CHAPTER 6

INDUCED FERROMAGNETISM IN NBT-BT CERAMICS
BY THE ADDITION OF TRANSITION METAL IONS

6.1 INTRODUCTION

Rapid advancement in data storage and device miniaturization strives for four-state memory where the data to be written electrically and read magnetically. This new generation memories and sensing/actuating devices powered by the materials that combine magnetism and ferroelectricity in an effective manner (Scott 2007). Using the coupling principle between electric and magnetic properties four-state memory has been demonstrated by Erenstein et al (2006). In two-state data storage process particularly in ferroelectric random access memory (FeRAM) large magnetic fields are needed to write the data and it creates problem while reading. By exploiting the advantages of FeRAM and magnetic storage four-state memory are being designed. Multiferroic materials are found to be quite interesting for memory and logic device applications (Ying Hao Chu et al 2008).

6.1.1 Multiferroics

Multiferroic are defined as a single phase material where two or all the three ferroic properties (ferroelectricity, ferromagnetism and ferroelasticity) are coexisting (Paval Lukashev et al 2008). Normally the existence of ferroelasticity (materials that exhibit spontaneous strain that is
stable and can be reversed by the applied stress) is rare. Generally simultaneous existence of ferroelectric and ferromagnetic is termed as multiferroics. This term not only comprises the ferro-electro magnets but also the coexistence of the following ferroic phases,

- **Ferroelectricity**- spontaneous polarization which can be reversed by external electric field
- **Antiferroelectricity**- ordered dipole moments which cancel each other within the crystallographic unit cell
- **Ferromagnetism**- spontaneous magnetization which can be reversed by the external magnetic field
- **Antiferromagnetism**- ordered magnetic moments which cancel each other within the crystallographic unit cell
- **Ferrimagnetism**- magnetic moments cancellation is incomplete in such a having net magnetization and that can be reversed by the external magnetic field

Figure 6.1 explains the inter relationship between the ferroelectric and ferromagnetic materials. In magneto-electric materials electric polarization is induced by the application of an external magnetic field or vice-versa (Cheong & Mostovoy 2007). The multiferroics and magneto-electric materials are found to be used in transducers, magnetic field sensors and data storage applications (Scoot 2007).
Though they are intriguing, the coexistence of ferroelectric and ferromagnetism is scarce in nature due to the following reason. The ferroelectricity requires fully filled $d$ or $f$ orbitals to induce surface charge. On contrary, the ferromagnetism requires partially and empty $d$ or $f$ orbitals for the spin interactions to occur (Yuan-Hua Lin et al 2008). In other words the ferroelectric materials exhibit a stable and switchable electrical polarization that is manifested in the form of cooperative atomic displacements where as the ferromagnetic materials exhibit a stable and switchable magnetization that arises through the quantum mechanical phenomenon of exchange (Erenstein et al 2006). Generation of ferromagnetism in non magnetic perovskite materials draws a continuous attention. To introduce a ferromagnetic property into a ferroelectric material originally with no ferromagnetism by itself is quite interesting. One of the common approaches is to dope magnetic impurities into the ferroelectric host material (Singh et al 2006). The other approach is to combine a ferroelectric material and a ferromagnetic material.

Figure 6.63 Inter relationship between magnetic and electrically polarizable materials
together into a composite material, which subsequently shows multiferroic properties (Zurbuchen et al 2005).

Most of the multiferroics synthesized so far are transition metal oxides with perovskite structures. The transition metal ions are interesting by their chemically inert and non toxic nature. Also the intermediate ionic-covalent nature of transition metal-oxygen bonds leads to strong polarizability which is a desirable property in ferroelectricity. The localized 3d electron in the transition metal ion provides a strong correlation associated with the exotic magnetic behavior also. The overall picture suggests that all conventional ferroelectric perovskite oxides contain transition metal ions with a configuration \( d^0 \), such as \( \text{Ti}^{4+}, \text{Ta}^{5+}, \text{W}^{6+} \) at B-sites of \( \text{ABO}_3 \) perovskite. The empty \( d \)-shell seems to be a prerequisite for ferroelectricity generation, the filled shell do not participate in magnetic ordering. The difference in filling the transition metal ion \( d \)-shells at the B-site, which is required for ferroelectricity and magnetism, makes these two ordered states mutually exclusive (Wang et al 2009).

