CHAPTER - IV
Characterization of Ba$_{0.7}$Ca$_{0.3}$TiO$_3$ (BCT), BaZr$_{0.2}$Ti$_{0.8}$O$_3$ (BZT), Ferroelectric Composite BCT-BZT and Co$_{0.9}$Ni$_{0.1}$Fe$_2$O$_4$ (CNFO)

4.1 Introduction

Ferroelectric Ba$_{0.7}$Ca$_{0.3}$TiO$_3$, BaZr$_{0.2}$Ti$_{0.8}$O$_3$ and the solid solution of both materials and ferromagnetic Co$_{0.9}$Ni$_{0.1}$Fe$_2$O$_4$ which are synthesized in nanopowder form are characterized to obtain their characteristic properties are discussed in this chapter. Different instruments are used for characterization purpose such as, x-ray diffractometer (XRD), scanning electron microscope/ field emission scanning electron microscope (SEM/FE-SEM), dielectric measurement unit (LCR-Q), Raman spectroscopy and vibrating sample magnetometer (VSM) for studying structural, morphological, and magnetic properties. Ba$_{0.7}$Ca$_{0.3}$TiO$_3$, BaZr$_{0.2}$Ti$_{0.8}$O$_3$ and Co$_{0.9}$Ni$_{0.1}$Fe$_2$O$_4$ materials are individually synthesized with coprecipitation method and processed with microwave sintering technique. After being processed with microwave technique the individual samples of each material are characterized by various techniques and the obtained results are analyzed. Followed by which ferroelectric compositions of x[Ba$_{0.7}$Ca$_{0.3}$TiO$_3$-(1-x)]BaZr$_{0.2}$Ti$_{0.8}$O$_3$] are studied for their various characteristic properties and obtained results are discussed in detail. For simplification the ferroelectric constituents Ba$_{0.7}$Ca$_{0.3}$TiO$_3$, BaZr$_{0.2}$Ti$_{0.8}$O$_3$ and ferromagnetic phase Co$_{0.9}$Ni$_{0.1}$Fe$_2$O$_4$ will be termed as BCT, BZT and its CNFO while the ferroelectric solid solution as xBCT-(1-x)BZT.

4.2 Characterization of Ba$_{0.7}$Ca$_{0.3}$TiO$_3$ (BCT)

Well synthesized nanopowders and pressed pellets, after being sintered at different temperatures (1100 °C and 1200 °C) are used structural, morphological, electrical characterization. The ceramics are sintered at the desired temperature with fast microwave sintering technique by maintaining holding time 30 min and 20 min for 1100 °C and 1200 °C respectively. The heating rate was maintained at 40 °C/min. Overall mechanism of sintering including cooling needs 2-3 hours only.

4.2.1 Structural analysis of BCT

After sintering using the microwave sintering technique at 1100 °C and 1200 °C, powder samples of BCT are characterized for structural analysis with x-ray diffraction. For
structural analysis the sample was scanned at 20° scale between 20° to 80° at room temperature while the scan rate was maintained at 3°/min. Figure 4.1 shows the diffraction patterns of Ba$_{0.7}$Ca$_{0.3}$TiO$_3$ (BCT) sintered at 1100 °C and 1200 °C. BCT is a perovskite ceramic, which is a solid solution of BaTiO$_3$ and CaTiO$_3$. At room temperature BaTiO$_3$ exhibits a tetragonal crystal structure while CaTiO$_3$ reveal orthorhombic structure [1-3]. Tetragonal peaks in the BCT ceramic are more and are in good agreement with JCPDS 81-1288, while orthorhombic peaks corresponding to CaTiO$_3$ are indexed according with JCPDS data card 75-2100 [4]. Calculated lattice parameters, tetragonal distortion ratio and volume of unit cell with average crystallite size measured from the highest intense peak of both the ceramic samples sintered at different temperatures are listed in table 4.1.

The highest intensity peak or most prominent peak of tetragonal side is (110) while peak indexed as (121) is the most prominent peak of the orthorhombic system and these peaks are almost coincide each other. Peak intensity of the ceramic sample sintered at 1200 °C is more which confirms the well diffusion of Ca$^{2+}$ ions in BT matrix. From the diffraction pattern the average crystallite size was estimated using the Debye-Scherrer equation.

![Figure 4.1 Room temperature x-ray diffraction pattern of Ba$_{0.7}$Ca$_{0.3}$TiO$_3$ sintered at 1100 °C and 1200 °C.](image-url)
Table 4.1 Lattice parameters, c/a ratio, unit cell volume and crystallite size of Ba$_{0.7}$Ca$_{0.3}$TiO$_3$ sintered at different temperature.

<table>
<thead>
<tr>
<th>Sintering Temperature and Time</th>
<th>Lattice parameters</th>
<th>Volume of Unit Cell $V = (a^2c)$</th>
<th>Crystallite size nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100 °C 30 min</td>
<td>3.9256 4.001 1.0192</td>
<td>63.87</td>
<td>35.56</td>
</tr>
<tr>
<td>1200 °C 20 min</td>
<td>3.9487 4.002 1.0134</td>
<td>63.98</td>
<td>38.33</td>
</tr>
</tbody>
</table>

\[ D = \frac{0.9\lambda}{\beta \cos \theta} \] ----- 4.1

It could be seen that the crystallite size increases with increase in the temperature on the other hand the tetragonal distortion ratio (c/a) slightly decreases. This may resulted as; with increase in temperature partial incorporation of Ca$^{2+}$ ions occurs at barium site. A Ca$^{2+}$ ion replaces Ba$^{2+}$ ions in the solid solution of the BCT and results in tetragonal crystal structural however the complete solubility occurs up to $x = 0.25$ and at $x = 0.3$ the solid solution becomes biphasic tetragonal and orthorhombic [3]. Addition of Ca ions over the solubility limit will results in formation of CaTiO$_3$ lattice and crystal structure exhibits diffraction peaks corresponding to CaTiO$_3$ phase as shown in figure.

4.2.2 Morphological and EDS analysis of BCT

Figure 4.2 (a) and (b) show the scanning electron microscope images of Ba$_{0.7}$Ca$_{0.3}$TiO$_3$ sintered at 1100 °C and 1200 °C respectively. Backscattered microstructural images were collected by using scanning electron microscope with energy dispersive spectrometer (JEOL JSM 6390). Figures reveal that sintered ceramics at different temperatures are dense; grains are formed with very less voids. Here, increase in temperature results in the increase in size of grains. Fast microwave sintering technique, which heats the surface of the material body from inside and heats all the area in equal magnitude results in more separation of the grains. Compact nature of grain structure of microwave sintered ceramic sample results in enhancement of electrical and physical properties of ceramic material. The presence of all the elements in stoichimetric proportion is confirmed by using Energy Dispersive Spectrometry (EDS). Figure 4.2 (c) and (d) show the EDS spectra of BCT ceramic sample sintered at 1100 °C and 1200 °C respectively. A
Table insight EDS spectrum gives the elemental composition (weight % and atomic (%) present in the final composition. As no other peak corresponding to any impurity phase is not detected from the EDS which confirms formation of pure phase Ba$_{0.7}$Ca$_{0.3}$TiO$_3$.

![Figure 4.2 Scanning electron microscope images of Ba$_{0.7}$Ca$_{0.3}$TiO$_3$ ceramic sintered at different temperature (a) 1100 °C and (b) 1200 °C.](image)

![Figure 4.2 Energy dispersive spectra (EDS) of Ba$_{0.7}$Ca$_{0.3}$TiO$_3$ ceramic sintered at different temperature (c) 1100 °C and (d) 1200 °C.](image)

**4.2.3 Dielectric measurements of BCT**

For measurement of electrical properties calcined nanopowders of BCT ceramic sample are pressed into pellets by using hydraulic press. Pressure was maintained at 5 kN/cm$^2$ to get the material in a disk shape having about 1 cm diameter and about 2 mm thickness. For binding purpose powder sample where mixed with polyvinyl alcohol solution (PVA), which will be removed at the time the time of sintering process. 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 measurements.
Programmable furnace was used for measurement of temperature dependent dielectric behaviour from room temperature to 200 °C. Heating rate was maintained at 1 °C/min. Capacitance (Cp) of the material was measured with variation of frequency and temperature. Capacitance was then converted to the dielectric constant by using the formula,

$$\varepsilon_r = \frac{C_p \times t}{\varepsilon_0 \times A}$$

where, $\varepsilon_r$ relative dielectric constant of material, Cp is capacitance measured in parallel mode, t is thickness of pellet under investigation; $\varepsilon_0$ is permittivity of air ($8.854 \times 10^{-12}$) and A is area of the circular pellet. Also dielectric loss tangent was calculated by using measuring Q value and converted by using the relation,

$$\tan \delta = \frac{1}{Q}$$

4.2.3.1 Frequency dependant dielectric measurement

Room temperature variation of dielectric constant with varying frequency of Ba$_{0.7}$Ca$_{0.3}$TiO$_3$ sintered at 1100 °C and 1200 °C is shown in figure 4.3 (a) and (b) respectively. Loss tangent with variation of frequency is also incorporated in the figure. The dielectric constant and dielectric loss tangent was measured in frequency range 100 Hz to 1 MHz. Ceramic sintered at both temperatures show the similar kind of variation with frequency. Both ceramic sample posses high dielectric constant at lower frequency and dielectric loss tangent is also has a high value. At lower frequency dielectric constant decreases rapidly and remains constant at higher frequencies, while the loss tangent also show similar kind of nature analogous to dielectric constant. Contribution of the different types of polarization i.e. interfacial, space charge, dipolar, electronic, and ionic polarization leads to the dielectric dispersion of ferroelectric materials. Rapid dielectric dispersion at lower frequency is due the contribution of interfacial polarization. This type of polarization might be resulted due to the inhomogeneous structures of the materials. At higher frequency the dielectric constant does not follow the applied alternating field and results in constant behaviour. It could be seen that the value of dielectric constant of ceramic sample sintered at 1200 °C is larger, and posses low dielectric loss value as compared to ceramic sample sintered at 1100 °C. Sintering at higher temperature increases the more diffusion of Ca$^{2+}$ ions which results in higher densification of sample, higher
density results in more improved electrical properties. At lower frequency the loss is higher and loss tangent value decreases with increase in frequency, which normal characteristic property of ferroelectric material.

