

## List of Figures

Figure 1.1: Schematic view of the ideal cubic perovskite structure: A cation occupy on the cubic corner position (0, 0, 0) (shown by blue sphere), B cation sits on the (1/2, 1/2, 1/2) position (shown by dark green sphere) and O anion sits on the face diagonal (1/2, 1/2, 0) positions (shown by red sphere). .....	2
Figure 1.2: Typical P-E hysteresis loop for ferroelectric materials. $P_S$ = Saturation polarization, $P_R$ = Remnant polarization, $E_C$ = Coercive field [3]. .....	3
Figure 1.3: Typical hysteresis loop for antiferroelectric materials [10]. .....	5
Figure 1.4: Schematic Brillouin zone of the cubic perovskite structure showing special points [11]. .....	7
Figure 1.5: Comparison between the properties of normal and relaxors ferroelectrics behaviour [25]. .....	10
Figure 1.6: M-H Hysteresis Loop for Ferromagnetic materials. $M_S$ is saturation magnetization, $M_R$ is remanent magnetization at $H = 0$ , $H_C$ is coercivity at $M=0$ [27]. ....	11
Figure 1.7: Temperature dependence of magnetization (M) and the inverse of the magnetic susceptibility ( $1/\chi$ ) for ferromagnetic material. Reproduced from [26]. .....	11
Figure 1.8: Temperature dependence of (M) and inverse of susceptibility ( $1/\chi$ ) for antiferromagnetic material. AF: Antiferromagnetic, P : Paramagnetic [26]. .....	12
Figure 1.9: Different types of spin structure resulting in different type (A-, C-, G-or E-type) antiferromagnetic ordering [28]. .....	13
Figure 1.10: Theoretical variation of reciprocal of susceptibility with temperature for a ferrimagnetic above the Curie point [26]. .....	14
Figure 1.11: Different types of mechanism responsible for multiferroicity in a multiferroic materials [32]. .....	16

Figure 1.12: Schematic representation of magnetic ground state in a triangular lattice by considering (a) ferromagnetic and antiferromagnetic nearest neighbour interactions and (b) shows the possible spin arrangement for nearest neighbour antiferromagnetic interactions [45]. ..... 19

Figure 1.13: (a) Schematic representation of RKKY interactions which take place in dilute metallic spin-glass system like CuMn (b) Schematic variation of  $J_{RKKY}(r)$  interaction with separation ( $r$ ) between the moments. .... 20

Figure 1.14: Temperature dependence of dc magnetic susceptibility curves of CuMn (3%) system measured under ZFC and FC conditions [46]. ..... 21

Figure 1.15: Temperature dependence of ac magnetic susceptibility curves of CuMn system showing cusp at  $T_{SG}$ . Inset depicts the frequency dispersion across  $T_{SG}$  [41]. ..... 22

Figure 1.16: Variation of the nonlinear susceptibility ( $\chi_3$ ) as function of temperature across the spin-glass transition at a frequency of  $10^{-2}$  Hz for AgMn system [47]. ..... 22

Figure 1.17: Temperature dependence of dc magnetic susceptibility of CuMn system measured at 0.5 Oe field under FC and ZFC conditions. Below  $T_{SG} = 57K$ , effect of aging, memory and rejuvenation is clearly demonstrated. Inset depicts a “hole burnt” at the waiting temperature ( $T_w$ ) [48]. ..... 24

Figure 1.18: The temperature dependence of magnetic contribution to the specific heat ( $C_m$ ) of CuMn system at various magnetic fields. Here, the  $T_f$  is 3.0 K and  $C_m$  exhibits maximum at 5K [41]. ..... 24

Figure 1.19: Phase diagram of  $BiFeO_3$  using ingredients  $Bi_2O_3$  and  $Fe_2O_3$  [67]. ..... 26

Figure 1.20: Crystal structure of  $BiFeO_3$ . Two simple perovskite unit cell are shown to illustrate the successive oxygen octahedra along the polar [111] axis rotate with opposite sense. Arrows on Fe atoms indicate the orientation of the magnetic moments in the (111) plane [78]. ..... 27

Figure 1.21: (a) Magnetic structure of BiFeO<sub>3</sub> [82] (b) The propagation wave vector **k** is along the [110]<sub>hex</sub> direction and lies in the plane of spin rotation (1-10) [71]. .....28

Figure 1.22: M-H hysteresis loop for BiFeO<sub>3</sub> measured at room temperature [71]. .....29