Until now, many multiferroic materials, such as \( \text{BiFeO}_3 \), \( \text{CdCr}_2\text{O}_4 \), \( \text{LuFe}_2\text{O}_4 \), \( \text{RE Mn}_3 \), and \( \text{REMn}_2\text{O}_5 \) where RE = Rare Earth, have been studied vastly (Ascher et al 1966; Wang et al 2003; Hemberger et al 2005; Ikeda et al 2005). Room temperature multiferroics are very limited because most of the currently known materials exhibit a low magnetic transition temperature in contrast to a high ferroelectric transition temperature. To find other new multiferroics materials with the magnetic and ferroelectric transition temperatures above the room temperature is of both fundamental and technological importance nowadays. It is well known that semiconductors have been successfully converted into diluted magnetic semiconductors (DMS) by doping with transition-metal elements (Fe, Ni, Co, etc.), and DMS have been considered as key functional components of many spin-based semiconductor devices (Ohno 1998). The method to obtain room temperature
ferromagnetism by doping semiconductors with transition metal atoms (Fe, Co, Ni, etc.) has offered an alternative approach to achieve room temperature ferromagnetism in ferroelectric materials.

For instance, the ferromagnetism in PbTiO$_3$ doped with Fe and Mn has been studied. By ab initio calculation, Nakayama et al (2001) reported that the BaTiO$_3$ doped with Fe, Co, Ni and Mn is the promising material to achieve the ferromagnetism. Room temperature ferromagnetism was achieved in Co doped BaSrTiO$_3$ thin films (Yuan-Hua Lin et al 2008). Ferromagnetic behavior of the Fe doped lead niobate-lead titanate (Cheng et al 2009), thickness dependence of ferromagnetism in Co doped BaTiO$_3$ (Luo et al 2008), Mn doped PbTiO$_3$ (Manoj Kumar et al 2007) were studied in detail. The Fe and Co ions implantation in BaTiO$_3$ single crystals shows the ferromagnetic behavior (Khalitov et al 2012) which gives the new insight for multiferroics. Ferroelectric behavior of Fe doped sodium bismuth titanate (NBT) was studied by Davies et al (2011).

NBT-BT is a ABO$_3$ perovskite type relaxor with the A-site is shared by the Na$^+$, Bi$^{3+}$ and Ba$^{2+}$ ions and the B-site is occupied by the Ti$^{4+}$ ions. The present chapter concentrates on the influence of Cr, Co, Ni, Mn and Fe on sodium bismuth titanate-barium titanate (NBT-BT) in the view of dielectric, ferroelectric and ferromagnetism. 0.5 wt% of MnO$_2$, NiO, Cr$_2$O$_3$, Fe$_2$O$_3$ and Co$_2$O$_3$ added 0.94Na$_{0.5}$Bi$_{0.5}$TiO$_3$-0.06BaTiO$_3$ ceramics were prepared by the conventional solid state reaction method. The dielectric, ferroelectric and ferromagnetic behaviors of the prepared ceramics were discussed in detail.

