Preface

Multiferroic materials that inherently possess two or more than two ferroic properties in the same phase have attracted unprecedented attention in recent times but are rare in nature. The co-existence of ferroic properties in multiferroic materials make it novel than those of conventional materials since they permit a mutual coupling between them. A material where such an interestingly phenomena present is referred to as Magnetoelectric (ME) multiferroic material. Moreover, materials with ME effect have potential applications for multifunctional device such as future generation four-state memory devices, spintronics, actuators, transducers and for profound physics of these materials. Therefore, this led to a huge attention of scientific community for its detailed study. Multiferroics are very rare in nature due to the chemical incompatibility and mutual exclusiveness of the ordered states. It is, therefore to combine electric and magnetic properties simultaneous at room temperature in the same phase becomes a major challenge from its discovery. Among the discovered multiferroics, Bismuth ferrite ($BiFeO_3$) with perovskite structure (ABX_3 type) has stayed as the model multiferroic because of its high ferroic transition temperature (T_C =1100 K) and antiferromagnetic temperature (T_N = 650 K) above the room temperature. The stereochemical activity of the Bi^{+3} $6s^2$ lone pair electrons are believed to the origin of ferroelectricity in $BiFeO_3$,while a modulated cycloidal spin structure of transition metal ion Fe^{+3} (d^5) on the B-site is responsible for canted G-type antiferromagnetism with periodicity 62nm. However, there are several problem like structural instability, low resistivity and leakage current can't still solved which restricted it for technology applications. Single phase polycrystalline $BiFeO_3$ shows weak magnetic and electric order and weak intrinsic ME coupling, consequence applied magnetic (electric) fields causing weak polarization (magnetization). With a specific end goal to illuminate this lacks of single phase $BiFeO_3$ multiferroics, our research work focus on the preparation of solid solution of $BiFeO_3$ with different magnetic and non-magnetic dopants (for example Ti, Al, and Co) and their composite with terbium manganites ($TbMnO_3$) to increase ME coupling mechanism and induce new exotic phenomena like exchange bias effect. So as to give systematic discussion this thesis has been shorted out into seven chapters, outline of each chapter is given below.

In chapter 1, the Physics of the broad area multiferroic and its related materials has been discussed in details. This chapter starts with brief introduction of multiferroic material,

classification of multiferroic, essential research literate survey for our research works. In this chapter, we have also discuss some other important issues like exchange bias effect, training effect, ME coupling etc. From view of literature, we have chosen Type–I multiferroic Bismuth ferrite ($BiFeO_3$) for our objective of the present investigation.

In chapter-2, we have explained the technique process and basic principle employed in the synthesis of sample, characterization, and measurements used in our research work. Room tempearture X-ray diffraction and Raman analysis have been emplyoed for structural and phase identification. The detail of Quantum Design MPMS magnetometer (MPMS) for the magnetic properties of the sample has been elucidated in detail. We have also discussed the working principal of X-Ray Absorption Spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) widely used for studying the electronic structure and magnetic origin of sample in this chapter. Some common measurements like dielectric measurement, UV-Vis. spectrophotometer and their working principles are also added in this chapter.

In Chapter 3, we have studied electrical and magnetic properties of $Bi_{0.5}La_{0.5}Fe_{0.5}Mn_{0.5-x}Ti_xO_3$ (where x=0 and 0.05) samples which were prepared by solid state method. The Rietveld refinement of X-ray diffraction (XRD) patterns show that the systems crystallize in orthorhombic phase with *Pnma* space group. Observed Raman modes support the XRD results. The appearance of prominent A_{1-3} and weak E_2 modes in $Bi_{0.5}La_{0.5}Fe_{0.5}Mn_{0.45}Ti_{0.05}O_3$ indicate the presence of chemically more active Bi-O covalent bonds. Ferromagnetism of $Bi_{0.5}La_{0.5}Fe_{0.5}Mn_{0.5}O_3$ is enhanced by Ti doping at Mn-site indicating that these particular samples might be interesting for device applications.

Chapter 4 deals with the structural and electrical properties of non-magnetic Al ion doped on $Bi_{0.5}La_{0.5}Fe_{0.5}Mn_{0.5}O_3$ multiferroic. X-ray diffraction, room temperature Raman analysis and dielectric measurement are performed on Al-doped $Bi_{0.5}La_{0.5}Fe_{0.5}Mn_{0.}5O_3$. X-ray diffraction analysis confirms the system crystallize in orthorhombic phase with *Pnma* space group. Observed Raman modes are also support the XRD outcomes. Dielectric study on $Bi_{0.5}La_{0.5}Fe_{0.5}Mn_{0.40}Al_{0.1}O_3$ indicates that ε' increases sharply and shows high dielectric constant with weak-temperature dependence. Dielectric constant of the system enhances sharply from $\sim 8.5\times10^3$ for $Bi_{0.5}La_{0.5}Fe_{0.5}Mn_{0.5}O_3$ to $\sim 1\times10^4$ for $Bi_{0.5}La_{0.5}Fe_{0.5}Mn_{0.40}Al_{0.10}O_3$ at room

temperature. All the results suggest that $Bi_{0.5}La_{0.5}Fe_{0.5}Mn_{0.40}Al_{0.10}O_3$ is very promising for device applications in the field of Spintronics, memory devices, high energy density capacitors etc.