Figure 1.23: (a) Variation of longitudinal polarization with magnetic field at 10 K [84] (b) Magnetization as a function of the magnetic field for H≤25T of a BiFeO<sub>3</sub> sample at 10 K [68]. .....30

Figure 1.24: Schematic representation of the planes of spiral rotation and spin cycloids **k** vector for the two polarization domains separated by a domain wall [85]. .....31

Figure 1.25: Composition dependence of magnetic satellite reflections measured using OSIRIS diffractometer at ISIS for BiMn<sub>x</sub>Fe<sub>1-x</sub>O<sub>3</sub> [76]. .....33

Figure 1.26: Left panel (a) and (b) show the temperature dependence of dc magnetization curves for polycrystalline and single crystals of BiFeO<sub>3</sub> measured under ZFC and FC conditions. Right panel (c) and (d) depicts the real and imaginary parts of ac susceptibility of single crystals of BiFeO<sub>3</sub> [102,103]. .....35

Figure 1.27: Phase diagram of (1-x)BiFeO<sub>3</sub>-xBaTiO<sub>3</sub> system [146]. .....38

Figure 1.28: The temperature dependence of dc magnetic susceptibility curves of Pb(Fe<sub>1/2</sub>Nb<sub>1/2</sub>)O<sub>3</sub> measured under ZFC and FC conditions [172]. .....40

Figure 1.29: (a) Schematic representation of the antiferromagnetic Fe<sup>3+</sup> clusters in Pb(Fe<sub>1/2</sub>Nb<sub>1/2</sub>)O<sub>3</sub> with projections of <111>-oriented spins viewed in (001) cross sections at different scales [171] and (b) Temperature dependence of the integrated intensity of the antiferromagnetic (AFM) peak intensity of PFN at Q = (½, ½, ½) [172]. .....41

Figure 1.30: The temperature dependence of dc magnetic susceptibility curves of Ca(Fe<sub>1/2</sub>Nb<sub>1/2</sub>)O<sub>3</sub> measured under ZFC and FC conditions [176]. .....43

Figure 2.1: Microstructure and EDX spectra for undoped and Mn-doped BiFeO<sub>3</sub> (a, b) in the grain and (c, d) around the grain boundary. ....53

Figure 2.2: High resolution synchrotron x-ray powder diffraction patterns collected at room temperature for (a) Undoped BiFeO<sub>3</sub> and (b) Mn-doped BiFeO<sub>3</sub>. All indices are with respect to a doubled pseudocubic cell.....55

Figure 2.3: Observed (filled circles), calculated (continuous line), and difference (bottom line) profiles obtained from the Rietveld analysis of the room temperature synchrotron x-ray powder diffraction data for (a) Undoped BiFeO<sub>3</sub> and (b) Mn-doped BiFeO<sub>3</sub> sample using R3c space group. The vertical tick marks above the difference profile represent the Bragg peak positions. Insets depicts the profile fits for 222<sub>pc</sub>, 400<sub>pc</sub>, and 440<sub>pc</sub> pseudocubic peaks. ....56

Figure 2.4: XPS Fe 2p core level spectra for (a) undoped BiFeO<sub>3</sub> (b) Mn-doped BiFeO<sub>3</sub>. Insets to figure 3(a) and (b) depict the fitted profile of 2p<sub>3/2</sub> peak. ....60

Figure 2.5: Temperature dependence of dc magnetization for (a-b) Undoped BiFeO<sub>3</sub> and (c-d) Mn- doped BiFeO<sub>3</sub> at an applied field of 500 Oe in two separate measurements from 2-300K and 300 to 750K range.....62

Figure 2.6: Temperature dependence of the real and imaginary parts of the ac susceptibility at various frequencies at an applied ac field of 5 Oe for (a, b) undoped BiFeO<sub>3</sub> and (c, d) Mn-doped BiFeO<sub>3</sub>.....63

Figure 2.7: ln(τ) vs ln(T<sub>f</sub>-T<sub>SG</sub>/T<sub>SG</sub>) plot. The solid line is the fit for the power law for (a) undoped BiFeO<sub>3</sub> (b) Mn-doped BiFeO<sub>3</sub>. Insets depicts ln(τ) vs 1/T plot.....65

Figure 2.8: Dielectric constant and dielectric loss as a function of temperature for undoped BiFeO<sub>3</sub> at 20 kHz frequency. Inset to figure show the anomaly around 25K.....67