### 6.2 EXPERIMENTAL METHODS

The conventional solid state reaction method was used to prepare all the ceramics. High purity (99.9%) Na$_2$CO$_3$, BaCO$_3$, Bi$_2$O$_3$, TiO$_2$, NiO, Cr$_2$O$_3$, Co$_2$O$_3$, Fe$_2$O$_3$ and MnO$_2$ were used as initial precursors. The oxides
and carbonates were weighed according to the composition of 0.94(Na\textsubscript{0.5}Bi\textsubscript{0.5}TiO\textsubscript{3})-0.06(BaTiO\textsubscript{3}) + 0.5 wt% of y (y = NiO, Cr\textsubscript{2}O\textsubscript{3}, Co\textsubscript{2}O\textsubscript{3}, Fe\textsubscript{2}O\textsubscript{3} and MnO\textsubscript{2}). The carbonates and oxides were mixed homogeneously in ethanol medium and calcined at 850°C for 4 hours. The calcined powders were reground and mixed with binder (polyvinyl alcohol). After drying, the pellets of the size 19 mm dia and 1 mm thickness were made by applying pressure of 300 MPa. The prepared discs were sintered at 1200°C for 4 hours. The obtained ceramics were finely ground and subjected to powder XRD in the range of 10° to 80° of 2θ with the step angle of 0.02° and step time 1s using PANalytical diffractometer (CuKα radiation) to confirm the phase formation and crystalline nature. Surface morphology of the gold coated sintered samples was studied by scanning electron microscopy (Carl Zeiss MA15/ EVO18). The variation of dielectric constant with temperature at different frequencies was studied from room temperature to 350°C using Agilent E4980A impedance analyser. Ceramics were poled by applying a field 20-25 kV/cm at room temperature for 20 min. The piezoelectric coefficient d\textsubscript{33} (pC/N) was measured using Piezometer (PM300, Piezotest). The P-E hysteresis loop was recorded by the P-E loop tracer at room temperature. The M-H loop was recorded by the Lakshore VSM 7410. The magnetic domain analysis was carried out by the Park XE -100 model Atomic Force Microscopy.

6.3 RESULTS AND DISCUSSION

6.3.1 Structural and Surface Analysis

The structure of the prepared ceramics was analyzed by means of powder XRD and the XRD patterns are shown in Figure 6.2 (a). The obtained XRD patterns were refined by FullProf suit and the lattice parameters are given in Table 6.1. It shows that the prepared ceramics all are in perovskite structure with R3c space group. The absence of secondary peaks in the XRD
pattern shows that the magnetic additives were diffused into the NBT-BT lattice and forms a complete solid solution. The addition of magnetic impurities Mn, Ni, Cr and Co shifts the XRD peaks towards the higher angle side whereas the Fe addition shifts towards the lower angle side. For better understanding the (110) peak shifting is shown in Figure 6.2 (b). The ionic radius of Ti$^{4+}$ (0.74 Å) is large when compared to the Mn$^{2+}$ (0.67 Å), Ni$^{2+}$ (0.70 Å), Cr$^{3+}$ (0.615 Å) and Co$^{3+}$ (0.65 Å). The replacement of Mn$^{2+}$, Ni$^{2+}$, Cr$^{3+}$, Fe$^{3+}$ and Co$^{2+}$ ions in the Ti$^{4+}$ site of NBT-BT results in lattice contraction and this leads to the shifting of XRD peaks towards the larger angle side except Fe-NBT-BT. The XRD peaks of Fe-NBT-BT shifts towards the higher angle side and the same nature is obtained for the Fe doped NBT and Fe doped BT (Davis et al 2011). The lattice parameter decreases after the addition of Fe in NBT-BT.

Figure 6.64 (a) Powder XRD patterns of the synthesized ceramics
Table 6.11 Lattice parameter and compositional analysis of synthesized ceramics

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice Parameter Å</th>
<th>O</th>
<th>Na</th>
<th>Bi</th>
<th>Ti</th>
<th>Ba</th>
<th>Others (Mn/Ni/Co/Cr/Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBT-BT</td>
<td>3.907</td>
<td>68.55</td>
<td>7.71</td>
<td>7.77</td>
<td>14.94</td>
<td>1.04</td>
<td>--</td>
</tr>
<tr>
<td>Cr-NBT-BT</td>
<td>3.909</td>
<td>65.48</td>
<td>7.21</td>
<td>8.82</td>
<td>17.05</td>
<td>1.58</td>
<td>0.13</td>
</tr>
<tr>
<td>Co-NBT-BT</td>
<td>3.908</td>
<td>66.18</td>
<td>7.54</td>
<td>8.51</td>
<td>16.53</td>
<td>1.10</td>
<td>0.15</td>
</tr>
<tr>
<td>Ni-NBT-BT</td>
<td>3.908</td>
<td>63.56</td>
<td>8.07</td>
<td>9.12</td>
<td>17.59</td>
<td>1.61</td>
<td>0.05</td>
</tr>
<tr>
<td>Mn-NBT-BT</td>
<td>3.907</td>
<td>65.98</td>
<td>7.45</td>
<td>8.05</td>
<td>16.92</td>
<td>1.52</td>
<td>0.09</td>
</tr>
<tr>
<td>Fe-NBT-BT</td>
<td>3.999</td>
<td>64.60</td>
<td>8.41</td>
<td>8.41</td>
<td>17.87</td>
<td>1.41</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Figure 6.2 (b) Enlarged view of (110) peak
Figure 6.3 Raman spectra of NBT-BT, Cr-NBT-BT, Co-NBT-BT, Ni-NBT-BT, Mn-NBT-BT and Fe-NBT-BT ceramics

