3\) and \(0.4\), whereas part of magnetic material kept unchanged throughout. This section includes only the properties of magnetodielectric composition having morphotropic phase boundary ferroelectric system i.e. 0.5BCT-0.5BZT. The synthesis process of particulate magnetodielectric composite is similar as discussed in chapter-III. Here the results obtained through application of various characterization techniques on CNFO-(0.5BCT-0.5BZT) MD bulk phase composite are presented in this section.

Now here the calcinated powders of ferroelectric (0.5BCT-0.5BZT) and ferromagnetic (CNFO) are used as two constituents and these powders are mixed as per formula,

\[
x[\text{Co}_{0.9}\text{Ni}_{0.1}\text{Fe}_2\text{O}_4] + (1-x) \{0.5[(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3-0.5[\text{Ba(Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3]]
\]

Where, \(x = 0.1, 0.2, 0.3\) and \(0.4\). These mixed powders are rigorously grinded for 4-5 hours for complete mixing of ferroelectric and ferromagnetic constituent to form the MD composite. These mix powder composites are compressed into disk shaped pellet form with the help of hydraulic press. PVA was used as binder, while the pressure was maintained at 4-5 tons. These pellets are small quantity of powder sample of each composition are sintered at 1100 \(^\circ\)C for 30 min and at 1200 \(^\circ\)C for 20 min with the microwave sintering technique. These samples were characterized by various characterization techniques and the results obtained are interpreted and discussed as below.

### 5.3.1 Structural analysis of xCNFO-(1-x)(0.5BCT-0.5BZT) MD particulate composite

Figure 5.8 shows the room temperature x-ray diffraction of the CNFO-(0.5BCT-0.5BZT) magnetodielectric composite sintered at 1100 \(^\circ\)C for 30 min mean while the diffraction patterns of individual phases of CNFO and 0.5BCT-0.5BZT phase are also included here. Whereas, figure 5.9 represents the room temperature x-ray diffraction pattern of only magnetodielectric composite with variation of x CNFO content sintered at 1200 \(^\circ\)C for 20 min. Now here from figure 5.8 it could be seen, the parent 0.5BCT-0.5BZT shows the perovskite polycrystalline crystal structure with coexistence of tetragonal and rhombohedral phase which can be characterized by splitting of the peaks at \(\sim 20 = 45^\circ\) of (002)/(200) and the peak (220)/(202) between \(20 = 65–66^\circ\). The peaks corresponding to the BCT-BZT matches well with JCPDS card no. 05-0626, 85-0368 [11] as reported in previous chapter. As there is no any impurity peaks are identified in the diffraction pattern it shows that Ca and Zr ions are well diffused into the BaTiO\(_3\) lattice which forms a
homogenous solid solution of BCT-BZT. The ferrite CNFO exhibits the spinel structure with space group Fd3m. All the peaks of CNFO are well matches with standard pattern (JCPDS card no. 22-1086) [14]. 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 \( x = 0.4 \). The magnetodielectric composite material sintered at both temperature shows similar behaviour. Also it is observed that the introduction of the ferrite phase in the piezoelectric material causes the splitting of the peaks of the ferroelectric phase [15], whereas here it could be seen that the x-ray diffraction angles of composites shifts towards slightly lower higher angles up to \( x = 0.2 \) and then again shifts slightly lower angle in case of MD composite sintered at 1200 °C while in composite sintered at 1100 °C shifting of diffraction peaks is occurs with alternative x content. This shifting of angles may due to more or less mixing of CNFO in ferroelectric phase. The calculated lattice parameters for composites sintered at 1100 °C and of ferroelectric, ferrite phase separate are listed in table 5.2, on the other the parameters observed from MD composites sintered at 1200 °C are listed in table 5.3. The crystallite size for BCT-BZT phase and of CNFO phase was calculated by using the Debye-Scherrer equation; the most prominent peaks of the respective phase with higher intensities are used for calculation of crystallite size.

![Figure 5.8 Room temperature x-ray diffraction pattern of 0.5BCT-0.5BZT, CNFO and (0.5BCT-0.5BZT)-CNFO MD composite sintered at 1100 °C.](image)
Table 5.2 Parameters obtained from the x-ray diffraction analysis of $x[\text{CNFO}]-(1-x)[0.5\text{BCT}-0.5\text{BZT}]$ for $x = 0, 0.1, 0.2, 0.3, 0.4$ and 1 sintered at 1100 °C.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Lattice parameters</th>
<th>Crystalite Size (nm)</th>
<th>Unit cell Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ferrite</td>
<td>Ferroelectric</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a=b=c$ (Å)</td>
<td>$a$ (Å)</td>
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<tr>
<td>50BCT-50BZT</td>
<td>-----</td>
<td>3.9615</td>
<td>3.9932</td>
</tr>
<tr>
<td>CNFO</td>
<td>8.37</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>10CNFO-90 (50BCT-BZT)</td>
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</tr>
<tr>
<td>20CNFO-80 (50BCT-BZT)</td>
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<td>30CNFO-70 (50BCT-BZT)</td>
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<tr>
<td>40CNFO-60 (50BCT-BZT)</td>
<td>8.40</td>
<td>4.0231</td>
<td>4.0538</td>
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</table>

