

Preface

Recent discovery of multiferroicity and magneto-electric effect in rare-earth manganites and hybrid organic-inorganic materials have led to intense search for finding new multiferroic materials for device applications. Multiferroics can be classified broadly in two categories depending on the correlation between magnetic and ferroic orders. Undoped and doped manganites are especially attractive due to their complex magnetic structure which can lead to ferroelectric order. Hybrid organic-inorganic or metal-organic frameworks (MOFs) have been recently identified as a class of type-I multiferroic system that consists of metal ions interlinked by bridging ligands (organic). The ferroelectric order in such materials is a result of hydrogen bond ordering and reorientation of organic cation present in the cavities of the framework. Detailed studies on such systems demand high quality single crystals.

This thesis relates to growth of single and poly crystalline samples of ABX_3 type of multiferroics and their characterization. Structural, magnetic, ferroelectric and thermal properties of manganites and hybrid organic-inorganic compounds are explored. By selectively tuning A, B and X components of the perovskite structure, specific magnetic and ferroelectric order can be realized. In this work, we discuss in detail the effect of A and B-site substitution in rare-earth manganites on the physical properties of the system. We have synthesized two series of Yttrium doped manganites to see the influence of rare-earth ion size on the magnetic phase transition and other physical properties, using magnetization, ac susceptibility and impedance studies. The double perovskite system was used to investigate the role of disorder at B-site on the physical characteristics of the system. In hybrid organic-inorganic compounds, we evaluated the magnetic and ferroelectric properties using various organic cations (A), anions (X) and transition elements. The work is organized into seven chapters in the thesis and the brief outline of each is given below.

Chapter 1 provides general introduction to multiferroics and a brief overview of perovskite geometry and lattice distortions. A basic introduction of ferroelectricity, dielectric relaxation and various fundamental magnetic interactions is provided which leads to the evolution of multiferroicity. The term multiferroicity is referred as the simultaneous existence of magnetic and electric order in a single phase

material. Classification of multiferroic materials depending on the correlation between various ferroic order is discussed briefly. The mechanism of multiferroic behaviour is outlined for few type-I and type-II systems as also spin-glass effects due to size-mismatch and disorder. A discussion on specific heat and critical point in manganites is also presented. The last section of this chapter includes the motivation and scope of work presented in this thesis.

Chapter 2 summarizes the crystal growth techniques and experimental methods employed. The basic working principles are briefly explained.

Chapter 3 deals with evolution of lattice and magnetic structure with substitution of Yttrium at rare-earth site of RMnO_3 manganites with $R = \text{Nd}, \text{Pr}$. Two series of single phase samples are synthesized with varying Yttrium content i.e, $\text{Nd}_{1-x}\text{Y}_x\text{MnO}_3$ ($0 \leq x \leq 0.5$) and $\text{Pr}_{1-x}\text{Y}_x\text{MnO}_3$ ($0 \leq x \leq 0.4$). Both series crystallize in $Pbnm/Pnma$ space group with O' type orthorhombic distortion. Lattice parameter, b increases with increase in Yttrium doping, while a , c and $\langle \text{Mn-O-Mn} \rangle$ bond angle decreases. Both series of compounds show antiferromagnetic transition at low temperature. The transition temperature decreases with decrease in $\langle \text{Mn-O-Mn} \rangle$ bond angle. At lower doping levels $x \leq 0.35$, rare earth ordering is observed in $\text{Nd}_{1-x}\text{Y}_x\text{MnO}_3$ whose virgin magnetization curves reveal step-like discontinuities at 5 K. This is reminiscent of spin reorientation or meta-magnetic effect. The interaction between Mn and Nd sub-lattices and their relative strength are a function of doping. This results in ferrimagnetic-like nature when $x = 0.35$. The magnetization of $\text{Nd}_{1-x}\text{Y}_x\text{MnO}_3$ series can be explained by assuming the competition between Mn and Nd sub-lattices combining with the scenario of phase separation for higher doping. A phase diagram is constructed using the data accumulated through our measurements. For $\text{Pr}_{1-x}\text{Y}_x\text{MnO}_3$ series, the magnetic structure is found to be $(A_x, F_y, 0)$ using Rietveld refinement of powder neutron diffraction data, thus confirming A-type antiferromagnetic order. The compounds are found to be Jahn-Teller distorted and Jahn-Teller distortion is evaluated as a function of temperature. Dielectric studies point to dominant Maxwell-Wagner polarisation and presence of different relaxation processes. It is observed that the relaxation mechanism also changes with change in doping.