Figure 2.9: Dielectric constant and dielectric loss as a function of temperature for Mn-doped BiFeO<sub>3</sub> at 20 kHz frequency. Inset to figure show the anomaly around 25K.....68

Figure 2.10: The evolution of x-ray powder diffraction profiles of the (222)<sub>pc</sub>, (400)<sub>pc</sub> and (440)<sub>pc</sub> reflections of pure BiFeO<sub>3</sub> sample with temperature showing the absence of any

structural phase transition. The Miller indices are written with respect to a doubled pseudocubic cell.....	69
Figure 2.11: The evolution of x-ray powder diffraction profiles of the $(222)_{pc}$ , $(400)_{pc}$ and $(440)_{pc}$ reflections of Mn-doped $\text{BiFeO}_3$ sample with temperature showing the absence of any structural phase transition. The Miller indices are written with respect to a doubled pseudocubic cell.....	70
Figure 2.12: Variation of unit cell parameters ( $a_{hex}$ , $c_{hex}$ and $V_{hex}$ ) with temperature obtained from the LeBail refinement of the x-ray powder diffraction data for pure $\text{BiFeO}_3$ sample. ....	71
Figure 2.13: Variation of unit cell parameters ( $a_{hex}$ , $c_{hex}$ and $V_{hex}$ ) with temperature obtained from the LeBail refinement using x-ray powder diffraction data for Mn doped $\text{BiFeO}_3$ sample. ....	72
Figure 3.1: Left panel depicts the scanning electron micrograph of BF-0.20BT sample. Right panel show the EDX spectrum.....	84
Figure 3.2: Synchrotron x-ray diffractogram of sintered and annealed powder of BF-xBT solid solutions for $0.10 \leq x \leq 0.60$ . All indices are with respect to a pseudocubic (pc) doubled perovskite cell. The 113 reflection is a superlattice peak due to the anti-phase tilting of the oxygen octahedra about the trigonal $[111]_{pc}$ axis that doubles the unit cell size. ....	85
Figure 3.3: Composition evolution of selected profiles of $400_{pc}$ , $440_{pc}$ and $444_{pc}$ reflection for BF-xBT in the composition range $0.10 \leq x \leq 0.60$ . ....	86
Figure 3.4: Rietveld refinement of the synchrotron x-ray diffractogram of $(1-x)\text{BiFeO}_3$ - $x\text{BaTiO}_3$ powders for representative compositions $x = 0.20, 0.40, 0.60$ using (a) Rhombohedral $R3c$ space group (b) Cubic $Pm\bar{3}m$ space group and (c) Cubic $Pm\bar{3}m$	

space group. Inset depicts the fits for the pseudocubic reflections $222_{pc}$ , $400_{pc}$ and $440_{pc}$ . .....	88
Figure 3.5: Variation of elementary perovskite (a) cell parameters (b) unit cell volume of BF-xBT as a function of composition (x) at room temperature. The structural parameters for $x = 0.0$ i.e. $\text{BiFeO}_3$ was taken from the previous chapter's analysis. ....	89
Figure 3.6: <b>(a)</b> ZFC DC magnetization versus temperature plot of BF-0.20BT for an applied field of 500 Oe <b>(b)</b> depicts the Curie-Weiss plot for BF-0.20BT above $T_N$ . ....	92
Figure 3.7: The M-H hysteresis loop at 300K for BF-0.20BT. ....	92
Figure 3.8: Neutron powder diffraction pattern of BF-0.20BT at room temperature. Arrow marks the antiferromagnetic peak. All the indices are written with respect to a doubled pseudocubic cell. ....	93
Figure 3.9: Temperature dependence of DC magnetization of BF-0.20BT under ZFC and FC conditions for an applied field of 500 Oe. ....	95
Figure 3.10: Variation of $\chi'$ ( $\omega$ , T) and $\chi''$ ( $\omega$ , T) in the temperature range 2-300K at various frequencies [47.3 Hz ( $\blacktriangleright$ ), 97.3 Hz ( $\blacktriangleleft$ ), 197.3 Hz ( $\blacktriangledown$ ), 297.3 Hz ( $\blacktriangle$ ), 397.3 Hz ( $\bullet$ ), 497.3 Hz ( $\blacksquare$ )]. Insets (i) and (ii) depict $\chi'$ ( $\omega$ , T) on a zoomed scale for SG 1 and SG 2, respectively. ....	98
Figure 3.11: $\ln(\tau)$ versus $1/T$ plot for (a) SG1 and (b) SG 2 transitions. Solid line is the least squares fit for Vogel-Fulcher law. ....	99
Figure 3.12: $\ln(\tau)$ versus $\ln(T-T_{SG}/T_{SG})$ plot for (a) SG1 and (b) SG2 transitions. Solid line shows the least squares fit for power law. ....	100
Figure 3.13: ZFC DC magnetization vs temperature plots of BF-0.20BT measured at different applied fields. Insets depict the magnified view around SG2 transition. ....	102
Figure 3.14: (a) de Almeida-Thouless (A-T) line for SG1 transition and (b) Gabay-Toulouse (G-T) line for SG2 transition. ....	103