Figure 4.3 (a) Variation of dielectric constant and loss tangent with frequency of Ba$_{0.7}$Ca$_{0.3}$TiO$_3$ sintered at 1100 °C.

Figure 4.3 (b) Variation of dielectric constant and loss tangent with frequency of Ba$_{0.7}$Ca$_{0.3}$TiO$_3$ sintered at 1200 °C.
4.2.3.2 Temperature dependent dielectric properties

Dielectric properties of the BCT samples are measured at various frequencies from 100 Hz to 1 MHz with the variation of temperature from room temperature to 200 °C. Figure 4.4 (a) and (b) show the variation of dielectric constant with temperature of Ba$_{0.7}$Ca$_{0.3}$TiO$_3$ samples sintered at 1100 °C and 1200 °C with microwave sintering respectively whereas, figure 4.4 (c) and (d) represents variation of dielectric loss tangent at respective sintering temperature value. Dielectric constant value increases with increase in temperature, reaches maximum and then starts to decrease. The point at which dielectric constant becomes maximum and start to decrease is called as Curie temperature. For both the samples it could be seen that, magnitude of relative permittivity decreases with increase in frequency and the maxima shifts towards higher temperature. Observation of broad dielectric maxima for ceramic sintered at both reveals the existence of diffused phase transition and relaxor behaviour of material [5]. Due to application of fast microwave sintering process grains growth is more with high density, well crystallinity and denser nature of grains enhances the permittivity value of ceramic material [6]. More over ferroelectric-paraelectric transition temperature (Tc) of ceramic material increases. Increase in transition temperature Tc may be resulted due to the microwave sintering, due to which microwave sintering may found suitable technique for processing of material for high Tc application. Transition temperature values of both samples are in between 155 °C to 160 °C at each value of applied frequency. Increment in sintering temperature results in more densification and well orientation of grains, as a result enhanced dielectric properties are observed for BCT ceramic sample sintered at higher temperature (1200 °C). Loss tangent also shows analogous behaviour to the dielectric constant nature. At lower temperature value of loss tangent is more and decreases with increases in temperature and again increases at higher temperature. As the magnitude of applied frequency increases the value of loss tangent decreases, lower values of loss tangent was observed at the highest frequency value 1 MHz, for BCT ceramic sintered at both temperatures. Increase in the loss tangent value at higher temperature may attributes to the increase in conductivity of the sample. Relatively this feature was observed at lower frequency value where as at higher frequency value the loss tangent remains almost constant throughout the given temperature range. At the transition temperature small peak is observed in the loss tangent vs. Temperature graph.
Figure 4.4 (a) Temperature dependent variation of dielectric constant ($\varepsilon_r$) of Ba$_{0.7}$Ca$_{0.3}$TiO$_3$ sintered at 1100 °C.

Figure 4.4 (a) Temperature dependent variation of dielectric constant ($\varepsilon_r$) of Ba$_{0.7}$Ca$_{0.3}$TiO$_3$ sintered at 1200 °C.
4.2.4 Ferroelectric properties of BCT

Polarization with applied electric field was measured at room temperature of ceramic samples sintered at both temperatures. Figure 4.5 shows the P-E hysteresis loop of...
Ba$_{0.7}$Ca$_{0.3}$TiO$_3$ samples sintered at 1100 °C and 1200 °C respectively. P-E hysteresis loop tracer from Marine India was used for measurement of P-E loops. Both samples show regular shape hysteresis loop as the ideal ferroelectric material. The saturation polarization (Ps), remanant polarization (Pr) and coercive field (Ec) of both the samples is tabulated in table 4.2. It could be seen that the sample sintered at higher temperature has higher saturation polarization, while the loop shape becomes slimmer as compared to sample sintered at lower temperature. Typical ferroelectric relaxor behaviour is confirmed with increasing temperature as the hysteresis loop becomes slimmer for BCT ceramic sintered at 1200 °C. Microwave sintering plays an important role on crystallinity and homogeneity of the material as a result materials processed with this method exhibits sharp ferroelectric behaviour. Also the increase in temperature improves the ferroelectric properties of the ceramic material, as the BCT ceramic sintered at 1200 °C shows increase in polarization saturation value.

![Hysteresis Loop](image)

**Figure 4.5** Room temperature ferroelectric hysteresis loop (P-E) of Ba$_{0.7}$Ca$_{0.3}$TiO$_3$ sintered at 1100 °C and 1200 °C.
Table 4.2 Parameters observed from ferroelectric measurement of Ba$_{0.7}$Ca$_{0.3}$TiO$_3$ sintered at different temperature.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Saturation Polarization (Ps) $\mu$C/cm$^2$</th>
<th>Remanant Polarization (Pr) $\mu$C/cm$^2$</th>
<th>Coercive Field (Ec) kV/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCT 1100 °C</td>
<td>1.89</td>
<td>0.55</td>
<td>14.34</td>
</tr>
<tr>
<td>BCT 1200 °C</td>
<td>1.96</td>
<td>0.42</td>
<td>4.99</td>
</tr>
</tbody>
</table>

4.3 Characterization of BaZr$_{0.2}$Ti$_{0.8}$O$_3$ (BZT)

As a part of lead free composition second constituent BaZr$_{0.2}$Ti$_{0.8}$O$_3$ (BZT) was synthesized by the similar method i.e. hydroxide coprecipitation. The whole synthesis procedure was mentioned in previous chapter. Here nanopowders of BZT ceramic are mixed with PVA which will act as binding reagent and pressed in to circular disk shape pellets the procedure was quite similar to the procedure done so for in the developing and characterization of Ba$_{0.7}$Ca$_{0.3}$TiO$_3$. Pellets and nanopowders of BZT are also sintered at 1100 °C and 1200 °C, after sintering process this ceramic material were characterized by various characterization techniques.

4.3.1 Structural analysis of BZT

Figure 4.6 shows the x-ray diffraction pattern obtained at room temperature of Ba(Zr$_{0.2}$Ti$_{0.8}$)O$_3$ (BZT) sintered at 1100 °C and 1200 °C by using microwave sintering technique. From diffraction pattern it could be seen that the perovskite ferroelectric (BZT) phase crystallizes into the single phase crystal with a cubic structure. All the peaks corresponding to the BZT are indexed according to the JCPDS 36-0019 [7-9]. Formation of the single phase perovskite structure without any unidentified peak suggests that the addition of the Zr in the BaTiO$_3$ lattice forms a stable solid solution. Macroscopically BZT is known to exhibit cubic crystal structure with space group Pm3m, but when it is considered as microscopically BZT shows the crystal phase rather than cubic crystal structure. As BZT is a constitution of two unit cells BTO and BZO it can be expected that the change in the crystal structure may result due to the local strain effect of these two unit cells. The lattice constant of BZO is (a = 4.15 Å) which is greater than lattice constant of
BTO (a = 4.00 Å) [9]. The calculated lattice constant for the BZT ceramic sintered at 1100 °C is (a = 4.026 Å) and that of for ceramic sintered at 1200 °C it is (a = 4.0208 Å), the volume of unit cell and crystallite size is listed in table 4.3.

Random distribution of BTO and BZO phases results in formation of solid solution of BZT, and due to random distribution it is possible that BTO cell may partially or completely surrounded by BZO or completely surrounded by another BTO unit cell. Partial surrounding of BTO by BZO unit cell or in either way, results in the creation of tensile or compressive strain between these two unit cells, due to these strain effects local symmetry of BZT solid solution lowers. If the BTO unit cell is completely surrounded by BZO unit cell it creates isotropic strain between them and results in cubic crystal symmetry. If BTO is completely surrounded by BTO unit cell then there is no strain effect between them and results in cubic crystal structure [9]. Hence the overall BZT ceramic material is known to exhibit cubic crystal structure at room temperature.

![Figure 4.6 Room temperature x-ray diffraction pattern of BaZr0.2Ti0.8O3 sintered at 1100 °C and 1200 °C.](image)

Calculated parameters from diffraction pattern show that lattice constant and volume of unit cell decreases with increase in temperature, on the other hand crystallite size increases. Decrease in lattice constant and unit cell volume is in agreement with well diffusion of Zr$^{4+}$ ions in to Ti$^{4+}$ ions in the BaTiO$_3$ lattice.
Increase in crystalline size with increase in temperature may attribute due to the formation of solid solution of BZO unit cell having slight higher lattice constant with BTO unit cell at higher temperature.

**Table 4.3 Lattice parameters, unit cell volume and crystallite size of BaZr_{0.2}Ti_{0.8}O_3 sintered at different temperature.**

<table>
<thead>
<tr>
<th>Sintering Temperature and Time</th>
<th>Lattice Constant a (Å)</th>
<th>Volume of Unit Cell V = a^3</th>
<th>Crystallite Size nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100 °C 30 min</td>
<td>4.026</td>
<td>65.07</td>
<td>36.93</td>
</tr>
<tr>
<td>1200 °C 20 min</td>
<td>4.0208</td>
<td>64.97</td>
<td>42.76</td>
</tr>
</tbody>
</table>

**4.3.2 Morphological and EDS analysis of BZT**

Microstructural analysis of BaZr_{0.2}Ti_{0.8}O_3 microwave sintered ceramic samples was done by using field emission scanning electron microscope (FE-SEM). For analysis purpose Zeiss Ultra 55 FE-SEM with Oxford EDS system was used. Figure 4.7 (a) and (b) are show the backscattered images of BZT nanoparticles sintered at 1100 °C and 1200 °C respectively. The micrographs show the well oriented grains, small pores are observed in BZT ceramic sintered at 1100 °C. With increase in temperature to 1200 °C results in formation of pore free BZT microstructure with high density. This may results due to complete diffusion of Zr^{4+} ions in to Ti^{4+} side at higher temperature which fill up the pores and makes more compact microstructure. Also, it is seen that average grain size is increased in the BZT sample sintered at higher temperature. Higher densification of ceramic sample plays an important role in enhancing the physical and electrical properties of the material. Figure 4.7 (c) and (d) show energy dispersive spectra (EDS) of BZT sample sintered at 1100 °C and 1200 °C respectively. Table inside EDS spectra show elemental composition for the ceramic sintered at respective temperature range. Here it is seen that all elements composed in BZT sample are present in stoichiometric amount. With variation of temperature observed weight (%) of respective element varies in the final composition. There is no any impurity peak is detectable in EDS spectra of sample sintered at both temperature suggests formation of pure BaZr_{0.2}Ti_{0.8}O_3 lattice.
4.3.3 Dielectric measurements of BZT