Raman spectra of the synthesized samples were recorded at room temperature (Figure 6.3) The spectrum is consistent with previous reports, where it was assigned as belonging to the pseudo-rhombohedral R3c phase, for which a total of 13 Raman-active modes are expected. No shift in the peaks position was observed but the intensity variation is there. However the intensity of the peaks decreases after the addition of Mn, Ni, Co and Cr and increase in the case of Fe addition in NBT-BT. The bands at 91 and 127 cm$^{-1}$ correspond to the Bi-O and A$_1$ symmetry particularly the Na-O vibrations respectively. 254 cm$^{-1}$ region are dominated by the A$_1$ mode and it matches to the Ti-O vibrations. The bands at 527 and 601 cm$^{-1}$ are attributed to the A$_{1g}$ [TiO$_6$] stretching vibrations (Jun et al 2013) and to the overlapping of E (LO) and E (TO) modes of vibrations (Xu et al 2008). The addition of Mn, Ni, Cr, Co and Fe in the NBT-BT constitute a small difference in atomic mass variation in NBT-BT hence no significant variation in the peak position was
observed. This is in accordance with observations from XRD and with the fact that generally Raman spectra are slightly affected for such small concentrations of modifiers.

Beside the influence on the ferroelectric properties, the added impurities alter the sinter ability of the ceramic. Figure 6.4 shows the surface morphology of the prepared ceramics. All the ceramics were dense and pore free. The NBT-BT ceramics are having cubic like structure. For Co, Mn and Ni added NBT-BT the grains are like pebbles. In this the edges of the grains are not sharp, which confirms the melting like nature of the grains. This shows that the sintering temperature is high for these ceramics and the grain boundary contributions are increasing. For the addition of Fe and Cr rectangular grains were formed. The minimum and maximum sizes of the grains were observed in Mn-NBT-BT and Fe-NBT-BT respectively. The added impurities are segregated at the grain boundary and inhibit the grain growth in the Cr, Co, Mn and Ni addition.

In addition, all the additives are acting like an acceptor dopant to the Ti$^{4+}$ site and oxygen vacancies are created to maintain the charge neutrality. These oxides precipitated at the grain boundary and controlled the grain growth (Majumdar et al 2001). The compositional analysis was carried by means of energy dispersive X-ray analysis coupled with SEM and it is shown in Figure 6.5 and the observed atomic % of each element is given in Table 6.1.
Figure 6.4  SEM micrographs of NBT-BT, Cr-NBT-BT, Co-NBT-BT, Ni-NBT-BT, Mn-NBT-BT and Fe-NBT-BT ceramics
Figure 6.5  EDX spectra of NBT-BT and Cr, Co, Ni, Mn, Fe added NBT-BT ceramics
6.3.2 Dielectric Analysis

The dielectric analysis was carried out from room temperature to 350°C for various frequencies and it is shown in Figure 6.6. The diffuse phase transition was observed in all the dielectric graphs. The dielectric maximum \( (\varepsilon_m) \) decreases as the measuring frequency increases and shifts toward the higher temperature side. This is the main characteristic of the relaxor ferroelectric materials and arises due to the disordered lattice structure. The presence of nano size polar regions which originates from the cation displacements in the oxygen octahedral is the main cause for relaxor nature in \( \text{ABO}_3 \) perovskites (Samara 2003).