Figure 3.15: Variation of thermoremanent remnant magnetization ( $M(t)$ ) with time at (a) 200 K and (b) 10 K for BF-0.20BT. .... 104

Figure 3.16: The evolution of x-ray powder diffraction profiles of the  $(222)_{pc}$ ,  $(400)_{pc}$  and  $(440)_{pc}$  reflections of BF-0.20BT with temperature showing absence of any structural phase transition. .... 106

Figure 3.17: Observed (filled circles), calculated (continuous line), and difference (bottom line) profiles obtained from Rietveld refinement using R3c space group at (a) 300K (b) 200K (c) 100K and (d) 12K. The vertical tick marks correspond to the position of all allowed Bragg reflections. .... 107

Figure 3.18: Observed (filled circles), calculated (continuous line), and difference (bottom line) profiles obtained from the Rietveld refinement using SXRD data at (a) 220K (b) 240K and (c) 260K using R3c space group for BF-0.20BT. The vertical tick marks above the difference profile represents the Bragg peak positions. .... 108

Figure 3.19: Variation of unit cell volume with temperature: XRD ( $\blacktriangle$ ) and NPD ( $\bullet$ ) data. Solid line ( $\text{—}$ ) is fit for Debye Grüneisen equation  $T_{SG1}$ . Inset shows the zoomed view around 140K and SG2 transitions. .... 110

Figure 3.20: Variation of volume strain ( $\Delta V/V$ ) against square of magnetization ( $M_s^2$ ) obtained by M-H loop. .... 111

Figure 3.21: The evolution of the neutron powder diffraction patterns with temperature in the limited  $2\theta = 15^\circ\text{--}57^\circ$  range. The first peak is due to AFM ordering. The Miller indices are written with respect to a doubled pseudocubic cell. .... 112

Figure 3.22: Observed (filled circles), calculated (continuous line), and difference (bottom line) profiles obtained from Rietveld refinement using R3c space group at (a) 300K (b) 200K (c) 100K and (d) 2.8K. Arrow indicates the AFM peak. The vertical tick

marks correspond to the position of all allowed Bragg reflections for the nuclear (top) and magnetic (bottom) reflections. .... 115

Figure 3.23: Temperature dependent variation of the integrated intensity of the AFM peak (111) of BF-0.20BT (The miller indices are with respect to a doubled pseudocubic cell). Solid line is fit for Brillouin function. .... 118

Figure 3.24: Temperature dependence of the fractional z coordinates of (a) Bi/Ba and (b) Fe/Ti. The x and y coordinates of O are shown in (c) and (d). All these coordinates were obtained from the Rietveld refinements using neutron powder diffraction data. .... 119

Figure 3.25: Temperature dependent variation of the spontaneous polarization calculated from the positional coordinates..... 120

Figure 3.26: (a) The variation of ZFC magnetization with temperature measured at a field of 500 Oe for various compositions in the range  $0.10 \leq x \leq 0.60$ . (b) shows first derivative of M (dM/dT) with respect to temperature for these compositions. .... 122

Figure 3.27: Left panel shows the variation of  $\chi'(\omega, T)$  of BF-xBT with temperature at 497.3 Hz frequency for various compositions in the range  $0.10 \leq x \leq 0.60$ . Right panel (a-c) as well as panel (d) depict the zoomed view around the SG1 transition. .... 123

Figure 3.28: The variation of ZFC magnetization of BF-xBT with temperature below 300K measured at field of 500 Oe for compositions (a)  $x = 0.10$ , (b)  $x = 0.20$ , (c)  $x = 0.30$  and (d)  $x = 0.40$ . .... 124