Similar type of experimental procedure as carried in case of BCT ceramic sample is also employed for BZT sample. Sintered pellets were coated with silver paste on both sides for conducting purpose and dried at 150 °C for 2 hours which adhere silver paste to the pellet very well. Capacitance of the of the material was measured with variation of frequency and temperature, measured capacitance was then converted to the dielectric constant by using the formula 4.1 as given above and loss tangent were calculated by using formula 4.2. Programmable furnace attached LCR meter was used for measurement of temperature dependent dielectric behaviour from room temperature to 200 °C, heating rate was maintained at 1 °C/min.
4.3.3.1 Frequency dependant dielectric measurement

Frequency dependent room temperature dielectric properties of BaZr₀.₂Ti₀.₈O₃ ceramic sintered at 1100 °C and 1200 °C are shown in figure 4.8 (a) and (b) respectively. Figures show variation of dielectric constant and loss tangent with applied frequency ranging from 100 Hz to 1 MHz. It could be seen that magnitude of dielectric constant decreases with increase in frequency, at lower frequency range dielectric constant shows higher value. Variation of the dielectric constant depends on the free dipoles which are oscillating in an alternating field. In lower range of frequency dipoles are act on the similar path as the alternating field, and the dielectric constant reaches maximum value. As frequency increases dipoles starts to follow opposite direction to that of alternating field due to which the value of dielectric constant decreases, at very high value of frequency dipoles does not follow the field path and results in very low value of dielectric constant [10]. Also different types of polarizations contribute to the dielectric permittivity of the material, mainly dipolar and electronic polarization contributes at higher frequencies while interfacial polarization resulted from inhomogeneous structures in material contributes at lower frequency. Here it could be seen that the dielectric constant increases with increase in sintering temperature and dielectric loss decreases. This increase in dielectric constant value and decreases in loss tangent value ascribed due to complete diffusion of Zr⁴⁺ ions in to Ti⁴⁺ ions at high temperature. Complete diffusion of ions makes high dense structure of material without any pores, with increase in density of material physical and electrical properties of material gets improved. Also fast microwave sintering technique plays an vital role in improvement of microstructural properties; as a result BZT ceramic material sintered at both temperatures has good physical and electrical properties. Meanwhile, the BZT ceramic sintered at 1200 °C shows improved microstructural and electrical properties. Variation of dielectric loss with frequency also included in similar figure, which reveals the loss tangent, has similar kind of variation to that of dielectric constant. High value of tanδ at low frequency may attributes due to presence of electrical conductivity in the material [10-11]. Small increase in dielectric constant and loss tangent is observed at higher frequency value, this may attributes due to presence of electrical polarization at high values of applied frequency.
Figure 4.8 (a) Variation of dielectric constant and loss tangent with frequency of BZT sintered at 1100 °C.

Figure 4.8 (b) Variation of dielectric constant and loss tangent with frequency of BZT sintered at 1200 °C.

4.3.3.2 Temperature dependent dielectric properties

Figure 4.9 (a) and (b) represents the variation of dielectric constant \((\varepsilon_r)\) with temperature of BZT ceramic sample sintered at 1100 °C for 30 min at 1200 °C for 20 min respectively while figure 4.9 (c) and (d) show variation of dielectric loss tangent of BZT samples sintered at respective temperature. Values dielectric constant and loss tangent are measured at various different frequencies ranging from 100 Hz to 1 MHz respectively. For
measurement of temperature dependent dielectric properties sample was placed in a furnace and heated from room temperature to 150 °C, heating rate was maintained as 1 °C/min and the capacitance and Q value across the both sides of pellets are measured at different frequencies. Concentration of Zr\textsuperscript{4+} ions strongly affects on dielectric properties of BZT. With increasing content of Zr ions Curie temperature decreases and goes below room temperature, again with increasing Zr concentration material becomes more relaxor type and exhibits diffuse phase transition [12]. The transition temperature at Zr = 0.2 exist near room temperature ~ 30 °C in this case. BZT samples sintered at both temperatures exhibits sharp transition near room temperature. Dielectric permittivity has very high value near transition temperature, due to which very small field can also induces polarization in the material [13]. Therefore BaTiO\textsubscript{3} ceramic containing 20% Zr ions expected to exhibit more dielectric non-linearity. Here density of material plays an important role, due to which the ceramic sintered at 1200 °C exhibits more dielectric constant and low value of dielectric loss, reaching at ferroelectric to paraelectric transition dielectric constant starts to decrease. Magnitude of dielectric constant decreases with increase in frequency value which may be resulted due to different types of polarizations contributions. At lower frequency value interfacial polarization contributes more which results in more dielectric dispersion at lower frequency range. Loss tangent also varies in accordance to variation of dielectric constant for both BZT samples sintered at different temperatures. Ceramic sintered at 1200 °C has lower value of dielectric loss as compared to ceramic material sintered at 1100 °C. Dielectric loss value in ceramic sintered at both temperatures decreases with increase in temperature and again starts to increase at higher temperature range. Increase in loss tangent at higher temperature may resulted due to increase in dc conductivity of material with temperature [10] as conductivity decreases Q value and results in increase in loss tangent (tan\(\theta\)).
Figure 4.9 (a) Temperature dependent variation of dielectric constant (\(\varepsilon_r\)) of BZT sintered at 1100 °C.

Figure 4.9 (b) Temperature dependent variations of dielectric constant (\(\varepsilon_r\)) of BZT sintered at 1200 °C.
Figure 4.9 (c) Temperature dependent variation of dielectric loss tangent (tanδ) of BZT sintered at 1100 °C.

Figure 4.9 (d) Temperature dependent variation of dielectric loss tangent (tanδ) of BZT sintered at 1200 °C.

4.3.4 Ferroelectric properties of BZT

For measurement of polarization with applied electric field, sample were kept inside the container contains silicon oil bath and hysteresis loop were measured at room
temperature. Hysteresis loop measured at room temperature for BZT sample sintered at 1100 °C and 1200 °C is shown in figure 4.10. Hysteresis loops show typical nature as of normal ferroelectrics. Hysteresis loop of sample sintered at 1200 °C saturates at high electric field as compared to the sample sintered at 1100 °C. This may resulted due to, at lower temperature some pores remains in sample which makes sample conducting with applied electric field and sample gets shorted at that field and results in decrease in saturation polarization. On the other hand increasing sintering temperature increases density and enhances electrical properties of material. Observed values of remanant polarization (Pr), coercive field (Ec) and saturation polarization (Ps) of both samples were listed in table 4.4.

![Figure 4.10 Room temperature ferroelectric hysteresis loop (P-E) of BZT sintered at 1100 °C and 1200 °C.](image)

Table 4.4 Parameters observed from ferroelectric measurement of BaZr$_{0.2}$Ti$_{0.8}$O$_3$ sintered at different temperature.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Saturation Polarization (Ps) $\mu$C/cm$^2$</th>
<th>Remanant Polarization (Pr) $\mu$C/cm$^2$</th>
<th>Coercive Field (Ec) kV/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>BZT 1100 °C</td>
<td>1.59</td>
<td>0.55</td>
<td>13.01</td>
</tr>
<tr>
<td>BZT 1200 °C</td>
<td>1.91</td>
<td>0.67</td>
<td>13.10</td>
</tr>
</tbody>
</table>
4.4 Characterization of ferroelectric composite $x[(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3]-(1-x)[\text{Ba(Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$]

The calcinated powders of BCT and BZT were used to prepare the ferroelectric composite of $x[(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3]-(1-x)[\text{Ba(Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$] where $x = 0.15, 0.3, 0.4$ and $0.5$. The individual powder samples are mixed in stoichiometric proportions and ground for 2–3 h. The mixed powder samples were pressed by using hydraulic press. The pressure applied is about 4-5 tons to get the material in a disk shape of 1 cm diameter and about 2 mm thickness. The synthesis procedure of BCT and BZT are reported in previous chapter, while its structural and electrical properties are mentioned in previous section. Green pellets of $x[(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3]-(1-x)[\text{Ba(Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$] for $x=0.4$ and $0.5$ are primarily sintered at $1100 \, ^\circ\text{C}$ with microwave sintering technique. At first the soaking time was maintained for quite longer time i.e. 80 min for preparation of final BCT-BZT ceramic composite. This developed ferroelectric samples are characterized by various characterization techniques to study its different properties. On analysis of results obtained through various techniques samples of $x[(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3]-(1-x)[\text{Ba(Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$] where $x=0.15, 0.3, 0.4$ and $0.5$ are prepared and sintered at $1200 \, ^\circ\text{C}$, here the soaking time maintained was very i.e. only 20 min on the other hand the rate of increase in temperature were kept at $40 \, ^\circ\text{C/min}$. Different properties of ferroelectric composite samples $x\text{ BCT-} (1-x)\text{ BZT}$ at $x = 0.15, 0.3$ and 0.4 and 0.5 sintered at $1200 \, ^\circ\text{C}$, and properties of ceramic samples with $x = 0.4$ and 0.5 sintered at $1100 \, ^\circ\text{C}$ for 80 min are included in this section.

4.5 Characterization of $x\text{BCT-}(1-x)\text{BZT}$ ($x = 0.4$ and $0.5$) sintered at $1100 \, ^\circ\text{C}$

After being structural analysis here all other different properties of $x\text{BCT-}(1-x)\text{BZT}$ ceramic samples sintered at $1100 \, ^\circ\text{C}$ are studied which are primarily represented in this section.