In all the dielectric graphs two dielectric anomalies were observed one at \( T_d \) (temperature corresponds to the transition from ferroelectric to anti ferroelectric) and the other one at \( T_m \) (temperature corresponds to the transition from antiferroelectric to paraelectric and the temperature where dielectric constant reaches its maximum, \( \varepsilon_m \)) was observed except in Fe-NBT-BT. In Fe-NBT-BT the dielectric anomalies were observed only after 1 MHz. The multi valance nature of Fe creates the electrical leakage problem and increase the conductivity of the sample. Similar effect was observed by Cheng et al (2008). The values of \( T_d, T_m \) and \( \varepsilon_m \) measured at 1 kHz frequency were tabulated in Table 6.2 for all the samples except Fe-NBT-BT, for this ceramic values corresponding to 1 MHz are listed as the diffuse transition was not observed at 1 kHz.

The reduction of dielectric constant after the addition Mn, Ni and Cr are due to the grain size effect. The addition of Co increases the grain growth and hence the dielectric constant rises. Similarly for Fe addition maximum grain size was observed and so it exhibits highest dielectric
constant compared to all the additives. The value of $T_d$ decreases after the incorporation of Cr, Co, Mn and Ni in NBT-BT whereas the value of $T_m$ increases. The decrease in $T_d$ is attributed to the decrease in grain size.

Table 6.12 Values obtained from dielectric characteristics of synthesized ceramics

<table>
<thead>
<tr>
<th>Sample</th>
<th>Frequency</th>
<th>$T_d$ (K)</th>
<th>$T_m$ (K)</th>
<th>$\varepsilon_m$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBT-BT</td>
<td>1 kHz</td>
<td>378</td>
<td>504</td>
<td>2680</td>
<td>1.79</td>
</tr>
<tr>
<td>Cr-NBT-BT</td>
<td>1 kHz</td>
<td>352</td>
<td>526</td>
<td>2023</td>
<td>1.70</td>
</tr>
<tr>
<td>Co-NBT-BT</td>
<td>1 kHz</td>
<td>372</td>
<td>530</td>
<td>3071</td>
<td>1.76</td>
</tr>
<tr>
<td>Ni-NBT-BT</td>
<td>1 kHz</td>
<td>373</td>
<td>536</td>
<td>2523</td>
<td>1.89</td>
</tr>
<tr>
<td>Mn-NBT-BT</td>
<td>1 kHz</td>
<td>357</td>
<td>534</td>
<td>2411</td>
<td>1.80</td>
</tr>
<tr>
<td>Fe-NBT-BT</td>
<td>1 MHz</td>
<td>--</td>
<td>518</td>
<td>8212</td>
<td>1.31</td>
</tr>
</tbody>
</table>

The experimental data of the dielectric constant are fitted to the modified Curie-Weiss law to analyze the diffusivity of the relaxation for all the samples. The calculated diffusivity parameter is listed in Table 6.2. Figure 6.7 shows the fit of modified Curie-Weiss law for Cr-NBT-BT at 1 kHz. The diffusivity of the transition is increased for Ni and Mn addition. For the Co, Cr and Fe addition $\gamma$ decreases. It has been suggested that the relaxor behavior results from the A-site and B-site cation disordering in ABO$_3$ perovskite structure. This reveals that the addition of Mn and Ni in NBT-BT strengthen the cation disordering and compositional disorder (Smolenskii et al 1961).
Figure 6.6  Variation of dielectric constant as a function of temperature for various frequencies for the synthesized ceramics
Piezoelectric and Ferroelectric Properties

The electroded samples were poled to 2-2.5 kV/cm for 20 min and P-E hysteresis and piezoelectric coefficient ($d_{33}$) was measured at 1 kHz applied frequency. The measured $d_{33}$ values were 209, 119, 120, 139, 135 and 105 pC/N for NBT-BT, Cr-NBT-BT, Co-NBT-BT, Ni-NBT-BT, Mn-NBT-BT and Fe-NBT-BT ceramics respectively. The $d_{33}$ was found to decrease after the addition of magnetic impurities. The added magnetic impurities are replaced the Ti site in ABO$_3$. The replacement in the B-site cation has detrimental effect on the piezoelectric properties (Yang et al 2008; Bao-Jin Chu et al 2002). As discussed already the oxygen vacancies restrict the grain growth and it leads to decrease the interaction between the neighboring dipoles which is the main cause for the ferroelectric properties and it encourages the domain wall pinning.