Figure 5.9 Room temperature x-ray diffraction pattern of $(0.5\text{BCT}-0.5\text{BZT})$-CNFO magnetodielectric composite sintered at 1200 °C.
Table 5.3 Parameters obtained from the x-ray diffraction analysis of x[CNFO]-[1-x][0.5BCT-0.5BZT] for x= 0.1, 0.2, 0.3, and 0.4 sintered at 1200 °C.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Lattice parameters</th>
<th>Crystal lattice Size (nm)</th>
<th>Unit cell Volume</th>
</tr>
</thead>
<tbody>
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<td></td>
<td>Ferrite a=b=c Å</td>
<td>Ferroelectric a(Å) c(Å) c/a</td>
<td>Ferrite a³</td>
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<tr>
<td>10CNFO-90 (50BCT-BZT)</td>
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<td>42.65</td>
<td>586</td>
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</tr>
<tr>
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<td>40CNFO-60 (50BCT-BZT)</td>
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<td>57.34</td>
<td>588</td>
</tr>
</tbody>
</table>

5.3.2 Surface morphology of xCNFO-(1-x)(0.5BCT-0.5BZT) MD composites

Figure 5.10 (a), (b), (c) and (d) show the FE-SEM images of [x CNFO-(1-x)(0.5BZT–0.5BCT)] for x = 0.1, 0.2, 0.3 and 0.4 multiferroic composite respectively sintered at 1100 °C. The micrographs show the agglomeration of ferroelectric and ferromagnetic phase. The composites are formed dense without any pores as seen in the micrographs. As the preparations of the composites were done in ferroelectric rich region spinel CNFO are well dispersed in the perovskite BCT-BZT matrix. The composites shows the compact arrangement of microstructure with the distinguishable phases which can be revealed from the images, which implies the successful formation of x(CNFO)-(1-x)(0.5BCT-0.5BZT) composites, may results in good magnetoelectric coupling. This is in well agreement with the x-ray diffraction pattern. The elemental distribution for all the composite samples is confirmed by the energy dispersive analysis (EDS) study. Figure 5.11 (a), (b), (c) and (d) shows the EDS spectrum of the MD composite sintered at 1100 °C, Inset of spectrum table gives the information of elements in the final composition in weight (%). The weight (%) of elements varies according with variation of CNFO concentration in MD composite. EDS shows the presence of all the elements in the composites without formation of any impurity phase. Similar MD composition was sintered at higher temperature (1200 °C) and characterized by FE-SEM. Figure 5.12 (a), (b), (c) and (d) show the microstructural images of xCNFO-(1-x)(0.5BCT-0.5BZT)
multiferroic composite at $x = 0.1, 0.2, 0.3$ and $0.4$ respectively. Here, from the microstructural images of MD composite sintered at relatively higher temperature, it is seen that the formation of grains were started and very less agglomeration is observed as compared with the MD composite sintered $1100 \, ^\circ C$. Again here the microstructural images reveal dense morphology for all MD composites. High dense composition with well orientation will improve the electrical as well as magnetic properties of the MD composition in equal. MD composite sintered at $1200 \, ^\circ C$ are also analysed by EDS and the observed elemental spectra is represented in figure 5.13 (a), (b), (c) and (d) with for $x = 0.1, 0.2, 0.3$ and $0.4$ respectively. Presence of all elements in weight (%) and atomic (%) were represented in table inset of each EDS spectrum which shows variation in the weight (%) and atomic (%) of each element as the concentration $x$ changes from 0.1 to 0.4. Spectrum reveals presence of elements only from CNFO and BCT-BZT phase in the MD composite.

Figure 5.10 FE-SEM images of $x$ (CNFO) - $(1-x)(0.5BCT-0.5BZT)$ magnetodielectric composite sintered at $1100 \, ^\circ C$ where (a) $x = 0.1$, (b) $x = 0.2$, (c) $x = 0.3$ and (d) $x = 0.4$. 

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Figure 5.11 EDS spectra of \( x \) (CNFO) - \((1-x)(0.5BCT-0.5BZT)\) magnetodielectric composite sintered at 1100 °C where (a) \( x = 0.1 \), (b) \( x = 0.2 \), (c) \( x = 0.3 \) and (d) \( x = 0.4 \).

Figure 5.12 FE-SEM images of \( x \) (CNFO) - \((1-x)(0.5BCT-0.5BZT)\) magnetodielectric composite sintered at 1200 °C where (a) \( x = 0.1 \), (b) \( x = 0.2 \).
Figure 5.12 FE-SEM images of x (CNFO) - (1-x)(0.5BCT-0.5BZT) magnetodielectric composite sintered at 1200 °C where (c) x = 0.3 and (d) x = 0.4.

Figure 5.13 EDS spectra of x (CNFO) - (1-x)(0.5BCT-0.5BZT) magnetodielectric composite sintered at 1200 °C where (a) x = 0.1, (b) x = 0.2, (c) x = 0.3 and (d) x = 0.4.