4.5.1 Structural analysis

Powder samples of $x[(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3]-(1-x)[\text{Ba(Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$] where $x= 0.15, 0.3, 0.4$ and $0.5$, after sintering through microwave technique are characterized by x-ray diffractometer for their structural analysis. Figure 4.11 shows room temperature x-ray diffraction pattern of $x[(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3]-(1-x)[\text{Ba(Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$] for $x=0.4$ and 0.5 sintered at $1100 \, ^\circ\text{C}$ for 80 min. X-ray diffraction pattern of $x\text{BCT-} (1-x)\text{BZT}$ ceramic samples measured between $2\theta = 20^\circ$ to $80^\circ$ and scan rate was maintained at $3^\circ/\text{min}$. diffraction
pattern shows pure perovskite phase with coexistence of tetragonal and rhombohedral crystal structures without any other impure phase. All the diffraction patterns of perovskite phase are assigned by the JCPDS card [05-626], [83-0368]. Existence of the polycrystalline perovskite structure without any secondary phase is in good agreement with the diffusion of Ca²⁺ and Zr⁴⁺ ions into BaTiO₃ lattice and confirms formation of stable solid solution [14-16]. Separation of reflection peak 002/200 around 2θ=45° and peak 202/220 at 2θ=66° confirms the existence tetragonal (T) and rhombohedral (R) structure respectively [16]. The splitting of peaks at the 2θ angles 45° and 66° sample sintered at 1100 °C was presented in figure inset. Biphasic structure is in good agreement with formation of stable composite of x[(Ba₀.₇Ca₀.₃)TiO₃]–(1-x)[Ba(Zr₀.₂Ti₀.₈)O₃] ceramic.

It could be seen that, diffraction peaks shift towards higher angles with increasing x content. This may be due to decrease in Zr as the content of Ba(Zr₀.₂Ti₀.₈)O₃ decreases in the composition. It might be due to the Zr⁴⁺ ion is chemically more stable than Ti⁴⁺, hence the substitution of Ti⁴⁺ by Zr⁴⁺ expands the lattice of ceramics as ionic radii of Zr⁴⁺ (86 pm) are larger than that of Ti⁴⁺ (60.5 pm). The lattice parameters are decreasing with decrease in Zr contents i.e. decreasing BZT content in the composition. The effect of increasing Ca contents with increasing (Ba₀.₇Ca₀.₃)TiO₃ content in composition adds on to this shifting to higher angles as lattice constant further shrinks with the increase in Ca²⁺ ions at the Ba²⁺ sites, due to smaller ionic radii of Ca²⁺ (114 pm) over Ba²⁺ (149 pm). With increasing BCT content, the doublets at (002)/(200) diffraction peak move further apart, which shows increase in tetragonality (c/a) ratio. Lattice parameters and unit cell volume with crystallite size measured at higher intense peak (100) for BCT-BZT ceramic sintered at 1100 °C were listed in table 4.5 Crystallite size was calculated using Debye-Scherrer method as given by equation 4.1.
Figure 4.11 Room temperature x-ray diffraction pattern of $x[(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3] - (1-x) [\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3]$ where $x=0.4$ and $0.5$ sintered at $1100 \, ^\circ\text{C}$.

Table 4.5 Lattice parameters, unit cell volume and crystallite size of $x\text{BCT} - (1-x)\text{BZT}$ sintered at $1100 \, ^\circ\text{C}$.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Lattice Parameters</th>
<th>Unit Cell volume V = (a²c)</th>
<th>Crystallite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a(Å)</td>
<td>c(Å)</td>
<td>c/a</td>
</tr>
<tr>
<td>0.5BCT-0.5BZT</td>
<td>3.9752</td>
<td>4.0028</td>
<td>1.0069</td>
</tr>
<tr>
<td>0.4BCT-0.6BZT</td>
<td>3.9675</td>
<td>3.9936</td>
<td>1.0065</td>
</tr>
</tbody>
</table>

4.5.2 Morphological and EDS analysis

Figure 4.13 (a) and 4.13 (b) show scanning electron microscope images of the $x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3-(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ ferroelectric composite for $x = 0.4$ and $0.5$ sintered at $1100 \, ^\circ\text{C}$ respectively. It shows agglomeration of $(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ ceramics with clusters having small pores distributed through the surface. The grains are formed with irregular shape attached with the clusters. The average grain size calculated from cluster free grains is about $\sim 0.5 \, \mu\text{m}$ for $0.4\text{BCT}-0.6\text{BZT}$ where as the average grain size of $0.5\text{BCT}-0.5\text{BZT}$ is $\sim 0.4 \, \mu\text{m}$ which is very small as compared to the solid state.
The average grain size decreases with increase in calcium content and decrease in Zr content as the average grain size of 0.5BCT-0.5BZT is smaller than 0.4BCT-0.6BZT. There is a loss of densification with increasing (Ba$_{0.7}$Ca$_{0.3}$)TiO$_3$ content as less heavier element like Ca$^{2+}$ start replacing Ba$^{2+}$ [2, 14]. The presence of all the elements in stoichiometric proportion is confirmed by using Energy Dispersive Spectrometry (EDS). Figure 4.13 (c) and (d) represents elemental analysis spectra of 0.4BCT-0.6BZT and 0.5BCT-0.5BZT sintered at 1100 °C respectively. A table inset gives the weight (%) and atomic (%) of elements presents in the final composition for a respective ferroelectric composition.

**Figure 4.12 SEM images of x(BCT)-(1-x)BZT ceramic samples sintered at 1100 °C where (a) x = 0.4 and (b) x = 0.5 respectively.**

**Figure 4.12 EDS spectra of x(BCT)-(1-x)BZT ceramic samples sintered at 1100 °C where (c) x = 0.4 and (b) x = 0.5.**

**4.5.3 Density measurement**

The bulk density of the sintered pellets of BCT-BZT ceramic samples is determined by Archimedes principle as given in the equation 4.4.
Bulk Density \( (\rho_{\text{d}}) = \frac{W_{d} \times \text{density of liquid}}{W_{s} - W_{a}} \) ----- 4.4

Where \( W_{d} \) is weight of the sample in dry, \( W_{s} \) weight of the soaked sample and \( W_{a} \) is weight of sample suspended in air. While, relative density of composite is calculated by the equation 4.5.

Relative Density \( (\rho) = \frac{\rho_{\text{th}}}{\rho_{\text{m}}} \) ----- 4.5

Where, \( \rho_{\text{th}} \) is the theoretical density of the BaTiO\(_3\), which is 6.02. The measured bulk density is 4.79 g/cc\(^{-3}\) and relative density 79.56% for BCT-BZT 0.4 and the bulk density is 4.47 g/cc\(^{-3}\) and relative density 74.25% for BCT-BZT 0.5. It is seen that lead free ferroelectric composite (BCT-BZT) sintered at 1100 °C shows lower values of density. More densification might be achieved by adding small amount of sintering aid or by sintering the compositions at higher temperatures.

4.5.4 Dielectric properties of \( x\text{(BCT)}-(1-x)\text{(BZT)} \) (\( x = 0.4 \) and 0.5)

4.5.4.1 Dielectric constant (\( \varepsilon_{r} \)) Vs temperature

The phase transition behavior of BCT–BZT ceramics is studied by temperature dependent dielectric spectroscopy measurements in the frequency range 1 KHz–1 MHz. Figure 4.13 (a) and (b) show the dielectric constant as function of temperature \( x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_{3}-(1-x)\text{Ba(Zr}_{0.2}\text{Ti}_{0.8})\text{O}_{3} \) for \( x = 0.4 \) and 0.5 respectively. A broad dielectric anomaly is observed for \( x=0.5 \) as compared to the \( x=0.4 \) BCT-BZT compositions. In analysis of XRD pattern it was observed that both the compositions shows a tetragonal crystal structure phase transition near room temperature which is also confirmed from the dielectric behavior. The phase transition temperature or Curie temperature (\( T_{c} \)) is observed between 120 °C to 130 °C for both of the compositions whereas dielectric maxima (\( \varepsilon_{m} \)) is observed at the maximum temperature (\( T_{m} \)) for 1 KHz. Both temperature-dependent dielectric permittivity and Curie temperatures (\( T_{c} \)) could be altered by substitution of various ions on the Ba or Ti sub lattice in BaTiO\(_3\) [14].

4.5.4.2 Loss tangent (\( \tan\delta \)) Vs temperature

Figure 4.13 (c) and (d) show the loss tangent (\( \tan\delta \)) as function of temperature for 0.4 and 0.5 BCT-BZT ceramics respectively. The loss tangent decreases initially with
increase in temperature and then increases further at higher temperatures. It could be seen that loss tangent is higher at low frequencies and posses low loss at higher frequencies. This might be due to interfacial polarization at grain-grain boundary interface [17]. The low loss tangent value indicates the low dielectric loss in both compositions. The observed behavior is a competitive phenomenon between the dielectric relaxation and the electrical conduction of relaxing species.

Figure 4.13 (a) Variation of dielectric constant ($\varepsilon_r$) with temperature for xBCT-(1-x)BZT where $x = 0.4$ sintered at 1100 °C.

Figure 4.13 (b) Variation of dielectric constant with temperature for xBCT-(1-x)BZT where $x = 0.5$ sintered at 1100 °C.
Figure 4.13 (c) Variation of loss tangent (tan\(\delta\)) with temperature for xBCT-(1-x)BZT where \(x = 0.4\) sintered at 1100 °C.

Figure 4.13 (d) Variation of loss tangent (tan\(\delta\)) with temperature for xBCT-(1-x)BZT where \(x = 0.4\) sintered at 1100 °C.