Figure 3.29: Phase diagram of BF-xBT. PM: Paramagnetic, SG: Spin glass, AFM: Antiferromagnetic, EM: Electromagnon. The SG2 transition temperatures (see the inset) shows the weakest composition dependence. The dotted lines through the data points depict the least squares fit for  $T_c \sim (x-x_c)^n$  type dependence with  $x_c = 0.55$  giving  $n = 0.30$ , 0.49, 0.33 and 0.08 for the AFM, SG1, electromagnon driven and SG2 transitions,



respectively. The exponent  $n \sim 1/2$  indicates the possibility of a quantum critical point at  $x_c \sim 0.55$ . ..... 125

Figure 4.1: Temperature dependence of total specific heat ( $C_p$ ), phonon contribution ( $C_l$ ) and magnetic contribution ( $C_m$ ) of BF-xBT for (a)  $x = 0$  (b)  $x = 0.10$  and (c)  $x = 0.20$ . ... 136

Figure 4.2: Left panel (a-c) shows the temperature evolution of Boson peak in the  $C_p/T^3$  versus T plot of BF-xBT as a function of composition (x). Right panel (d-f) depicts the temperature variation of magnetic Boson peak in the  $C_m/T^3$  versus T plot of BF-xBT as a function of x. .... 139

Figure 4.3: Left panel (a) and (b) shows the temperature dependence of total specific heat ( $C_p$ ) and Boson peak of BF-xBT for  $x = 0.40$ . Right panel (c) and (d) shows the temperature dependence of total specific heat ( $C_p$ ) and Boson peak for  $x = 0.60$ . .... 140

Figure 4.4: Variation of Boson peak temperature with composition. It follows  $(x-x_c)^{1/2}$  type dependence suggesting possibility of a quantum critical point at  $x_c \approx 0.55 \pm 0.01$ . ... 142

Figure 4.5: Temperature dependence of magnetic contribution to specific heat for BF-0.20BT in the range 1.8-40K. Solid line is the fit using  $AT^3$ -type dependence of  $C_m$ . Inset depicts the fit on a magnified scale. .... 143

Figure 4.6: Temperature dependence of magnetic contribution to specific heat for BF-0.20BT in the range 1.8-40K. Solid line is the fit using  $C_m = AT$ -type dependence. Inset depicts the fit on a magnified scale. .... 144

Figure 4.7: Temperature variation of magnetic contribution ( $C_m$ ) to specific heat for BF-0.20BT in the range 1.8 to 40K. Solid line is the fit corresponding to different model (a)  $C_m = aT^{1/2}\exp(-\Delta E/k_B T)$ , (b)  $C_m = aT\exp(-\Delta E/k_B T)$  (c)  $C_m = aT^{-2}\exp(-\Delta E/k_B T)$  below the Boson peak temperature. .... 145

Figure 4.8: The fit to  $C_m$  versus T plot of BF-0.20BT using (a)  $C_m = AT^3 + B\exp(-\Delta E/k_B T)$  and (b)  $C_m = AT^3 + BT$  type function dependence. The quality of the fits can be

seen from the insets where a magnified view is plotted. In contrast,  $C_m = AT^3 + BT$  type dependence gives poor fit as can be seen from the inset of bottom panel (b) given on the left-hand corner. The goodness of fit  $\chi^2$  is better for the  $AT^3 + B\text{Exp}(-\Delta E/k_B T)$  dependence..... 147

Figure 4.9: The fit to  $C_m$  vs  $T$  plot of BF-xBT using  $C_m = AT^3 + B\text{Exp}(-\Delta E/k_B T)$  type function for (a)  $x = 0$ , (b)  $x = 0.10$ . The quality of the fits can be seen in the insets where a magnified view is plotted..... 148

Figure 5.1: Scanning electron micrograph and EDX spectra of  $\text{Ca}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ . ..... 155

Figure 5.2: X-ray powder diffraction patterns of (a)  $\text{CaCO}_3$  (b)  $\text{Fe}_2\text{O}_3$  (c)  $\text{Nb}_2\text{O}_5$  and (d)  $\text{Ca}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ . The positions of superlattice reflections for the orthorhombic structure with the Pbnm space group, are marked by arrows. All the indices are written with respect to the double cubic perovskite cell..... 157