5.3.3 Dielectric properties of xCNFO-(1-x)(0.5BCT-0.5BZT) MD composites

Dielectric properties of the MD composite samples are measured using the circular pellet samples sintered at 1100 °C and 1200 °C respectively. Here the dielectric constant
and loss tangent was measured at room temperature by varying frequency. The temperature dependent dielectric properties are measured at different frequency range.

5.3.3.1 Frequency dependant room temperature dielectric properties

Room temperature frequency dependence behaviour of dielectric constant ($\varepsilon_r$) and loss tangent (tan $\delta$-inset) is as shown in figure 5.14 (a) and 5.14 (b) for $x$(CNFO)-1-$x$(0.5BCT-0.5BZT) where $x = 0.1$, 0.2, 0.3 and 0.4 sintered at 1100 °C and 1200 °C respectively using the microwave sintering. All the four composites constituted with ferroelectric and ferrite phase sintered at different temperatures are exhibiting an identical behaviour. It is observed that, at lower frequencies the value of dielectric constant decreases for ferrite-ferroelectric composite up to $x = 0.3$ and it again increases at $x = 0.4$ for MD composition sintered at 1100 °C. The increase in the relative permittivity at $x = 0.4$ might be due to the main contribution of the space charge polarization at the lower frequencies beyond $x = 0.3$ ferrite contain in the composite. Also at $x = 0.4$ in the magnetodielectric composite, it is expected that the Co$^{2+}$ and/ or Fe$^{3+}$ ions of ferrite side will enter in to the ferroelectric side straight forward which causes disorder in ion arrangement on the ferroelectric side. This disordered arrangement leads to dipolar or space charge polarization at lower frequency [16]. Now here the magnetodielectric composites sintered at 1200 °C for 20 min show (as shown in fig. 5.13 (b) that the at lower magnitude of frequency dielectric constant increases with increase in magnetic phase (CNFO) content in the MD composition except at $x = 0.3$ it slightly decreases. The dielectric dispersion in the low frequency region can be explained on the basis of Maxwell- Wagner polarization theory. Heterogeneous composites having the material phases with significantly different conductivities Maxwell–Wagner type interfacial space charge polarization mechanism plays an important role in these types composite materials. At higher frequency the dielectric constant ($\varepsilon_r$) possesses nearly constant behavior might be possibly due to the inability of various polarizations to follow the applied alternating field. In composites, the electron hopping between Fe$^{2+}$-Fe$^{3+}$ results in orientational polarization and at higher frequency this hopping of electron between Fe$^{2+}$-Fe$^{3+}$ does not follow the applied electric field [17]. The dielectric loss tangent observed (shown as inset of both figures) from the composites sintered at 1100 °C and 1200 °C has similar type of behaviour, loss tangent increases with increase in CNFO content at lower frequency, whereas decreases with increase in frequency. With increasing frequency decrease of the relative permittivity and the loss tangent is observed in the normal dielectric materials. To describe with frequency
dielectric dispersion in material Maxwell-Wagner polarization theory (interfacial polarization theory) or Koop’s phenomenological theory can be used. Due to inhomogeneous dielectric structure, the contribution of the space charge polarization at lower frequencies is more which results in the high values of the dielectric constant at lower frequencies. In the magneto-electric composites the two mediums i.e. ferrite phase and the ferroelectric phase have the dissimilar permittivity and the resistivity, when an electrical field is applied to the composite; space charges provided by the ferrite phase accumulate at the interface of the two phases. The high value of permittivity observed in the lower frequency range are not usually intrinsic but are attributed to the fact that ferroelectric regions are bounded by non-ferroelectric regions as in case of relaxor ferroelectric materials. With the increasing frequency the dielectric constant decreases and remains constant at higher frequencies. As in inhomogeneous dielectric structure the space charge carriers requires limited time to line in the axes parallel to the applied frequency, due to this the dielectric constant decreases as frequency increases [17].

Figure 5.14 (a) Room temperature frequency dependent dielectric properties of x(CNFO)-(1-x)0.5BCT-0.5BZT sintered at 1100 °C.
5.3.3.2 Temperature dependent dielectric properties