4.5.4.3 Diffuse phase transition (DPT)

Figure 4.14 (a) and (b) show the diffuse phase transition (DPT) behavior of 0.4 BCT-BZT and 0.5 BCT-BZT respectively. The graph of \(1000/\varepsilon_r\) is plotted with temperature to study the DPT nature of the compositions. For all the frequencies the maxima of dielectric
constant is observed at maximum temperature which is in between 390-400°K for both the compositions. Comparing with the earlier reports the DPT values observed are high and improved [18]. In the paraelectric phase the ferroelectric materials obeys the Curie-Weiss law and it is given by the equation 4.6.

\[
\frac{1}{\varepsilon_r} = \frac{T - T_0}{C} \quad \text{Where} \quad (T \geq T_0) \quad ----- 4.6
\]

Where \( \varepsilon_r \) is dielectric constant, \( T \) is the Absolute temperature, \( T_0 \) is the curie temperature and \( C \) is the Curie-Weiss constant. The graph of inverse the dielectric constant with temperature in the frequency range 1 KHz to 1 MHz and the corresponding fitted curve in the paraelectric region gives the Curie-Weiss behavior or the degree of diffuseness (\( \Delta T_m \)) as given by equation 4.7 [19].

\[
(\Delta T_m) = T_{cw} - T_m (^{\circ}C) \quad ----- 4.7
\]

Where \( T_{cw} \) represents the temperature from which the dielectric constant (\( \varepsilon_r \)) starts to follow the Curie-Weiss law and \( T_m \) denotes the maximum temperature at which the dielectric constant is maximum. The estimated value of \( \Delta T_m \) is found to be \(~ 30 \)°C. Evaluation of the phase transition mode is done by using the empirical comprehensive power law [20-21]. This law is applicable for the dielectric spectra which shows neither normal nor relaxor type of ferroelectric and is given by

\[
\frac{1}{\varepsilon_r} - \frac{1}{\varepsilon_{rm}} = \frac{(T - T_m)^\gamma}{C} \quad ----- 4.8
\]

Where \( \gamma \) is diffuseness factor and \( C \) is the Curie-Weiss constant. The estimated value of \( \gamma \) are 1.61 and 1.32 for \( x(Ba_{0.7}Ca_{0.3})TiO_3-(1-x)Ba(Zr_{0.2}Ti_{0.8})O_3 \) solid solutions for \( x = 0.4 \) and 0.5 respectively, which are calculated from the slope of log (\( 1/\varepsilon_r - 1/\varepsilon_{rm} \)) vs. log (\( T-T_m \)) graph as shown in the figure 4.14 (c) and (d) respectively.
Figure 4.14 (a) Diffuse phase transition behaviour of xBCT-(1-x)BZT at x = 0.4 sintered at 1100 °C.

Figure 4.14 (b) Diffuse phase transition behaviour of xBCT-(1-x)BZT at x = 0.5 sintered at 1200 °C.

Generally the $\gamma$ value founds between 1 and 2 depending on the phase transition modes. The $\gamma = 1$ value shows normal ferroelectric and $\gamma = 2$ shows the relaxor type of ferroelectric phase transition. Hence it is concluded that the present solid solutions are neither normal ferroelectrics nor the relaxor type of ferroelectrics.
4.5.5 Ferroelectric properties

Figure 4.15 shows well saturated hysteresis loops with regular shape, typical of ferroelectric materials, observed for both of the compositions. It could be seen that 0.5BCT-BZT exhibits anomaly ferroelectric properties such as the highest spontaneous polarization (Pm), highest remnant polarization (Pr) and relatively low coercive field (Ec). It might be due the MPB (morphotropic phase boundary) transitions in 0.5BCT-BZT. This
fact indicates that some interaction exists between the two phases i.e. ferroelectric R (BZT side) and T (BCT side) phases separated by MPB. A decrease in remanant polarization with the increase in zirconium content is indicative of changes in crystal structure and predominance of relaxor behavior. With increase of Ca contents, the remanant polarization is decreased due to loss of crystallinity. The polarization enhances the polarizability and domain rotation ability of the ceramics during the external electric field application. Therefore, the related parameters like dielectric constant and remanant polarization of the ceramics increase [22]. Parameters like spontaneous polarization, remanant polarization, coercive field and saturated electric field for x[(Ba_{0.7}Ca_{0.3})TiO_3]-1-x[Ba(Zr_{0.2}Ti_{0.8})O_3] for x = 0.4 and 0.5 are as listed in the table 4.6.

Figure 4.15 Ferroelectric hysteresis loop (P-E) of BCT-BZT 0.4 and 0.5 sintered at 1100 °C.
Table 4.6 Parameters observed from ferroelectric measurement of xBCT-(1-x) BZT sintered at 1100 °C.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Remanant Polarization Pr (μC/cm²)</th>
<th>Saturation Polarization Ps (μC/cm²)</th>
<th>Coercive Field Ec (kV/cm)</th>
<th>Maximum Field Emax (kV/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4BCT-0.6BZT</td>
<td>0.24</td>
<td>1.28</td>
<td>8.35</td>
<td>21.33</td>
</tr>
<tr>
<td>0.5BCT-0.5BZT</td>
<td>0.32</td>
<td>1.95</td>
<td>5.61</td>
<td>32.45</td>
</tr>
</tbody>
</table>

4.6 Characterization of xBCT-(1-x)BZT (x = 0.15, 0.3, 0.4 and 0.5) sintered at 1200 °C

It is seen that, ceramic materials synthesized by microwave sintering method at 1100 °C show less density. Due to lower density ceramics sintered at this temperature has meagre electrical and physical properties. To achieve enhancement in physical and electrical properties with higher density, xBCT-(1-x)BZT ferroelectric compositions are again synthesized and sintered at higher temperature (1200 °C) with microwave sintering technique with variation of some parameters. Here the sintering rate was kept at 40 °C/min where as the sample heating time is reduced to 20 min only. Here the process of sintering is completed within 2 hours including cooling process. After processing this ferroelectric composite samples are checked for their different properties as similar in previous section. All the results observed with characterization through different techniques for ferroelectric composition \( x[(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3]-(1-x)[\text{Ba(Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3] \) where \( x = 0.15, 0.3, 0.4 \) and 0.5 are mentioned in the following section.

4.6.1 Structural analysis

After being sintered at 1200 °C powder samples of ferroelectric composition \( x[(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3]-(1-x) [\text{Ba(Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3] \) where \( x = 0.15, 0.3, 0.4 \) and 0.5 are analysed with x-ray diffraction for confirmation of crystal structure. Here the samples of BCT-BZT exhibits similar kind of biphasic crystal structure as observed for samples sintered at 1100 °C. Again here also the x-ray diffraction pattern of xBCT- (1-x)BZT ferroelectric composite samples measured between \( 20 = 20° \) to \( 80° \) and scan rate was maintained at \( 3°/\text{min} \). Diffraction pattern confirms existence biphasic crystal structure i.e. tetragonal and
rhombohedral crystal structures in perovskite ferroelectric composition. All the diffraction patterns of perovskite phase are assigned by the JCPDS card [05-626], [83-0368] and no evidence was found related to any impurity peak from the crystal structure. Formation of polycrystalline perovskite structure without exhibiting any secondary phase is in good agreement with diffusion of Ca$^{2+}$ and Zr$^{4+}$ ions in to BaTiO$_3$ lattice and formation of BCT-BZT stable solid solution [14-16]. Separation of reflection peak 002/200 around 2θ=45° and peak 202/220 at 2θ=66° confirms the existence tetragonal (T) and rhombohedral (R) structure respectively [16]. The splitting of peaks at the 2θ angles 45° and 66° sample for xBCT-(1-x)BZT samples with variation of x value i.e. for x =0.15, 0.3, 0.4 and 0.5 respectively is represented in figure 4.16 (b).

Here it is seen that the diffraction peaks shifts towards higher 2θ angle with increasing BCT content in the composite BCT-BZT. Shifting of peaks may results due to reduction of BZT side in the composition, as Zr$^{4+}$ ion is chemically more stable than Ti$^{4+}$ and substitution of Zr ions with larger ionic radii results in expansion of lattice structure. With increasing BCT content, the doublets at (002)/(200) diffraction peak move further apart, which shows increase in tetragonality (c/a) ratio. Lattice parameters and unit cell volume with crystallite size measured at higher intense peak (100) for BCT-BZT ceramic table 4.7

Figure 4.16 (a) Room temperature x-ray diffraction pattern of x[(Ba$_{0.7}$Ca$_{0.3}$)TiO$_3$]–(1-x) [Ba(Zr$_{0.2}$Ti$_{0.8}$)O$_3$] sintered at 1200 °C.
Figure 4.16 (b) Splitting of diffraction peaks at $2\theta = 45^\circ$ and $2\theta = 65^\circ-66^\circ$ of xBCT-(1-x)BZT ceramic sintered at 1200 °C at various x content.

Table 4.7 Lattice parameters, unit cell volume and crystallite size of xBCT-(1-x)BZT sintered at 1200 °C at various x content.

<table>
<thead>
<tr>
<th>X- Content</th>
<th>Lattice Parameters</th>
<th>Unit Cell Volume</th>
<th>Crystallite Size</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a(Å)</td>
<td>c(Å)</td>
<td>c/a</td>
</tr>
<tr>
<td>X=0.15</td>
<td>4.0034</td>
<td>4.039</td>
<td>1.0001</td>
</tr>
<tr>
<td>X=0.3</td>
<td>3.9946</td>
<td>4.037</td>
<td>1.0106</td>
</tr>
<tr>
<td>X=0.4</td>
<td>3.9926</td>
<td>4.034</td>
<td>1.0103</td>
</tr>
<tr>
<td>X=0.5</td>
<td>3.9878</td>
<td>4.035</td>
<td>1.0118</td>
</tr>
</tbody>
</table>

4.6.2 Morphological and EDS analysis

Microstructural analysis of $x[(Ba_{0.7}Ca_{0.3})TiO_3]-1-x[Ba(Zr_{0.2}Ti_{0.8})O_3]$ was done by field emission scanning electron microscope with EDAX. Figure 4.17 (a), (b), (c) and (d) represents FESEM images of xBCT-(1-x)BZT ceramic samples sintered at 1200 °C for x = 0.15, 0.3, 0.4 and 0.5 respectively. Dense nature of grains having irregular shaped grains was observed for each x value. Higher sintering temperature affects directly on
microstructure of ceramic material, which results in pore free compact structure, also fast microwave sintering technique is found to be effective technique over conventional sintering technique due to its internal direct heating mechanism of material, which results higher dense structured material. It is seen that, average grain size varies between 0.4 μm to 0.9 μm as the x content varies from x = 0.15 to x = 0.5 in general the average grain size increase with increase in x content. The density was calculated by the similar Archimedes principal, and it is found that the ceramic sintered at 1200 °C has higher density than the ceramics sintered at 1100 °C in previous section. The measured bulk densities are 5.63 g/cc, 5.58 g/cc, 5.79 g/cc and 5.62 g/cc for x= 0.15, 0.3, 0.4 and 0.5 respectively while the relative density is found between 90 % to 96 %. Densification of ceramics above 90% is found more important feature in case of ceramic materials. Dense pore free structure of ceramic sample results in improvement of electrical and physical properties as there is minimum possibility flow of leakage current through sample. For confirmation of elemental analysis in composition, all ceramic samples were analysed by energy dispersive electron spectroscopy (EDS). It is found all the elements are found in composition with their respective stoichimetric amount. Figure 4.18 (a), (b), (c) and (d) represents EDS spectra of ferroelectric composition xBCT-(1-x)BZT for x = 0.15, 0.3, 0.4 and 0.5 respectively. Tables inset of each figure gives weight (%) and atomic (%) of each element in the final composition. The elemental weight (%) and atomic (%) varies in accordance with variation of x concentration. No peak corresponding any impurity was observed in EDS spectrum suggests formation of ferroelectric BCT-BZT composition.

