Chapter 7 Summary and Suggestions for Future Work

7.1. Summary of the present work:

In the present thesis, low temperature magnetic transitions in the well-known multiferroic $BiFeO_3$ (BF) and a potential multiferroic compound $Ca(Fe_{1/2}Nb_{1/2})O_3$ (CFN) were investigated. In addition, three solid solution compositions (1-x)$BiFeO_3$-x$BaTiO_3$ (BF-xBT), (1-x)$Ca(Fe_{1/2}Nb_{1/2})O_3$-x$BiFeO_3$ (CFN-xBF) and (1-x)$Ca(Fe_{1/2}Nb_{1/2})O_3$-x$LaFeO_3$ (CFN-xLF), based on the two compounds, were also investigated. The major emphasis of the thesis was on the spin-glass (SG) transition in these systems (chapters – II, III, IV and V). One chapter (VI) was dedicated to long range ordering (LRO) transition also in the CFN-xBF and CFN-xLF solid solutions in relation to pure CFN.

All the samples were synthesized by the conventional solid state route and were characterised for their phase purity, crystal structure, microstructure and composition using laboratory/synchrotron XRD, neutron powder diffraction, SEM, EDX and EPMA. Further, temperature dependent DC magnetization (M(T), M(H), M(T,H), M(t)), and AC susceptibility ($\chi(\omega,T)$) measurements were carried out to explore the low temperature magnetic transitions, especially the spin-glass transition in these systems. These studies were complemented with temperature dependent neutron and/or X-ray diffraction studies to capture the signatures of SG and LRO transitions as well as magnetoelectric and/or magnetoelastic couplings at the SG transitions. In addition, specific heat and dielectric measurements were also carried out on some of the samples to explore the role of magnons and magnetodielectric coupling in these systems.

The results of these investigations have been summarised at the end of each chapter (II to VI) and have been consolidated below:

In chapter II, we investigated the role of 0.3 wt% MnO_2 doping in $BiFeO_3$ used by various workers on the oxygen ion vacancy and Fe^{2+} ion concentration, on one hand, and the low temperature magnetic transitions, on the other. Iodometric titration and XPS studies reveal that the oxygen ion vacancy and Fe^{2+} ion concentrations decrease significantly as a result of Mn doping and acquire near stoichiometric proportions in the doped samples. The low temperature transitions occurring around 25 K, 150 K and 260 K are common to both the undoped and doped samples. However, the spin glass transition reported around 50 K by earlier workers, is absent in the Mn-doped $BiFeO_3$ and may be associated with the higher concentration of oxygen ion vacancies and Fe^{2+} ions in the undoped samples. The spin glass character of the transition around 25K is confirmed in both the samples and a significant change in the unit cell volume is observed around this transition confirming that this transition is a bulk behaviour and not due to the isolated superparamagnetic impurities. No signature of the other transitions is seen in ($\chi(\omega,T)$) plots suggesting that they may be of non-spin glass type.

In chapter III, evidence for two spin-glass transitions (SG1 and SG2) with T_f~ 250K and 25K in a solid solution of $BiFeO_3$ containing 20% $BaTiO_3$ (BF-0.20BT) was presented using a series of bulk measurements revealing history dependent effect, critical slowing down of the spin dynamics leading to ergodicity breaking at two characteristic spin glass transition temperature T_{SG1}~219K and T_{SG2}~18K, existence of A-T and G-T lines due to freezing of the longitudinal and transverse components of the spins and stretched exponential type decay of the thermoremanent magnetization. Using neutron powder diffraction (NPD) measurements, which provide evidence on microscopic scales, the two spin-glass transitions are shown to occur on the same magnetic sublattice in coexistence with the long range ordered antiferromagnetic phase with. The spontaneous polarization (P_s) and unit cell volume (V), obtained from the Rietveld analysis of low temperature NPD and XRD data, respectively, show significant variation across the SG1 and SG2 transitions confirming the presence of magnetoelectric and magnetoelastic couplings, respectively. These couplings, and possibly the presence of electromagnons not investigated in the present work, constitute unique features of a multiferroic spin-glass system like BF-xBT that distinguish it from the conventional spin glass systems. Our results provide the first unambiguous evidence for the theoretical predictions on concentrated Heisenberg systems with low single ion anisotropy about the occurrence of a succession of two spin glass transitions due to the freezing of longitudinal and transverse components in coexistence with the LRO phase. This chapter also gives a complete magnetic phase diagram for the BF-xBT solid solution system upto the critical percolation threshold value x_c~0.55.

Chapter IV is devoted to the study of low temperature magnetic transitions in the BF-xBT solid solution compositions using temperature dependence of specific heat (C_p). Both the total specific heat and the magnetic contribution (C_m), obtained after subtracting phonon contributions, show the presence of a Boson peak in the C_p/T^3 or C_m/T^3 vs T plots whose peak temperature varies as T_{Boson}~$(x - x_c)^{1/2}$ suggesting the possibility of a quantum critical point at x_c~0.55. The magnetic specific heat (C_m) below the Boson peak temperature cannot be explained without considering coexistence of spin glass and LRO AFM phases. It is shown than C_m in the temperature range 1.8 to 12 K is best described using a functional dependence $C_m = AT^3 + BT\exp(-\Delta E/k_BT)$ where the AT^3 term is due to the long-range ordered (LRO) antiferromagnetic (AFM) phase and the exponential term is due to gapped magnons in the spin-glass (SG) phase. We believe that this is the first evidence for the coexistence of LRO and SG phases in concentrated systems using specific heat studies.