Figure 5.15 (a), (b), (c) and (d) show the temperature dependant variation of dielectric constant of $x$[CNFO]-(1-$x$)[0.5BCT-0.5BZT] magneto-dielectric composites for $x = 0.1, 0.2, 0.3$ and 0.4 respectively sintered at 1100 °C, in the temperature range from room temperature up to 500 °C at different applied frequencies between 500 Hz - 1 MHz. It is observed that for each value of $x$ dielectric constant of the magneto-dielectric constant increases with the temperature. Two peaks are observed where the dielectric constant have higher values depending on the temperature in each of the composition, one is of the ferroelectric to paraelectric transition of 0.5BCT-0.5BZT at lower temperature (120 °C - 130 °C) [13] and other one corresponds to the magnetic transition temperature of CNFO (~ 500 °C) [15] at higher temperature. The phase transition in magnetolectric composite can be explained on the basis Landau-Devonshire theory, according to which magnetolectric coupling in the composites may give rise to anomaly in the dielectric constant [13, 18]. The observation of two dielectric anomalies one at lower temperature and another at higher temperature strongly indicates presence of Magneto-electric/Magneto-dielectric coupling effect in the CNFO-[BCT-BZT] composite. Increase in the ferrite phase causes the shifting of dielectric anomaly of the ferrite phase towards higher temperature. This may be ascribed to the fact that electric field inducing magnetic phase transition depends on the strength of electromagnetic interactions between constituent phases, which in fact depends on the
molar ratio of the phases. All the magneto-dielectric composites indicate the relaxor behaviour as the dielectric anomaly shifts towards the higher temperature with frequency increasing. Disorder in the allocation of the dissimilar ions on the equivalent lattice sites is responsible for the origin of relaxor behaviour [13, 15]. Dielectric constant increases with increase in the temperature. This increment in the dielectric constant may be due to the conduction mechanism at higher temperature. At higher temperature it is expected that there is a electronic hopping between the Fe$^{2+}$/Fe$^{3+}$ ions and hole hopping between Co$^{2+}$/Co$^{3+}$, and Ni$^{2+}$/Ni$^{3+}$ ions. This hopping between the electrons and holes causes the conduction in the ferrite phase at higher temperature [18]. Hopping ascribe the local displacement in the direction of applied electric field which causes polarization in ferrites. As the charge hopping is temperature dependent process, dielectric polarization increases with increase temperature causes an increase in dielectric constant. Depending on the frequency different types of polarizations contributes to the dielectric constant of the material, mainly dipolar, electronic and interfacial polarization. A Dipolar and interfacial polarization contributes significantly at lower frequency while at higher frequency only the electronic polarization is more significant. As a result, the increase in dielectric constant is more at lower frequency (1 KHz) as compared to higher frequency (above 100 KHz) [18].

Figure 5.15 (a) Temperature dependent variation of dielectric constant ($\varepsilon_r$) and dielectric loss tangent (tanδ) (inset) of 0.1(CNFO)-0.9[0.5BCT-0.5BZT] sintered at 1100 °C.
Figure 5.15 (b) Temperature dependent variation of dielectric constant ($\varepsilon_r$) and dielectric loss tangent (tan$\delta$) (inset) of 0.2(CNFO)-0.8[0.5BCT-0.5BZT] sintered at 1100 °C.

Figure 5.15 (c) Temperature dependent variation of dielectric constant ($\varepsilon_r$) and dielectric loss tangent (tan$\delta$) (inset) of 0.3(CNFO)-0.7[0.5BCT-0.5BZT] sintered at 1100 °C.
Figure 5.15 (d) Temperature dependent variation of dielectric constant ($\varepsilon_r$) and dielectric loss tangent (tan$\delta$) (inset) of 0.4(CNFO)-0.6[0.5BCT-0.5BZT] sintered at 1100 °C.

Figures inset of 5.15 (a) - 5.15 (d) show the temperature dependent loss tangent (tan$\delta$) variation of $x$ [CNFO]-$(1-x)[0.5BCT-0.5BZT]$ magneto-dielectric composites for $x = 0.1, 0.2, 0.3$ and 0.4 at different applied frequency respectively. The shifting in the loss tangent towards the higher temperature with increasing frequency prominently indicates the relaxor behaviour of the composites. It can be seen that, for all the magneto-dielectric composites the value of loss tangent show constant nature up to certain temperature (~ 300 °C) after which, at higher temperatures the value of loss tangent (tan$\delta$) of each composite increases rapidly. The similar type of behaviour is observed for with temperature dependent dielectric constant behaviour. As the hopping of electrons between Fe$^{3+}$ and Fe$^{2+}$ increases with increasing temperature ascribe space charge conduction, results in the rapid increase in value of loss tangent (tan$\delta$). Frequency of hopping is equal to the frequency of applied field, at the maximum value of tangent loss which can be described by the Koop’s theory [13]. Similar kind of behaviour was observed in temperature dependent dielectric properties for the MD compositions sintered at 1200 °C, but here the loss tangent values has lower values this may due to well formation of grains of CNFO in ferroelectric rich region. Figure 5.16 (a), (b), (c) and (d) represents temperature dependent dielectric properties of $x$ [CNFO]-$(1-x)[0.5BCT-0.5BZT]$ MD composite sintered at higher temperature at $x = 0.1, 0.2, 0.3$ and 0.4 respectively. Figures inset of show the variation of dielectric loss tangent (tan$\delta$) at each $x$ concentration.
Figure 5.16 (a) Temperature dependent variation of dielectric constant ($\varepsilon_r$) and dielectric loss tangent (tan\(\delta\)) (inset) of 0.1(CNFO)-0.9[0.5BCT-0.5BZT] sintered at 1200 °C.

Figure 5.16 (a) Temperature dependent variation of dielectric constant ($\varepsilon_r$) and dielectric loss tangent (tan\(\delta\)) (inset) of 0.2(CNFO)-0.8[0.5BCT-0.5BZT] sintered at 1200 °C.
Figure 5.16 (d) Temperature dependent variation of dielectric constant ($\varepsilon_r$) and dielectric loss tangent ($\tan\delta$) (inset) of 0.3(CNFO)-0.7[0.5BCT-0.5BZT] sintered at 1200 °C.