Figure 4.17 FE-SEM images of xBCT-(1-x)BZT sintered at 1200 °C where (a) X=0.15, and (b) X=0.3.
Figure 4.17 FE-SEM images of xBCT-(1-x)BZT sintered at 1200 °C where (c) x=0.4 and (d) x=0.5.

Figure 4.18 EDS spectra of xBCT-(1-x)BZT sintered at 1200 °C where (a) x = 0.15, (b) x = 0.3, (c) x = 0.4 and (d) x = 0.5.

4.6.3 Dielectric properties of xBCT-(1-x)BZT (x = 0.15, 0.3, 0.4 and 0.5)

Pellet samples of ferroelectric composite xBCT-(1-x)BZT after sintering at 1200 °C are used for dielectric property measurement. Here, for measurement purpose both side surface of each pellet were coated using silver and dried under IR lamp (Temp ~ 150 °C)
for 2 hours. Pellets of all four ceramic samples were characterized for their electrical properties and presented here.

4.6.3.1 Dielectric constant ($\varepsilon_r$) and loss tangent (tanδ) with temperature

Dielectric constant was calculated by measuring parallel capacitance, while the Q value also measured in parallel process which was further used for calculate dielectric loss tangent as per formulas given in previous section. Capacitance and Q value were measured at different frequencies, at 500 Hz, 1 KHz, 5 KHz, 10 KHz, 100 KHz, 500 KHz, and 1 MHz with variation of temperature from -10 °C to 200 °C. Figure 4.19 (a), (b), (c) and (d) show the dielectric constant versus temperature nature of $x[(Ba_{0.7}Ca_{0.3})TiO_3]-1-x[Ba(Zr_{0.2}Ti_{0.8})O_3]$ where x= 0.15, 0.3, 0.4 and 0.5 respectively.

All four samples has unique characteristic of dielectric constant behaviour, i.e. relative dielectric constant ($\varepsilon_r$) of each ceramic sample increases with increase in temperature, reaches maximum and then start decreasing with further increment in temperature. Decrease in the dielectric constant from the specific temperature is called as phase transition, above this temperature the ferroelectric material act as a paraelectric material. Temperature at which one phase of material gets converted to another phase is called as transition temperature or Curie temperature (Tc) [23]. Therefore relative dielectric behaviour with applied temperature can be utilised to study structural changes in the ceramic material. It could be seen that, all four ceramic sample posses high value of dielectric constant at Tc. The transition temperature (Tc) increases with increase in BCT content in the BCT-BZT composition, while the value of dielectric constant slightly decreases. Here, as mentioned in previous section BCT side has the higher transition temperature (155 °C) but the relative dielectric permittivity is lower in case of Ca doped BaTiO₃, on the other hand Zr doped BaTiO₃ has higher relative permittivity with transition temperature near room temperature (~ 35 °C for 20 % Zr content).This may be due to more chemically stability of Zr⁴⁺ ions than Ti⁴⁺ side which enhances the electrical properties of the material. due to this the transition temperature of BCT-BZT composition increase with increase in BCT content, highest transition temperature (~140°C) with fine dielectric properties was observed in case of 0.5BCT-0.5BZT ceramic. More over the fast microwave sintering improves crystallinity and microstructure in of the ceramic material which results in enhancement of transition point temperature than the ceramic material processed with conventional method [24]. Also ceramic samples posse’s one more
dielectric anomaly near room temperature (20 °C - 35 °C) with variation of x content. This lower temperature anomaly may result due to rhombohedral-tetragonal (R-T) phase transition at room temperature. With lower dielectric anomaly and ferroelectric to paraelectric phase transition, composition with x = 0.5 is known to have morphotropic phase boundary near room temperature. These properties of BCT-BZT lead-free piezoelectric ceramic are comparable with lead-containing piezoelectric material like PbZrTiO₃ [25]. Magnitude of dielectric constant decreases with increase in frequency, this may due to at lower field the electrons follow applied a.c. field path while at higher field they start decline applied field path which lowers the value of capacitance. Values of Tc, εr and tanδ at transition temperature point for each x content was listed in table 4.8.

Loss tangent properties of xBCT-(1-x)BZT samples at all frequencies with increase in temperature are shown in figure 4.20 (a), (b), (c) and (d) for x = 0.15, 0.3, 0.4 and 0.5. The loss tangent with temperature has similar kind of nature as dielectric constant, it also show a lower temperature anomaly. Loss tangent value decreases with further increase in temperature, and shows sudden increase after certain value of temperature depending on applied magnitude of frequency. This sudden increment in loss tangent is due over certain range of temperature material start to become conducting at higher temperature and low applied frequency. Analogous behavior is observed for temperature dependent dielectric loss tangent (tanδ) in all four samples.

Table 4.8 Parameters observed from dielectric measurement and average grain size of xBCT-(1-x) BZT sintered at 1200 °C.

<table>
<thead>
<tr>
<th>Composition (x-value)</th>
<th>Tc (°C)</th>
<th>εr at Tc (freq= 1 KHz)</th>
<th>tan δ at Tc (freq= 1 KHz)</th>
<th>Average Grain Size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R-T</td>
<td>T-C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X=0.15</td>
<td>30 °C</td>
<td>95 °C</td>
<td>6470</td>
<td>0.04649</td>
</tr>
<tr>
<td>X=0.3</td>
<td>25 °C</td>
<td>115 °C</td>
<td>4273</td>
<td>0.03199</td>
</tr>
<tr>
<td>X=0.4</td>
<td>25 °C</td>
<td>130 °C</td>
<td>3464</td>
<td>0.01856</td>
</tr>
<tr>
<td>X=0.5</td>
<td>25 °C</td>
<td>140 °C</td>
<td>3282</td>
<td>0.02673</td>
</tr>
</tbody>
</table>
Figure 4.19 (a) Variation of dielectric constant ($\varepsilon_r$) with temperature of 0.15BCT-0.85BZT sintered at 1200 °C.

Figure 4.19 (b) Variation of dielectric constant ($\varepsilon_r$) with temperature of 0.3BCT-0.7BZT sintered at 1200 °C.
Figure 4.19 (c) Variation of dielectric constant ($\varepsilon_r$) with temperature of 0.4BCT-0.6BZT sintered at 1200 °C.

Figure 4.19 (d) Variation of dielectric constant ($\varepsilon_r$) with temperature of 0.5BCT-0.5BZT sintered at 1200 °C.
Figure 4.20 (a) Variation of dielectric loss tangent (tanδ) with temperature of 0.15BCT-0.85BZT sintered at 1200 °C.

Figure 4.20 (b) Variation of dielectric loss tangent (tanδ) with temperature of 0.3BCT-0.7BZT sintered at 1200 °C.
Figure 4.20 (c) Variation of dielectric loss tangent (tanδ) with temperature of 0.4BCT-0.6BZT sintered at 1200 °C.

Figure 4.20 (d) Variation of dielectric loss tangent (tanδ) with temperature of 0.5BCT-0.5BZT sintered at 1200 °C.

4.6.3.2 Diffuse phase transition (DPT)

Ferroelectric diffuse phase transition was confirmed with Curie-Weiss law, which is applicable for dielectric constant behaviour above Curie temperature of normal ferroelectric materials. Curie-Weiss law can be represented as equation 4.6 mentioned in earlier section. Existence of diffuse phase transition (DPT) can established with
temperature dependent variation of $1000/\varepsilon_r$. In general the DPT behaviour was plotted at higher temperature range. Figure 4.21 (a), (b), (c) and (d) show the DPT behaviour of $x[(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3]-1-x[\text{Ba(Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3]$ where $x= 0.15$, 0.3, 0.4 and 0.5 respectively sintered at 1200°C with applied frequency 1 KHz. The dielectric maxima of all four samples was observed at maximum temperature which is in between 368-412 °k, while it could be seen that the maximum temperature increases with increasing x (BCT) content in the composition. Therefore the 0.5BCT-BZT ceramic has maximum temperature value (Tm) at 1 KHz. dielectric constant of ferroelectric material, which exhibits DPT behaviour decreases above Curie temperature where it follows Curie-Weiss law up to certain range of temperature called as Curie region. The degree of deviation, represented as $\Delta T_m$, the value of $\Delta T_m$ can be calculated by using equation 4.7 given as per earlier where the notations have the usual meaning. The observed values $\Delta T_m$, with microwave sintered ceramic samples has higher magnitude are in good agreement with the $\Delta T_m$ values reported by conventional sintering method earlier [18, 26]. The obtained $\Delta T_m$ values are 38 °C, 18 °C, 18 °C, 34 °C for $x$BCT-(1-$x$)BZT ceramic materials where $x= 0.15$, 0.3, 0.4 and 0.5 respectively. Other parameters observed from DPT study are listed in table 4.9. This observed values shows that the two samples 0.15BCT-0.85BZT and 0.5BCT-0.5BZT has nearly equal and enhanced DPT behaviour, which shows that the dielectric constant peaks posses broad structure in this at $x= 0.15$ and 0.5. On the other hand the ceramics with $x=0.3$ and 0.4 are shows equal DPT region, implies that there is less broadening in nature of dielectric constant.

Dielectric behaviour of complex ferroelectric materials, which are known to exhibit diffuse phase transition (DPT), can be explained on the basis of empirical comprehensive power law as given by equation 4.8. This law is applicable for ferroelectric materials which are neither normal or has no relaxor type of behaviour. With the use of this power the diffuseness factor ($\gamma$) can be calculated, on the basis of observed gamma values the behaviour of material could be decided, in general $\gamma=1$ for material with normal ferroelectric properties and $\gamma=2$ for material having relaxor type of ferroelectric properties. Gamma ($\gamma$) values can be calculated by plotting the graph as, log $(1/\varepsilon_r - 1/\varepsilon_{rm})$ versus log (T-Tm). Inset figure 4.21 (a), (b), (c), and (d) shows the observed gamma values for $x$BCT-(1-$x$)BZT ceramic samples sintered at 1200 °C which are calculated at an magnitude of 1 KHz frequency. Observed gamma values shows that the BCT-BZT material exhibits a
ferroelectric behaviour, which is neither normal nor relaxor type. Whereas with increasing $x$ from 0.15 to 0.5 material inclines towards relaxor type of ferroelectric ceramic.