The P-E hysteresis loops were shown in Figure 6.8. A well shaped P-E loop was observed for the Co-NBT-BT. The coercive field ($E_c$), remnant polarization ($P_r$) and the saturation polarization ($P_s$) were listed in Table 6.3.
The saturation polarization originates from the displacement of B-site cation in ABO$_3$ perovskite. Except Ni-NBT-BT, $P_s$ increases for all other samples. The coercivity decreases considerably after the addition of magnetic impurities which enable them to pole at higher field also.

6.3.4 Ferromagnetic Properties of Synthesized Ceramics

6.3.4.1 M-H curve analysis

To study the magnetic properties, M-H curves for the prepared ceramics were recorded at room temperature (Figure 6.9). The M-H curve analysis show that the NBT-BT ceramics are diamagnetic in nature. After the addition of ferromagnetic additives Co, Cr, Mn and Ni, the NBT-BT transforms to the ferromagnetic nature whereas the addition of Fe in NBT-BT retains the diamagnetic type. The magnetic ions Co$^{3+}$, Cr$^{3+}$, Mn$^{2+}$ and Ni$^{2+}$ are the promising candidates for the observed magnetic property in NBT-BT. The disordered distribution and lower concentration of magnetic additives in NBT-BT makes the M-H loop was very narrow. The slim hysteresis loop shows that the prepared ceramics are of soft magnetic type. The oxygen
vacancies are created by these impurities for the charge neutrality (Lina Gao et al 2009). The super exchange interaction between the magnetic ions in different occupational sites is facilitated by these oxygen vacancies. The coupling between the mixed valence states of Mn ion provides a possibility to induce the double exchange effect of Mn$^{2+}$ and Mn$^{3+}$ or Mn$^{4+}$ and thus brings the magnetic property in Mn doped PbTiO$_3$ (Manoj Kumar & Yadav 2007).

Table 6.13  Ferroelectric and ferromagnetic properties of synthesized ceramics

<table>
<thead>
<tr>
<th>Prepared Samples</th>
<th>Ferroelectric Hysteresis Loop</th>
<th>Ferromagnetic Hysteresis Loop</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$P_s$ (μC/cm$^2$)</td>
<td>$P_r$ (μC/cm$^2$)</td>
</tr>
<tr>
<td>NBT-BT</td>
<td>4.39</td>
<td>2.77</td>
</tr>
<tr>
<td>Cr-NBT-BT</td>
<td>4.66</td>
<td>1.83</td>
</tr>
<tr>
<td>Co-NBT-BT</td>
<td>7.35</td>
<td>4.14</td>
</tr>
<tr>
<td>Ni-NBT-BT</td>
<td>2.58</td>
<td>0.77</td>
</tr>
<tr>
<td>Mn-NBT-BT</td>
<td>7.74</td>
<td>2.89</td>
</tr>
<tr>
<td>Fe-NBT-BT</td>
<td>4.57</td>
<td>1.60</td>
</tr>
</tbody>
</table>

The Mn is having three ionic states Mn$^{2+}$, Mn$^{3+}$ and Mn$^{4+}$. Though the stable state of Mn is Mn$^{2+}$ sintering at high temperature oxidizes Mn$^{2+}$ to higher valance states like Mn$^{3+}$ or Mn$^{4+}$. The different valence of Mn determines the various properties of the materials. The Mn$^{3+}$ and Mn$^{4+}$ will not have any influence on the grain growth and it increases the dielectric constant thereby improving the ferroelectric properties. Contrarily the Mn$^{2+}$ will decrease the grain size when it replaces the higher valance states (e.g. Ti$^{4+}$) (Yang et al 2008). In the present investigation all the above phenomenon has been resulted and it confirms the existence of different ionic states of Mn in NBT-BT lattice. The multi valence nature of the Mn in NBT was studied.
by ESR analysis (Wenwei Ge et al 2008). The observed ferromagnetism in Mn-NBT-BT is due to the double exchange interactions between these Mn$^{2+}$ and Mn$^{4+}$ ions.