Figure 5.16 (d) Temperature dependent variation of dielectric constant ($\varepsilon_r$) and dielectric loss tangent ($\tan\delta$) (inset) of 0.4(CNFO)-0.6[0.5BCT-0.5BZT] sintered at 1200 °C.
5.3.4 Magneto-dielectric properties of xCNFO-(1-x)(0.5BCT-0.5BZT)

The variation of dielectric constant on application of magnetic field is one of the most interesting and important part of the present investigation. Magnetodielectric variation is calculated in percentage called as magnetocapacitance (%) or MD (%). Figure 5.17 (a) and 5.17 (b) show the variation of magneto-capacitance (MC %) with the applied magnetic field from 0 to 10 KOe at the constant frequency 5 KHz for x [CNFO]-(1-x) [0.5BCT-0.5BZT] for x = 0.1, 0.2, 0.3 and 0.4 sintered at 1100 °C and 1200 °C respectively. The magnetocapacitance is defined as [13],

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

Where, \(\varepsilon(H)\) and \(\varepsilon(0)\) is the observed dielectric constant in the presence and absence of the magnetic field. Almost analogous magneto capacitive behaviour was observed for the MD compositions sintered at both temperatures. Here, It could be seen that the magneto-capacitance increases with increase in the CNFO concentration except at x=0.3 drastic decreases in magnetocapacitance is observed. This may due to the inhomogeneities present in this system such as, impurities, porosity and change in grain structure. It is expected that the grain boundaries are found to be more resistive than grains, due to the formation of barrier layer. As a result most of the field is dropped across the layers, and results in an increased capacitance. On the application of magnetic field to a magnetoelectric material, the material gets strained, and this strain further induces stress which gives rise to an electric field. As this generated field causes orientation in the ferroelectric domains results in change of dielectric constant [18]. The observed magnetocapacitance can be discussed according to the two effects viz. first is the Grindev’s effect and other is the Catalan-type effect [19].

The dielectric constant (\(\varepsilon_r\)) decreases due to the increased polarization due to the induced stress in the piezomagnetic system. The stress induced by the magnetic field would be positive or negative depending on the sign of magneto-striction \(\lambda\). For positive value of \(\lambda\), stress will increase with increase in the applied magnetic field (H) while in case of negative value of \(\lambda\) the stress will decrease with field (H). \(\varepsilon_r\) increases with increase in H for the negative value of \(\lambda\), while it decreases with increase in H for positive \(\lambda\) [20]. Increase in the stress will cause increase in polarization and therefore the dielectric constant (\(\varepsilon_r\)) decreases for increase in stress and vice versa this type of effect is said to be a
Grindev’s effect [19], while increase in \((\varepsilon_r)\) with decrease in stress is due to the contribution of Catalan-type effect [21-22]. Here in this case it expected that in the CNFO-[BCT-BZT] composites the \((\varepsilon_r)\) increases with increase in the field \((H)\), as the CNFO possesses negative value of magnetostriction \((\lambda)\). According to Catalan, the magneto-capacitance \((\text{Mc})\) could be positive or negative depending on the nature of the composite. The magneto-capacitance is predictable to be negative, in those cases the composite appears as a multilayer laminate or similar super lattice, while it is positive for 3-0 type connectivity of the composite [22]. Here it could be seen that the MD composites sintered at lower temperature \((1100 \, ^\circ C)\) posses positive magnetocapacitance and the numerical value of magnetocapacitance at maximum applied magnetic field at \(x=0.2\) and 0.4 are high \((6-7\%)\) as compared reported elsewhere [13, 18], which is a prominent evidence shows that the coupling effect occurs at room temperature for \(x\) [CNFO-(1-x) [0.5BCT-0.5BZT] multiferroic composites, resulted from the magnetoelectric coupling. On the other hand the MD composites sintered at 1200 \(^\circ C\) posses the magnetocapacitance values which negative as well positive depending on the variation of CNFO content. Here the maximum value magnetocapacitance is again observed at \(x=0.2\) and 0.4 \((2-3\%)\) which is also a prominent value of magnetocapacitance. This decrease in magnetocapacitance may result due to more effect of ferroelectric material reacts more effectively with increasing temperature in the MD composition. Magnetocapacitance increases with increase in the field from 0 to 1 Tesla. The observed values of magnetocapacitance at \(x=0.1\) and 0.3 are lower than observed at \(x=0.2\) and 0.4. The magnetoelectric coupling effect is not the main factor which contributes to change in the dielectric constant on the application of the magnetic field to magnetoelectric composites but also the other factors such as magnetostriction effect, which is resulted from the change, occurs in the lattice parameter under the influence of magnetic field. Therefore the magnetostriction effect, i.e. change in the dimension of sample by the magnetic field could be also considered as the origin of the observed magnetocapacitance [13, 15, 18].The observed values of magnetocapacitance for CNFO-[0.5BCT-0.5BZT] composites sintered 1100 \(^\circ C\) at the maximum magnetic field measured at different frequency where listed in table 5.4, while for magnetodielectric composite sintered at 1200 \(^\circ C\) the magnetocapacitance values are listed in table 5.5.
Figure 5.17 (a) Variation of MC (%) with applied magnetic field for $x$(CNFO)-(1-x) (0.5BCT-0.5BZT) magnetodielectric compositions sintered at 1100 °C.