Figure 4.21 (a) Diffuse phase transition behaviour of 0.15BCT-0.85BZT sintered at 1200 °C measured at 1 kHz (figure inset are log $(1/\varepsilon_r - 1/\varepsilon_m)$ versus log $(T - T_m)$ plot.

Figure 4.21 (b) Diffuse phase transition behaviour of 0.3BCT-0.7BZT sintered at 1200 °C measured at 1 kHz (figure inset are log $(1/\varepsilon_r - 1/\varepsilon_m)$ versus log $(T - T_m)$ plot.
Figure 4.21 (c) Diffuse phase transition behaviour of 0.3BCT-0.7BZT sintered at 1200 °C measured at 1 kHz (figure inset are log (1/εr - 1/εrm) versus log (T - Tm) plot.

Figure 4.21 (d) Diffuse phase transition behaviour of 0.3BCT-0.7BZT sintered at 1200 °C measured at 1 kHz (figure inset are log (1/εr - 1/εrm) versus log (T - Tm) plot.
Table 4.9 Parameters observed from DPT behaviour and diffuseness factor ($\gamma$) of xBCT-(1-x) BZT sintered at 1200 °C.

<table>
<thead>
<tr>
<th>Composition (X value)</th>
<th>$T_m$(°C)</th>
<th>$\Delta T_m$(°C)</th>
<th>$T_0$(°C)</th>
<th>$T_{cw}$(°C)</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0.15</td>
<td>95</td>
<td>38</td>
<td>102</td>
<td>134</td>
<td>1.55</td>
</tr>
<tr>
<td>x = 0.3</td>
<td>110</td>
<td>18</td>
<td>115</td>
<td>127</td>
<td>1.85</td>
</tr>
<tr>
<td>x = 0.4</td>
<td>130</td>
<td>18</td>
<td>138</td>
<td>148</td>
<td>1.66</td>
</tr>
<tr>
<td>x = 0.5</td>
<td>139</td>
<td>35</td>
<td>153</td>
<td>174</td>
<td>1.93</td>
</tr>
</tbody>
</table>

4.6.4 Ferroelectric properties

Figure 4.22 shows the room temperature electric field dependent polarization (P-E) properties of x(BCT)-(1-x)BZT samples sintered at 1200 °C measured at 100 KHz frequency. Well saturated ferroelectric hysteresis loops are observed for all four ceramic samples. From the figure it could be seen that ferroelectric hysteresis properties are strongly composition dependent as, the value of $P_r$ increase with increase in x composition (BCT), 0.5BCT-0.5BZT composition has the highest value of remanant polarization ($P_r$) at room temperature implies the MPB behaviour of ceramic at 50BCT-50BZT [25,27]. This MPB behaviour was also confirmed by x-ray diffraction and dielectric behaviour. Also the value of spontaneous polarization increases with increasing x content, again the ceramic composition with x=0.5 has highest spontaneous polarization, which suggest dielectric breakdown occurs at higher field in this composition. Magnitude of coercive field decreases with increase in x=0.2 content, and it increase at x=0.4 again. Again the enhanced results are observed than the ceramic sintered at lower temperature (1100 °C) mentioned as in earlier section. Parameters like saturation polarization ($P_s$), coercive field ($E_c$), remanant polarization ($P_r$) are tabulated in table 4.10.
Figure 4.22 Room temperature ferroelectric hysteresis loop (P-E) of xBCT-(1-x)BZT sintered at 1200 °C.

Table 4.10 Parameters observed from room temperature ferroelectric hysteresis loop of xBCT-(1-x) BZT sintered at 1200 °C.

<table>
<thead>
<tr>
<th>Composition (x –value)</th>
<th>Coercive Field (Ec) kV/cm</th>
<th>Remanant Polarization (Pr) μC/cm²</th>
<th>Spontaneous Polarization (Ps) μC/cm²</th>
<th>Maximum field Emax kV/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0.15</td>
<td>5.14</td>
<td>0.76</td>
<td>5.80</td>
<td>54.18</td>
</tr>
<tr>
<td>x = 0.3</td>
<td>2.48</td>
<td>0.66</td>
<td>6.61</td>
<td>46.02</td>
</tr>
<tr>
<td>x = 0.4</td>
<td>3.65</td>
<td>1.29</td>
<td>7.18</td>
<td>33.12</td>
</tr>
<tr>
<td>x = 0.5</td>
<td>5.02</td>
<td>1.78</td>
<td>7.38</td>
<td>32.16</td>
</tr>
</tbody>
</table>

4.6.5 Raman spectroscopy

Room temperature Raman spectra of x[(Ba_{0.7}Ca_{0.3})TiO₃]-1-x[Ba(Zr_{0.2}Ti_{0.8})O₃] where x= 0.15, 0.3, 0.4 and 0.5 respectively represented as in figure 4.23. The Raman vibrational observed for all BCT-BZT samples are specified in the graph and this observed Raman modes well matches with those Raman modes observed in polycrystalline BaTiO₃.
ceramic sample [28]. Broad Raman peaks are observed for all BCT-BZT ceramic samples at room temperature, broadening of peaks can be assigned with mutual existence of rhombohedral and tetragonal phases. Ceramic sample sintered with both methods exhibits some weak modes at 142 cm\(^{-1}\), 174 cm\(^{-1}\), with broad peak at 242 cm\(^{-1}\) are assigned to \(A_1(\text{TO})\) phonon mode and at 272 cm\(^{-1}\) assigned \(B_1\) and/or \(E(\text{TO} + \text{LO})\) [15, 30]. Asymmetric peak at 500 cm\(^{-1}\) and broad weak peak at 710 cm\(^{-1}\) are assigned to \(A_1(\text{TO})\) and/or \(E(\text{TO})\) and \(A_1(\text{LO})\) and/or \(E(\text{LO})\) respectively [15, 28]. The modes \(A_1(\text{TO})\) and \(E(\text{TO})\) are all assigned to Ti – O bonds, and the modes \(A_1(\text{LO})\) and \(E(\text{LO})\) are contributed to Ba – O bonds [28]. Also weak Raman active asymmetric breathing mode (\(A_1(\text{g})\)) was seen at 819 cm\(^{-1}\) [29]. 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 500, 710 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 [29]. A Raman peak at 275 and 710 cm\(^{-1}\) confirms existence of tetragonal symmetry at room temperature in BCT-BZT ceramic samples [15].

![Raman spectra of xBCT-(1-x)BZT](image)

Figure 4.23 Room temperature Raman spectra of xBCT-(1-x)BZT where \(x = 0.15, 0.3, 0.4\) and 0.5 respectively sintered at 1200 °C.
4.7 Characterization of Co$_{0.9}$Ni$_{0.1}$Fe$_2$O$_4$ (CNFO) ferrite

As a part of present research work here we have selected Co$_{0.9}$Ni$_{0.1}$Fe$_2$O$_4$ (CNFO) as a ferromagnetic phase, which will be further used with ferroelectric phase (BCT-BZT) in formation of magnetodielectric (MD) composite. Before implementation in MD composition as like ferroelectric constituent, ferromagnetic phase of CNFO was also separately studied and obtained structural, morphological, electrical and magnetic properties are presented in this section.

As per discussed in previous chapter after synthesis by implementing hydroxide coprecipitation method, CNFO nanoparticles and pressed pellets are sintered at 1100 °C for 30 min. The heating process was carried out by using microwave sintering process, while the heating rate was maintained at 30 °C/min. The sintering temperature was selected as per literature [31].

4.7.1 Structural analysis of CNFO

The powder samples of CNFO after being sintered at 1100 °C was characterized for its structural phase confirmation using x-ray technique. Figure 4.24 shows the room temperature x-ray diffraction pattern for CNFO ferromagnetic material. It could be seen that as prepared CNFO powder crystallize into a single phase face centered cubic spinel structure with Fd3m space group. Observed all the diffraction patterns are well matches with standard pattern (JCPDS card no. 22-1086) [31], without any excessive peak which confirms formation of cubic spinel phase. All the peaks as represented in figure are indexed to cubic spinel structure. The lattice constant of CNFO particle sintered at 1100 °C was calculated by using equation 4.9 [32].

\[ a = d_{hkl} \sqrt{h^2 + k^2 + l^2} \]  

Where, d is the interplanar distance, a, is the lattice parameter and (hkl) are Miller indices. Cubic spinel structure in present study has lattice constant a = b = c = 8.37Å, while the unit cell volume is V = 586.37. Average crystallite size of magnetic CNFO particles was derived from Scherrer equation as given in earlier section. Average crystallite size of sintered CNFO particles calculated from FWHM at highest intense peak (311) founds to be D = 62.13 nm.
Figure 4.24 Room temperature x-ray diffraction pattern of Co$_{0.9}$Ni$_{0.1}$Fe$_2$O$_4$ powder sintered at 1100 °C.