In Chapter 5, we have incorporated $TbMnO_3$ (which shows strongest ME coupling) into $BiFeO_3$ in a single material and got exotic phenomena exchange bias at room temperature. The magnetic property of $0.7BiFeO_3$-$0.3TbMnO_3$ composite has been studied in detail and compared with that of the $0.8BiFeO_3$-$0.2TbMnO_3$. The magnetic property in $0.7BiFeO_3$-$0.3TbMnO_3$ is improved in manifold compared to $BiFeO_3$. An exchange bias (H_{EB}) is observed in both the compositions of these hard and soft antiferromagnetic composites. The H_{EB} varies between 5-180 Oe with a maximum at ~ 275 K. Isothermal remanent magnetization measurements at room temperature indicate the presence of an interfacial layer of a 2 dimensional dilute antiferromagnet in a field (2D DAFF). The presence of exchange bias can be explained on the basis of a strong strain-mediated magnetoelectric coupling induced exchange interaction and the creation of 2D DAFF layer at the interface. The properties of this layer are defined by canting and pinning of BFO spins at the interface with TMO due to Fe and Mn interaction. X-ray Magnetic Circular Dichroism (XMCD) confirms the presence of canted antiferromagnetic ordering of $BiFeO_3$, charge transfer between Mn ions and different magnetically coupled layers which play vital role in the exchange bias.

Chapter 6 presents the systemically studied of magneto-structural and magneto-electric coupling in multiferroic composite $BiFeO_3$-$TbMnO_3$. Anomalous softening of the phonon modes was observed at ~ 210 K near the spin reorientation transition temperature (T*) in the temperature dependent Raman spectra which is a result of spin phonon coupling in the lattice. Relaxor type ferroelectric behaviour was observed in the temperature dependent dielectric measurements where the relaxation was found near (T*). The frequency dependent dielectric study and the impedance spectroscopy revealed that the dielectric properties are a mixture of intrinsic Debye relaxation and Maxwell-Wagner relaxation arising from the space charge polarization at the interface of the two materials. A large positive magneto-dielectric (MD) coupling was found near the relaxation temperature which is understood to be originated as a result of the magneto-structural coupling in the system.

In **chapter 7**, we have studied band structure, transport and magnetic properties of $BiFeO_3$-$TbMnO_3$ composite. A narrower band gap is estimated from the UV-visible absorption spectrum from that of BiFeO3 and $TbMnO_3$. With known value of band gap, the band structure was estimated from the valence band x-ray photoemission spectra (XPS) and ultra violet photoemission spectra (UPS). The valence and conduction band was found at 1.0 eV and 0.45 eV above and below the Fermi level respectively. Thus the insulating behavior of the system is understood from the reconstruction of the energy bands at the interface which happens due to lattice mismatch of the two materials. The large coercivity and the increase on the magnetization value are understood to be due to superexchange interaction between different Mn ions (Mn^{2+}, Mn^{3+} and Mn^{4+}). From the composition study of EDXA and core level x-ray photoemission spectra oxygen vacancy was found which in turn creates the mixed valence state of Mn to maintain the charge neutrality.

Chapter 8 is devoted to multifunctional properties and magneto-dielectric (MD) response of $Bi_{0.5}La_{0.5}Fe_{0.5-x}Co_xMn_{0.5}O_3$ (with x= 0.10) multiferroic, synthesized using solid state reaction. Room temperature X-ray diffraction (XRD) pattern and Raman spectrum revealed that the $Bi_{0.5}La_{0.5}Fe_{0.4}Co_{0.1}Mn_{0.5}O_3$ crystallizes in orthorhombic crystal structure (space group *Pbnm*). Magnetic measurements exhibited that the partial substitution of Co at Fe-site induces a weak ferromagnetism as a result of Fe-O-Co superexchange interaction. More interestingly, meta-magnetic hysteresis loop behavior, a rare phenomenon for $BiFeO_3$ based system, was found from the M-H measurements at 80 K. A significant enhancement in dielectric permittivity (~5%) with the application of external magnetic of 1T has been observed near room temperature at 1 kHz frequency which confirms the presence of magneto-dielectric (MD) coupling in the system. Our work describes a new pathway to control improved multiferroic properties at room temperature which favour their application in future multiferroics devices.

Chapter 9 gives the brief conclusion and glimpse of future research work carried out in this material.