Figure 5.17 (b) Variation of MC (%) with applied magnetic field for $x$(CNFO)-(1-x) (0.5BCT-0.5BZT) magnetodielectric compositions sintered at 1200 °C.
Table 5.4 Magnetocapacitance (%) values at different frequencies for x(CNFO)-(1-x) (0.5BCT-0.5BZT) MD composites sintered at 1100 °C (applied field 1 tesla).

<table>
<thead>
<tr>
<th>MD Composition (x)</th>
<th>MC (%) at 100 Hz</th>
<th>MC (%) at 1 KHz</th>
<th>MC (%) at 5 KHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0.1</td>
<td>31.98</td>
<td>8.43</td>
<td>3.22</td>
</tr>
<tr>
<td>x = 0.2</td>
<td>13.81</td>
<td>9.73</td>
<td>6.67</td>
</tr>
<tr>
<td>x = 0.3</td>
<td>2.98</td>
<td>2.29</td>
<td>1.29</td>
</tr>
<tr>
<td>x = 0.4</td>
<td>34.12</td>
<td>9.73</td>
<td>5.48</td>
</tr>
</tbody>
</table>

Table 5.5 Magnetocapacitance (%) values at different frequencies for x(CNFO)-(1-x) (0.5BCT-0.5BZT) MD composites sintered at 1200°C (applied field 1 tesla).

<table>
<thead>
<tr>
<th>MD Composition (X)</th>
<th>MC (%) at 100 Hz</th>
<th>MC (%) at 1 KHz</th>
<th>MC (%) at 5 KHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0.1</td>
<td>-2.94</td>
<td>-0.82</td>
<td>-0.90</td>
</tr>
<tr>
<td>x = 0.2</td>
<td>-0.44</td>
<td>1.73</td>
<td>0.18</td>
</tr>
<tr>
<td>x = 0.3</td>
<td>-3.84</td>
<td>-0.20</td>
<td>-0.46</td>
</tr>
<tr>
<td>x = 0.4</td>
<td>9.87</td>
<td>3.27</td>
<td>2.28</td>
</tr>
</tbody>
</table>

5.3.5 Magnetolectric (ME) properties of xCNFO-(1-x)(0.5BCT-0.5BZT)

Multiferroic materials are composites with the substantial mixture of ferroelectric and magnetic phase having different chemical compositions which are insoluble in each other. Coupling between the piezoelectric effect of ferroelectric material and magnetostrictive effect of magnetic material are mainly responsible for the ME effect in the composites. To achieve the large ME values in the composites the materials should have the ferroelectric phase having large piezoelectric value and the magnetic material possessing large magnetostriction coefficient. The ME effect in the composite can be represented as [13].
Now here the custom designed circuit was used for measurement of ME in the magnetodielectric sample, where the frequency has constant magnitude 4 KHz. whereas, the linear and quadratic magnetoelectric coefficients $\alpha$ and $\beta$ are determined from the following formulae [19].

$$\alpha = \frac{dE}{dH} = \frac{dv}{dH \times t} \quad \text{----- 5.4}$$

$$\beta = \frac{dv}{dH \times 2h_o \times t} \quad \text{----- 5.5}$$

Where, t is thickness of sample, v is the root mean square value of AC voltage developed across the sample h is the AC magnetic field and H DC magnetic field. Now figure 5.18 (a) and (b) represents the variation of linear magnetoelectric coefficient ($\alpha$) and quadratic magnetoelectric coefficient ($\beta$) for samples sintered at 1100 °C and 1200 °C respectively. Here it could be seen that the ($\alpha$) has maximum value at $x=0.2$ for compositions sintered at 1100 °C, on the hand compositions sintered at 1200 °C maximum value was observed for $x = 0.4$ composition. Also it could be seen that with increase in sintering temperature magnitude of $\alpha$ increase. This may be due enhancement in grain structure and size with increase in temperature, results in the improved magneto-mechanical coupling [19].

Observation of maximum value at $x = 0.4$ attributed to $y \times (y-1)$ type of proportionality of $\alpha$ in this case of two phase magnetodielectric composite system. Now the measurement of $\beta$ was done under the applied magnetic field from 0 to 2.5 kG. The lower magnitude of $\beta$ value is seems preferable from the application point of view of magnetodielectric materials. From the figure another thing was observed that the $\beta$ also has higher magnitude at the respective composition where $\alpha$ is maximum. Therefore it could be predicted that the both the magnetoelectric coefficients exhibits analogous behaviour. The observed values are listed in table 5.6.
Figure 5.18 (a) Variation of linear magnetoelectric coefficient ($\alpha$) with CNFO content of MD composition sintered at 1100 °C and 1200 °C.

Figure 5.18 (b) Variation of quadratic magnetoelectric coefficients ($\beta$) with CNFO content of MD composites sintered at 1100 °C and 1200 °C.
Table 5.6 Magnetoelectric coefficients observed for CNFO-(0.5BCT-0.5BZT) MD composite sintered at 1100 °C and 1200 °C respectively.