Figure 5.3: Observed (red dots), calculated (black continuous line) and difference (green continuous line) profiles obtained by Rietveld refinement using synchrotron x-ray data of  $\text{Ca}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  at room temperature using (a) monoclinic  $P2_1/n$  (b) orthorhombic Pbnm space groups. Vertical tick marks above the difference profile represent the Bragg peak positions. Arrow marked the expected positions of superlattice peak at 2.63, 3.75 and 4.62 degree for the monoclinic phase. The absence of these peaks rules out the monoclinic structure. (c) depicts the crystal structure of  $\text{Ca}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  along with tilted octahedra. .... 161

Figure 5.4: Temperature dependence of dc magnetization of  $\text{Ca}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  measured at 100 Oe field in warming cycle for both zero-field cooled (ZFC) and field cooled (FC) conditions. The inset gives a magnified view of the  $M(T)$  to reveal a small dip (marked with an arrow) in the FC  $M(T)$  below  $T_f$ . .... 163

Figure 5.5: Temperature dependence of the real part ( $\chi'(\omega, T)$ ) of ac magnetic susceptibility of  $\text{Ca}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  measured at various frequencies as labelled in the plot for an applied ac drive field of 1 Oe. The main panel **(b)** depict  $\ln(\tau)$  versus  $\ln(T_f/T_{SG}-1)$  plot, where  $\tau = 1/(2\pi f)$ . Inset to panel **(b)** depict the  $\ln(\tau)$  versus  $1/T$  plot. The solid line represents the least-squares fit for critical power law and Vogel-Fulcher law..... 166

Figure 5.6: Temperature dependence of the zero-field cooled (ZFC) and field-cooled (FC) dc magnetization plots of  $\text{Ca}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  at various applied magnetic fields. The arrow pointing downwards represents the irreversibility ( $T_{irr}$ ) temperature while the arrow pointing upwards corresponds to the peak ( $T_f$ ) in the ZFC  $M(T)$ ..... 168

Figure 5.7: Plot of  $T_{irr}$  versus  $H^{2/3}$  as well as  $T_f$  versus  $H^{2/3}$  showing the presence of de Almeida-Thouless (A-T) line..... 169

Figure 5.8: Time dependence of thermoremanent magnetization of  $\text{Ca}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  sample at 15 K for 1000 Oe cooling field and wait time of 1000s. The solid line is the best fit for stretched exponential function to the data. .... 171

Figure 5.9: Temperature dependence ZFC magnetization of  $\text{Ca}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  recorded at 100 Oe field with ( $\bullet$ ) and without ( $\circ$ ) intermediate stop at  $T_w=15\text{K}$  for a wait time ( $t_w$ ) of  $10^4\text{s}$ . **(b)** depicts the difference  $\Delta M(T) = M_{wait}^{ZFC}(T) - M_{ref}^{ZFC}(T)$  vs temperature ( $T$ ) plot from which it is evident that a sharp dip occurs exactly at the waiting temperature ( $T_w$ ).  
..... 173

Figure 5.10: Temperature dependence dc magnetization of  $\text{Ca}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  recorded at 100 Oe field in three different cycles as labelled in the plot. The field is set to zero during the intermittent wait of cooling temperature  $T_w = 50\text{K}, 15\text{K}$  for 3 hours. The cooling and heating rate of measurement is  $2\text{K}/\text{min}$ . The pronounced steps in the cooling curve occurs at  $15\text{K}$  and no such step is seen above the spin-glass freezing temperature (i.e. at  $50\text{K}$ ).  
..... 174

Figure 5.11: Magnetic relaxation of  $\text{CaFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$  sample at 15 K for 100 Oe field with temporary cooling (i.e. negative cycling) at 10K using (a) the ZFC and (b) FC protocols. The insets show the same data versus total time spent at 15K. The relaxation curve clearly reveals that, the curve during  $t_3$  is in continuation of the curve during  $t_1$  (memory effect). ..... 176

Figure 5.12: Magnetic relaxation of  $\text{CaFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$  sample at 15K for 100 Oe field with temporary heating (i.e. positive cycling) at 20K using (a) the ZFC and (b) FC protocols. The relaxation curve clearly reveals that during heating cycle the curve during  $t_3$  is not in continuation of the curve during  $t_1$  which is consistent Hierarchical model. .... 177