The stable state of Cr, Co and Ni in the present case is Cr$^{3+}$, Co$^{3+}$ and Ni$^{2+}$ respectively. The other ionic states of these ions are possible only in O$_2$ or vacuum annealing. Hence the super exchange interactions between Cr$^{3+}$-Cr$^{3+}$, Co$^{3+}$-Co$^{3+}$ and Ni$^{2+}$-Ni$^{2+}$ ions different occupational sites associated with oxygen vacancies are expected to produce the observed ferromagnetism in Cr-NBT-BT, Co-NBT-BT and Ni-NBT-BT.

Fe doped NBT ceramics showed diamagnetism till 0.6 mol% of Fe and with further increase of Fe concentration the ferromagnetism was observed. In the present case also the Fe added NBT-BT retained the diamagnetic behavior. This may be due to the distance between (Fe-Fe) may be large in the case of Fe-NBT-BT which cannot transfer spins to create the global magnetic property (Nakayama et al 2001).

6.3.4.2 Magnetic force microscopy (MFM)

Magnetic domain analysis was carried out by means of Magnetic Force Microscopy (MFM). MFM is a valuable tool to study the ferromagnetic domain structure and distribution of the sample with the high lateral resolution. The MFM images correspond to the magnetic force emerging from the sample surface only. In the present case the cantilever was magnetized by an external magnet for 20 min to align the magnetic dipoles of the tip normal to the sample surface. The tip magnetization was negligible in all the measurements. The cantilever is in perpendicular orientation hence it is responsive only to the x component of the spins which are in front and back of the cantilever (Rugar et al 2004). In the MFM mode the cantilever operates in non-contact and lift mode. To catch the magnetic signals the tip is elevated at the lift mode.
Figure 6.9 M-H loop of synthesized ceramics at room temperature

The tip to sample distance was maintained at 30 nm. Figure 6.10 shows the topography, MFM phase and the corresponding line profiles. As the roughness of Fe-NBT-BT sample is in the order of 50 μm atomic force microscope (AFM) analysis cannot be carried out. From the Figure 6.10 there is no correlation between the topography and the MFM image as expected, which shows these two signals are different. To stress that the line profile of these two things are shown in right corner of the Figure 6.10 for all the samples. Due to the magnetic interactions there are bright and dark regions in the MFM images and they correspond to the magnetic domains of opposite polarity. The presence of magnetic impurities is the sole responsibility for the ferromagnetism observed in NBT-BT. The micrometer sized domains indicate the strong agglomeration of magnetic additives in NBT-BT ceramics. Among all the samples, maximum magnetic domain size was observed in Mn-NBT-BT and minimum was observed in Ni-NBT-BT.
Figure 6.10 Topography, MFM phase and the line profile of synthesized ceramics
6.4 CONCLUSION

The structural, dielectric, ferroelectric, piezoelectric and ferromagnetic properties were discussed in detail for the Cr, Co, Ni, Mn and Fe added NBT-BT ceramics. The complete solid solution formation of ferromagnetic additives in NBT-BT was observed in XRD analysis. From the diffuse phase transitions in the relaxor nature of the synthesized ceramics was confirmed. The creation of oxygen vacancies by the B-site substitution decreases the dielectric constant and the piezoelectric properties. The room temperature M-H hysteresis loop confirms the ferromagnetic nature. The exchange interaction between the ferromagnetic ions induces ferromagnetic nature in the diamagnetic NBT-BT. The ferromagnetic domain structures were analyzed by MFM. The coexistence of ferroelectric and ferromagnetic was found in Mn-NBT-BT, Ni-NBT-BT, Cr-NBT-BT and Co-NBT-BT ceramics. The order of the best multiferroics in the present work is Mn-NBT-BT > Cr-NBT-BT > Ni-NBT-BT > Co-NBT-BT. A detailed ferromagnetic analysis will be the future scope of this work.