<table>
<thead>
<tr>
<th>Composition</th>
<th>α (mV/Oe.cm)</th>
<th>β (mV/Oe.cm) X 10⁻⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ts = 1100 °C</td>
<td>Ts = 1200 °C</td>
</tr>
<tr>
<td>x = 0.1</td>
<td>9.59</td>
<td>15.04</td>
</tr>
<tr>
<td>x = 0.2</td>
<td>10.35</td>
<td>16.81</td>
</tr>
<tr>
<td>x = 0.3</td>
<td>8.29</td>
<td>18.38</td>
</tr>
<tr>
<td>x = 0.4</td>
<td>9.25</td>
<td>21.6</td>
</tr>
</tbody>
</table>

5.3.6 Raman spectroscopy analysis of xCNFO-(1-x)(0.5BCT-0.5BZT) MD composite

Figure 5.19 shows the room temperature Raman spectra for x(CNFO)-(1-x)(0.5BCT-0.5BZT) MD compositions sintered at 1200 °C, where x = 0.1, 0.2, 0.3 and 0.4. It could be seen that all the vibrational modes seen in the ferroelectric phase are exist prominently in the MD compositions; this may attributes due to formation of composite in the ferroelectric rich region. Also here with increasing the CNFO content in the composition the Raman vibrational peaks corresponding to Fd3m ferrite increase gradually. Observation of vibrational modes related to ferroelectric and ferromagnetic material in the composition confirms the formation of magnetodielectric multiferroic composite. Vibrational modes observed at 142 cm⁻¹, 186 cm⁻¹, with broad peak at 242 cm⁻¹ are assigned to A₁(TO) phonon mode [2]. Whereas shoulder peak at 302 cm⁻¹, asymmetric peak at 519 cm⁻¹ and broad weak peak at 721 cm⁻¹ are assigned to B₁ and/or E(TO+LO), A₁(TO) and/or E(TO) and A₁(LO) and/or E(LO) respectively [2]. The modes A₁(TO) and E(TO) are all assigned to Ti – O bonds, and the modes A₁(LO) and E(LO) are contributed to Ba – O bonds [8]. Also weak Raman active asymmetric breathing mode (A₁g) was seen at 816 cm⁻¹. These observed vibrational modes are corresponds with ferroelectric phase (0.5BCT-0.5BCT) in the MD composition. Whereas, vibrational modes at 186 cm⁻¹, 212 cm⁻¹, 268 cm⁻¹, 308 cm⁻¹, 473 cm⁻¹ and 692 cm⁻¹ respectively, with some less intense shoulder peaks at 172 cm⁻¹, 252 cm⁻¹, 369 cm⁻¹, 401 cm⁻¹, 577 cm⁻¹ and 623 cm⁻¹ respectively are peaks corresponding to spinel ferrite phase i.e. CNFO. It could be seen
that the Raman vibrational mode at 692 cm\(^{-1}\) has a shoulder peak at lower wave number (625 cm\(^{-1}\)) these bands are assigned to \(A_{1g} (1)\) and \(A_{1g} (2)\) modes. Therefore, Raman spectroscopy confirms the presence of mix phase structure, reveals formation of CNFO-0.5BCT-0.5BZT MD composite.

![Raman spectra](image)

**Figure 5.19 Raman spectra of CNFO-(0.5BCT-0.5BZT) MD composition sintered at 1200 °C.**

### 5.3.7 Ferroelectric (P-E) hysteresis measurement \(x\)CNFO-(1-x)(0.5BCT-0.5BZT)

Ferroelectric properties at room temperature i.e. polarization versus electric field hysteresis loops of \(x\)CNFO-(1-x)(0.5BCT-0.5BZT) where \(x = 0.1, 0.2, 0.3\) and 0.4 MD composites sintered at 1100 °C are demonstrated in figure 5.20 (a) and the P-E hysteresis loop of MD compositions sintered at 1200 °C was represented in figure 5.20 (b). From the figure it could be seen that, ferroelectric hysteresis loop of pure BCT-BZT (not shown) has a higher value of saturation polarization. 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 as the ferrite materials consisting of mixed valance states of Fe\(^{3+}\) and Fe\(^{2+}\) has a higher leakage current density than the ferroelectric phase [23]. The values of various parameters obtained from the ferroelectric hysteresis loop characterization of MD composites listed in table 5.7. Here with the increase in CNFO concentration area under the curve of P-E hysteresis loop increases and the curves becomes more and more circular with unsaturated polarization,
while the electric loss also increase this may attributed to increase in ionic conductivity and decrease in the values of resistivity with increase in ferrite concentration. It could be seen that P-E hysteresis loops of sample sintered at higher temperature has more ferroelectric nature as compared with the MD composites sintered at lower temperature, this may due to with increasing temperature the grains of ferroelectric phase are more improved.

![Figure 5.20 (a) Ferroelectric hysteresis (P-E) loops of CNFO-(0.5BCT-0.5BZT) MD composites sintered at 1100 °C.](image)

![Figure 5.20 (b) Ferroelectric hysteresis (P-E) loops of CNFO-(0.5BCT-0.5BZT) MD composites sintered at 1200 °C.](image)
Table 5.7 Values observed from P-E hysteresis loop of x(CNFO)-(1-x)(0.5BCT-0.5BZT) sintered at 1100 °C and 1200 °C.