Figure 5.13: Panel (a) depicts neutron powder diffraction patterns of  $\text{Ca}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  collected at 300K, 100K and 5K. The patterns are shifted vertically for the purpose of presentation. Inset of (a) depicts the enlarged scale of broad diffuse magnetic scattering peak corresponding to short-range antiferromagnetic correlations. Panel (b) depicts the deconvolution of the NPD profile peaks at 5K. Insets of panel (b) shows enlarged scale of deconvoluted peaks at 5K. .... 179

Figure 6.1: (a) Microstructure and (b) EDX spectra of CFN-0.10BF ceramic sample... 189

Figure 6.2: Observed (red dots), calculated (black continuous line) and difference (green continuous line) profiles obtained from Rietveld refinement using x-ray diffraction data of (a)  $\text{Ca}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  (b)  $\text{Ca}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-}0.10\text{BiFeO}_3$  (c)  $\text{Ca}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-}0.10\text{LaFeO}_3$  at room temperature using Pbnm space group. Vertical tick marks above the difference profile represent the Bragg peak positions. .... 191

Figure 6.3: Left panel (a, c, e) depicts the ZFC and FC dc magnetization versus temperature plots for CFN, CFN-0.10BF and CFN-0.10LF, respectively and right panel (b, d, f) shows the corresponding Curie-Weiss plot using ZFC  $M(T)$  data. .... 194

Figure 6.4: Temperature dependent evolution of NPD patterns of CFN-10BF over a limited  $2\theta$  range 5 to 70 degrees. Arrow marks the antiferromagnetic (AFM) ordering peak. ....196

Figure 6.5: Temperature dependent evolution of NPD patterns of CFN-0.10LF over a limited  $2\theta$  range 5 to 70 degrees. Arrow marked the antiferromagnetic (AFM) ordering peak. ....197

Figure 6.6: Observed (filled circles), calculated (continuous line), and difference (bottom line) profiles obtained from Rietveld refinement using NPD data of CFN-0.10BF at 100K for propagation vector  $k = (0,0,0)$  and the irreducible representations (a)  $\Gamma_1$  (b)  $\Gamma_3$  (c)  $\Gamma_5$  and (d)  $\Gamma_7$ . Arrow marked the AFM peak. The vertical tick marks correspond to the position of all allowed Bragg reflections for the nuclear (top) and magnetic (bottom) reflections.....199

Figure 6.7: The magnetic structure of 0.90CFN-0.10BF corresponding to representation (a)  $\Gamma_1$  (G-type AFM ordering) (b)  $\Gamma_3$  (A-type AFM ordering) (c)  $\Gamma_5$  (C-type AFM ordering) and (d)  $\Gamma_7$  (FM-type Ordering).. ....200

Figure 6.8: Observed (filled circles), calculated (continuous line), and difference (bottom line) profiles obtained from Rietveld refinement using NPD data at 100K for (a) CFN-0.10BF and (b) CFN-0.10LF for propagation vector  $k = (0,0,0)$  and the irreducible representation  $\Gamma_1$ . The vertical tick marks correspond to the position of all allowed Bragg reflections for the nuclear (top) and magnetic (bottom) reflections. ....201

Figure 6.9: (a) Temperature evolution of NPD patterns of  $\text{Ca}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  in the 4 to 300K range and (b) shows the temperature evolution of diffuse magnetic peak on a magnified scale. ....204

Figure 6.10: (a) Shows the deconvoluted peak profiles for diffuse magnetic peak using Gaussian function at (a) 250K and (b) 100K for CFN. Insets depict the magnetic diffuse peak on a magnified scale. ....205

Figure 6.11: Variation of correlation length ( $\xi$ ) with temperature for CFN. ....206

Figure 6.12: (a to d) Observed (red dots), calculated (black continuous line) and difference (green continuous line) profiles obtained from Rietveld refinement using NPD patterns of  $\text{Ca}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  at 4K,100K 200K and 300K, respectively, for Pbnm space group. Vertical tick marks above the difference profile represent the Bragg peak positions. Here, we have excluded the magnetic diffuse scattering region on the refinement. ....208

Figure 6.13: Temperature variation of lattice parameters (a to c) and unit cell volume (d) of  $\text{Ca}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  obtained from Rietveld refinement using NPD patterns. ....209

Figure 6.14: Temperature variation of in-phase ( $\varphi$ ) and antiphase ( $\gamma$ ) tilt angles of CFN. ....211

Figure 6.15: Temperature dependence of dielectric permittivity ( $\epsilon'$ ) of CFN. Insets depict the magnified scale across the AFM and SG transitions. ....212