Chapter V presents results of low temperature magnetic transition in $Ca(Fe_{1/2}Nb_{1/2})O_3$ (CFN) using M(T), χ (ω,T), M(T, H), M(T, t) and neutron scattering measurements. Analysis of the dc magnetization measurements reveals a spin-glass (SG) transition with T_f ~25K with characteristic history dependent irreversibility. Analysis of the ac susceptibility data reveals power law/Vogel-Fulcher type critical spin dynamics with a time scale of τ_0~10^{-6}s which suggests the existence of a cluster spin-glass (CSG) state in CFN with T_{SG}~24K. The field dependence of the irreversibility temperature T_{irr} (H) and the peak temperature T_f(H) of the ZFC M(T) falls on the A-T line in the T_{irr}(H)/T_f (H) versus $H^{2/3}$ plot. The zero-field SG freezing temperature $T_f(0)$ = 25.2K, obtained from the extrapolation of T_f(H) versus $H^{2/3}$ plot to H = 0, is in close agreement with the ergodicity breaking temperature T_{SG}~24K obtained from the analysis of the ac susceptibility $\chi(\omega, T)$ data. The observation of slow relaxation of thermoremanent magnetization, memory and rejuvenation effects below the SG transition temperature T_{SG}~24K supports the presence of glassy phase. Neutron diffraction study confirms the absence of any long-range AFM ordering but shows diffuse scattering due to the presence of short-range ordered (SRO) AFM spin clusters with a correlation length ξ ~2nm which are involved in the CSG freezing. The present results raise doubts about the origin of the spin glass transition in the related compound $Pb(Fe_{1/2}Nb_{1/2})O_3$ in terms of the freezing of the transverse component of the Fe^{3+} spins whose longitudinal component continues to remain long-range ordered.

Chapter VI addresses a long standing puzzle about the absence of LRO AFM phase in Pb^{2+} free complex perovskites $A(Fe_{1/2}B_{1/2})O_3$, where A = Ba, Sr, Ca and B = Nb, Ta, W, taking $Ca(Fe_{1/2}Nb_{1/2})O_3$ as an example. Theoretically all these compounds should exhibit LRO AFM transition since the Fe^{3+} ion concentration is above the percolation threshold value required for stabilizing the LRO percolative phase. Results of dc magnetization and neutron scattering measurements on CFN as well as its solid solutions containing 10% $BiFeO_3$ or $LaFeO_3$ (i.e., CFN-0.10BF and CFN-0.10LF) reveal that only a slight increase in Fe^{3+} ion concentration in CFN helps stabilise the LRO AFM phase with T_N~ 175K. Neutron diffraction measurements reveal that CFN is an incipient AFM whose SRO AFM correlation length starts growing at T≲175K, but the size of the AFM spin-clusters remains limited to ~2 nm even at the lowest temperature (4K). This shows that CFN is at the verge of acquiring LRO AFM state below T_N~175K. ZFC M(T) measurements reveal that the LRO AFM phase gets stabilised by increasing the Fe^{3+} ion concentration slightly (~ 5%) in CFN through a substitution of $BiFeO_3$ and $LaFeO_3$, This was confirmed by neutron diffraction studies on CFN-0.10BF and CFN-0.10LF which reveal AFM phase with G-type LRO AFM state below T_N. Presence of significant magnetoelastic and magnetodielectric coupling below T≲175K in CFN suggests that CFN could become a multiferroic also through suitable compositional engineering. The results presented in this thesis demonstrate the role of critical percolation threshold composition for stabilising LRO AFM phase in CFN.

7.2. Suggestions for future study

Notwithstanding the strong experimental evidences presented in this thesis for the existence of spin glass phase in $BiFeO_3$ (BF), solid solutions of BF with $BaTiO_3$ (BT) (i.e., BF-xBT) and $Ca(Fe_{1/2}Nb_{1/2})O_3$ (CFN), the following aspects need further investigation in a future study:

1. The occurrence of spin glass transition in an ordered compound like $BiFeO_3$ is quite intriguing in the absence of any apparent disorder and randomness. While spin glass transition in recent years has been reported in some ordered compounds but the magnetic interactions in such systems are geometrically frustrated. In such

systems, even infinitesimal disorder due to magnetoelastic strains has been shown to stabilize spin glass phase at low temperature. While we have presented evidence for magnetoelastic strain accompanying spin glass transition, there in no evidence for geometrical frustration in $BiFeO_3$. Thus the origin of spin glass phase in $BiFeO_3$ remains an open issue and requires further exploration.

2. While the robust evidence presented for the succession of two spin glass transitions due to the freezing of the transverse and longitudinal components of the Fe^{3+} spins in coexistence with LRO AFM is in broad agreement with theoretical predictions for concentrated systems with Heisenberg spins, the origin of magnetoelectric coupling mediated by isostructural phase transitions needs more theoretical investigation. There is a need to revisit the existing theories of spin glass transitions to take into account the magnetoelastic and magnetoelectric coupling terms in the Hamiltonian for understanding the characteristic of spin glasses in multiferroic systems.
3. We presented experimental evidence for incipient AFM nature of $Ca(Fe_{1/2}Nb_{1/2})O_3$ and the stabilization of LRO AFM phase below T_N~175K due to 10% substitution by $BiFeO_3$ (BF) or $LaFeO_3$ (LF). More theoretical work is required to calculate the percolation threshold for $Ca(Fe_{1/2}Nb_{1/2})O_3$ taking into account the nearest and higher neighbour superexchange interactions.
4. Below the LRO AFM phase transition temperature T_N~175K, there is evidence for two more transitions in M(T) plots in solid solutions of $Ca(Fe_{1/2}Nb_{1/2})O_3$ with $BiFeO_3$ and $LaFeO_3$. Understanding the nature and the origin of these transitions needs further investigation. In particular, it needs to be understood if the drop in the ZFC magnetization at T~50K below the AFM T_N~175K is due to the appearance of a re-entrant spin glass phase.