<table>
<thead>
<tr>
<th>x value</th>
<th>Pr (μC/cm²)</th>
<th>Pmax (μC/cm²)</th>
<th>Ec (Kv/cm)</th>
<th>Pr/Pmax</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1100°C</td>
<td>1200°C</td>
<td>1100°C</td>
<td>1200°C</td>
</tr>
<tr>
<td>x = 0.1</td>
<td>3.31</td>
<td>1.29</td>
<td>8.37</td>
<td>6.67</td>
</tr>
<tr>
<td>x = 0.2</td>
<td>2.94</td>
<td>3.18</td>
<td>6.42</td>
<td>7.74</td>
</tr>
<tr>
<td>x = 0.3</td>
<td>4.08</td>
<td>4.16</td>
<td>8.85</td>
<td>7.71</td>
</tr>
<tr>
<td>x = 0.4</td>
<td>7.54</td>
<td>4.18</td>
<td>11.15</td>
<td>9.59</td>
</tr>
</tbody>
</table>

5.3.8 Magnetic properties of xCNFO-(1-x)(0.5BCT-0.5BZT) MD compositions

In general the dc hysteresis loop gives the magnetic characteristics or magnetic behaviour of a sample when the sample excited by an external magnetic field. Fig 5.21 (a) and 5.21 (b) shows the magnetization versus magnetic field (M-H) behaviour for x [CNFO]-[1-x] [0.5BCT-0.5BZT] for x = 0.1, 0.2, 0.3, 0.4 and 1 magnetolectric composites sintered at 1100 °C and 1200 °C using the microwave sintering technique investigated at room temperature respectively. Vibrating sample magnetometer (VSM) is used to measure the magnetization with the applied magnetic field in the range −50 kOe ≤ H ≤ 50 kOe. Observation of the typical ferromagnetic loops is prominent evidence, which show the presence of ordered magnetic structure in the ferrite-ferroelectric composites. The values of coercive field (Hc), remanant magnetization (Mr), saturation magnetization (Ms) and magnetic moment (μB) of MD/ME composite samples sintered at both temperatures are listed in Table 5.8. Magnetic moment is calculated in terms of Bohr magnetron by using the relation as follows [13]

\[
\mu_B = \frac{M_s}{5585}
\]

Where, M is molecular weight, Ms is the saturation magnetization and 5585 is the magnetic factor. Smaller values of remanant magnetization and saturation magnetisation
are observed in the composites as compared to the CNFO ferrite, also the smaller values of coercive magnetic field is a prominent indication of easy magnetization characteristic of ferromagnetic phase in ferroelectric matrix. The variation of Ms and magnetic moment ($\mu_B$) as a function of ferrite CNFO concentration is shown in Fig. 5.22 (a) and (b) for MD composition sintered at different temperature 1100 °C and 1200 °C respectively. 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 which can be seen in the figure inset of 5.20 (a) and (b) respectively. This may be due to, the change in the total magneto crystalline anisotropy energy due to the ME coupling resulted from the disordered arrangement of lattices between the CNFO and BCT-BZT ferrites or may be distribution of ferrite particles in the composites [13]. The increase in saturation magnetization and magnetic moment with increasing CNFO content may due to the fact that the each grain of the CNFO contributes in the saturation magnetization as a centre of magnetization and the total saturation magnetization is a vector sum all these individual contributions. Also it is noted that the ferroelectric grains in ferrite phase act as pores in the presence of applied magnetic field and break the magnetic circuit. Increase in CNFO concentration results in decrease of the pores and interaction between the CNFO increases with reduction in domain wall [18].

![Figure 5.21 (a) Magnetic hysteresis (M-H) loop of CNFO-(0.5BCT-0.5BZT) sintered at 1100 °C.](image)

Figure 5.21 (a) Magnetic hysteresis (M-H) loop of CNFO-(0.5BCT-0.5BZT) sintered at 1100 °C.
Figure 5.21 (b) Magnetic hysteresis (M-H) loop of CNFO-(0.5BCT-0.5BZT) sintered at 1200 °C.

Table 5.8 Room temperature magnetic parameters observed from M-H hysteresis loop of x(CNFO)-(1-x)(0.5BCT-0.5BZT) sintered at 1100 °C and 1200 °C.

<table>
<thead>
<tr>
<th>x value</th>
<th>1100 °C</th>
<th>1200 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mr emu/gm</td>
<td>Ms emu/gm</td>
</tr>
<tr>
<td>x = 0.1</td>
<td>0.093</td>
<td>5</td>
</tr>
<tr>
<td>x = 0.2</td>
<td>1.68</td>
<td>12.50</td>
</tr>
<tr>
<td>x = 0.3</td>
<td>3.03</td>
<td>18.25</td>
</tr>
<tr>
<td>x = 0.4</td>
<td>3.30</td>
<td>23.30</td>
</tr>
</tbody>
</table>
Figure 5.22 (a) Variation of Mr, Ms, and $\mu_B$ with Variation of CNFO concentration for MD composite sintered at 1100 °C.

Figure 5.22 (b) Variation of Mr, Ms, and $\mu_B$ with variation of CNFO concentration for MD composite sintered at 1200 °C.
References