4.7.2 Morphology and EDS analysis

Figure 4.25 (a) shows the field emission scanning electron microscope (FE-SEM) image of CNFO. Image represents well orientation of grains with uniform grain size. Here the microwave sintering plays an important role in the formation of controlled grains, as the microwave sintering is well known technique which provides rapid heating and as a result jumping of ions from the concave to convex side during grain growth as in case of conventional sintering is avoided in case of microwave sintering. FE-SEM image shows that the CNFO particles are grown as like octahedron in shape. Average grain size estimated from FESEM is ~ 0.3 μm and is found to be greater than the crystallite size calculated from x-ray diffraction pattern, indicates grains are formed by assortment of no of crystallites. Figure 4.25 (b) represents energy dispersive spectroscopy image (EDS) of CNFO. It is seen that the all the elements present in the prepared ferrite sample which indicates the quantitative presence of Co, Ni, Fe and O which concludes the formation of spinal ferrite sample without any other impurity as revelled by x-ray diffraction. Table inset of EDS spectrum gives the quantitative information in weight and atomic (%) of the elements, which are included in the CNFO ferrite sample.
4.7.3 Raman scattering analysis

Raman spectroscopy is one of the most important and a highly powerful and perceptive technique which found very useful for analysis of structural transition, distribution of local cations, local cation distribution, study of lattice distribution and magnetic ordering. Figure 4.26 represents the room temperature Raman scattering of as synthesized CNFO powder sample. CNFO ferrite exhibits inverse cubic spinel structure of AB₂O₄ type and belongs to Fd-3m space group with eight formula units per unit cell. There are 56 total atoms are consisted in the full unit cell of cubic symmetry, while the smallest Bravais cell can contain only 14 atoms due this type of symmetry can have 42 possible vibrational modes. According to group theory optical phonon distribution 5T₁u + A₁g + E₉ + 3T₂g are known as IR active modes while the other five first order (A₁g + E₉ + 3T₂g) are regarded as Raman active modes [33]. Symmetric stretching of oxygen atoms along with metal atom (Fe-O) creates tetrahedral bonding between those atoms results in A₁g(1) mode, whereas symmetric and asymmetric bonding of oxygen atoms with Fe metal atoms give rise to E₉ and T₂g(3) vibrational modes respectively. Asymmetric stretching of Fe-O bond results in T₂g(2) and T₂g(1) is due to translational movement of the whole tetrahedron (Fe₂O₄) [34].

Here the as synthesized CNFO material has 6 intense 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. Almost all the peaks are typically active vibrational modes of cubic spinel structure. 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, reflects the stretching of vibration between \(Fe^{3+}\) and \(O^{2-}\) ions in tetrahedral side. The other modes at lower frequencies are assigned to \(T_{2g}\) and \(E_{g}\) modes which reflects the vibration of that site respectively. It could be seen that the Raman modes in CNFO splits in small doublets this may be resulted due to the distribution in bond distance as in Co/Ni doped Fe\(_2\)O\(_4\), Co, Ni and Fe ions occupies the octahedral sites while only Fe ions are situated at tetrahedral. Difference in the ionic radii of Co/Ni and Fe ions results in the bond distance (Fe/Ni/Co-O) distribution which attributes to doublet like structures in ferrites [35]. One peak in the doublet like structure represents the unit cell containing all Fe Ions only while other peak corresponds to unit cell with mixed (Co/Ni) and Fe ions.

Figure 4.26 Raman spectra of CNFO sample sintered at 1100 °C.

4.7.4 Dielectric properties

Dielectric constant (\(\varepsilon_r\)) and loss tangent are studied with variation of frequency (100 Hz - 1MHz) at room temperature. Figure 4.27 shows the room temperature variation of the dielectric constant and loss tangent with applied frequency from 100 Hz to 1 MHz. Dispersion relation is observed in the variation of the dielectric constant with frequency. The dielectric constant (\(\varepsilon_r\)) decreases as the frequency increases and remains constant at the higher frequencies. The dielectric constant of any material depends on the various types of polarizations, the dipolar, inter-facial, ionic, and an electronic polarization contributes to the dielectric constant. The dipolar and interfacial polarizations are found to be effective at
low frequencies while the electronic polarization is found to be effective at higher
frequencies. Also in ferrites the variation in ions Fe\textsuperscript{2+} and Fe\textsuperscript{3+} concentration affect on
variation of dielectric constant with the applied frequency. Thus, polarization and dielectric
constant were also expected to vary accordingly with the concentration of Fe\textsuperscript{2+} and Fe\textsuperscript{3+}
ions. At lower frequencies the initial decrease in dielectric constant with frequency can be
explained by the phenomenon of dipole relaxation process [33]. In case of lower
frequencies, polarization attributed to electronic exchange between Fe\textsuperscript{3+} to Fe\textsuperscript{2+} ions
situated octahedral site of ferrite. Presence of the Ni\textsuperscript{3+}/Ni\textsuperscript{2+} and Co\textsuperscript{3+}/Co\textsuperscript{2+} ions on the
octahedral B site yields p-type charge carrier and the Fe\textsuperscript{3+}/Fe\textsuperscript{2+} ions n-type charge carrier.
The local displacement of these n-type and p-type charge carrier contributes to the net
polarization. Due to the hopping of electrons beyond certain limit of the frequency,
dielectric constant may decrease with increasing frequency. The polarization from the p-
type charge carrier is smaller and rapidly decreases due to its low mobility. Variation of
dielectric loss with frequency has similar kind of dispersion relation is observed as in case
of the dielectric constant. The loss tangent shows high values at lower frequency while it
shows low values at higher frequency [31].

Figure 4.28 (a) and (b) represents the temperature dependent dielectric constant and
loss tangent of CNFO ferrite. It could be seen that, the dielectric constant continuously
increases with increase in dielectric constant reaches maximum at higher temperature and
slightly decreases. This temperature at which dielectric constant reaches maximum and
start to decrease is called as magnetic transition temperature \(\sim 500 \degree C\) in this case where
the ferromagnetic phase becomes paramagnetic material. Increase in dielectric constant
with increasing temperature may be due to conduction mechanism. As with increase in
temperature hopping of electrons between Fe\textsuperscript{2+}/Fe\textsuperscript{3+}, Co\textsuperscript{2+}/Co\textsuperscript{3+}, and Ni\textsuperscript{2+}/Ni\textsuperscript{3+} ions
increases which results in higher conduction in ferrite samples. This conduction
mechanism also results in higher values of dielectric loss in ferrite samples. High values of
dielectric loss may due to increased space charge conduction which is further related to the
movement of oxygen vacancies towards dielectric-electrode interface. Conduction
mechanism in ferrites can be derived on the basis of Verwey de Bohr mechanism,
according to this theory the exchange of electrons between ions of same elements existing
in more than one valence state and are randomly distributed over equivalent
crystallographic lattice sites [36].
4.7.5 Magnetic Properties of CNFO

Figure 4.29 shows the field cool (FC) and zero field cool (ZFC) versus temperature (T°k) curve for Co$_{0.9}$Ni$_{0.1}$Fe$_2$O$_4$ ferrite at an applied magnetic field of 100 Oe between temperature range from 5 °k to 350 °k. Observed FC and ZFC curves tends towards each other in a opposite direction reaches one symmetry point at the critical temperature called
as blocking temperature ($T_B \sim 340 \, ^\circ k$). ZFC increases up to critical temperature point and start to decreases after the critical point on the other hand FC decreases continuously. Here the blocking temperature ($T_B$) represents the temperature point above which magnetization in the material is due to the thermal activation energy only, as result ferrimagnetic material changes phase to superparamagnetic material. Below the blocking temperature range the material exhibits higher values of coercivity ($M_c$), high saturation magnetization ($M_s$) and high remanant magnetization ($M_r$) as shown in figure 4.30. Above the blocking point magnetic hysteresis feature in the magnetic particles gets vanished and the material will start to exhibit superparamagnetic behaviour. Above the blocking temperature the particles obey Curie–Weiss law [37].

Figure 4.30 shows the magnetisation verses applied magnetic field curve (M-H hysteresis loop) of $Co_{0.9}Ni_{0.1}Fe_2O_4$ nanoparticles sintered at $1100 \, ^\circ C$ at temperature range ($5 \, ^\circ k$, $150 \, ^\circ k$, and $300 \, ^\circ k$) respectively. Figure inset shows the enlarged view of M-H loop at the respective temperature value Magnetisation of the magnetic sample was measured by applying the magnetic field from 50 KOe to -50 KOe. The highest magnetic moment was achieved at temperature $5k$ with high coercive field and remanant magnetisation as shown in inset figure. The magnetic parameters such as saturation magnetisation ($M_s$), coercive magnetic field ($H_c$), remanance magnetisation ($M_r$) and the loop squareness factor ($M_r/M_s$), was listed in table 4.10. The magnitude of magnetic properties decreases with increase in temperature. At room temperature ($300 \, ^\circ k$) the material has low values of all magnetic parameters. This decrease in magnetic parameters results due to over a blocking temperature point the phase change occurs in magnetic material and the material will behave as a superparamagnetic material as seen in FC-ZFC curve. Increase and decrease in the crystallite size with also plays an important role in enhancing or lowering the magnetic parameters in the magnetic sample. Generally in ferrimagnetic ferrite materials the magnetisation due to tetrahedral and octahedral sublattices is antiparallel to each other. The maximum $M_r/M_s$ value is 0.79 founds at temperature $5k$ this may be resulted due to enhanced cubic anisotropy at lower temperature range. Therefore high values of saturation magnetisation ($M_s$) and coercive field ($H_c$) can be expected at lower temperature [38]. Magnetic moment is calculated in terms of Bohr magnetron ($\mu_B$) by using the relation as follows [36].

\[
\mu_B = \frac{M_h}{5585} \quad \text{----- 4.10}
\]
Where, $M$ is the molecular weight, $Ms$ is the magnetization per gram mol of the sample and 5585 is the magnetic factor and magnetic moment found to be decrease with increase in temperature.

**Table 4.11 Parameters observed from M-H hysteresis loop of Co$_{0.9}$Ni$_{0.1}$Fe$_2$O$_4$.**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Ms (emu/gm)</th>
<th>Hc (Oe)</th>
<th>Mr (emu/gm)</th>
<th>Mr/Ms</th>
<th>$\mu_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 k</td>
<td>64.15</td>
<td>5517</td>
<td>51.09</td>
<td>0.79</td>
<td>2.69</td>
</tr>
<tr>
<td>150 k</td>
<td>62.44</td>
<td>2553</td>
<td>38.70</td>
<td>0.62</td>
<td>2.62</td>
</tr>
<tr>
<td>300 k</td>
<td>55.75</td>
<td>883</td>
<td>21.36</td>
<td>0.39</td>
<td>2.34</td>
</tr>
</tbody>
</table>

**Figure 4.29 FC-ZFC curve of Co$_{0.9}$Ni$_{0.1}$Fe$_2$O$_4$ (CNFO) at 100 Oe.**
Figure 4.30 M-H hysteresis loop of Co$_{0.9}$Ni$_{0.1}$Fe$_2$O$_4$ measured at different temperature (figure inset shows enlarged view of coercivity).
References