Chapter 4 elaborates the multiglass properties of $\text{Nd}_2\text{NiMnO}_6$ double perovskite

compound. The compound is crystallized in either $Pbnm$ or $P2_1/n$ space group, depending on the synthesis conditions (disorder). It has ordered Ni and Mn atoms at B-site and display ferromagnetic behaviour at low temperature. Another magnetic transition is observed at low temperature, which is investigated by ac susceptibility technique. Results confirm the presence of re-entrant spin glass phase. A critical behaviour study in the vicinity of paramagnetic–to–ferromagnetic transition reveals critical exponents as, $\beta = 0.452 \pm 0.001$, $\gamma = 1.251 \pm 0.005$ and $\delta = 3.76 \pm 0.02$, which do not match with any of the conventional theories i.e mean field, 3D Heisenberg and 3D Ising. However close resemblance with $\text{La}_2\text{NiMnO}_6$ suggests a 3D Heisenberg ferromagnet with short range magnetic interactions. Dielectric response indicate colossal value of dielectric constant due to Maxwell-Wagner effect. A relaxor like behaviour points to glassy dielectric behaviour. The glassy nature is not intrinsic but rather owes to crossover in relaxation times associated with electrically different regions, within the homogeneous sample. The relaxation times observed for grain boundary is 4 orders of magnitude higher than the values observed for grain contribution which indicates electrical heterogeneity. Impedance data provides different conduction mechanisms for grain and grain boundary contribution often related to polaronic conduction.

Chapter 5 concerns with the new class of multiferroic, hybrid organic-inorganic perovskite compounds of the type $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{MCl}_4$. Magnetic, dielectric and pyroelectric properties of $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4$ have been studied which confirm its multiferroic nature. Magnetic measurements reveal that the compound is antiferromagnetic with weak ferromagnetism below 10.2 K. Ferromagnetically ordered layers are stacked antiferromagnetically along the long-axis of the crystal. The interlayer antiferromagnetic interaction is dependent on the size of organic cations, which are sandwiched between layers of CuCl_6 octahedrons. For compounds with larger organic cation such as $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{MCl}_4$, ferromagnetic behaviour is noticeable below 8.5 K, and another spin-reorientation transition is observed around 6 K. The real part of dielectric permittivity for $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4$ single crystals has an anomaly at 247 K reminiscent of improper ferroelectric phase transition. There is one more broad maxima observed near 232 K. This is believed to be due to structural ordering. The anomalies in dielectric constant originate from order-disorder transitions associated with the reorientation of organic cation as a whole. A large magnitude of electric polarization, $P_a = 17 \mu\text{C}/\text{cm}^2$ is seen

below 247 K from the pyroelectric data. To confirm the role of organic cation reorientation in driving structural transitions, Raman and dielectric measurements were performed on $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4$ single crystals. The results indicate that hydrogen bond ordering is the key driving force for the structural transitions.

Chapter 6 presents hybrid perovskite compounds with general formula $\text{AB}(\text{HCOO})_3$, where A is organic cation $(\text{CH}_3)_2\text{NH}_2^+$, $\text{C}(\text{NH}_2)_3^+$ and B is a transition element (Mn, Cu, Co). Single crystals of both series of MOFs are grown using solvothermal process and characterized by magnetic, dielectric and thermal data. The compounds have a NaCl-type framework of $\text{B}(\text{HCOO})_3$ where transition metal ions sit at the corners of the cube (unit cell) and are connected with each other via coordination bonding with oxygen of the formate ion. The organic cation is located at the centre of the cavity in BO_6 octahedrons. The amine hydrogen atoms participate in hydrogen bonds $\text{N}-\text{H}\cdots\text{O}$ with oxygen atoms of the metal-formate framework. For the $(\text{CH}_3)_2\text{NH}_2\text{M}(\text{HCOO})_3$ series, the nitrogen atom of ammonium group is disordered over 3 equivalent positions at room temperature. Upon cooling, the organic cation orders leading to a structural phase transition. The structural transition is seen as an anomaly in dielectric measurement, which is regarded as the order-disorder ferroelectric transition. For $(\text{CH}_3)_2\text{NH}_2\text{Co}(\text{HCOO})_3$ compound ferroelectric hysteresis loops were seen below transition temperature, while no hysteresis is seen above T_c , further confirming the ferroelectric phase below 155 K. No dielectric anomaly is observed in $\text{C}(\text{NH}_2)_3\text{B}(\text{HCOO})_3$ series of compounds. All compounds of both series show 3D antiferromagnetic nature with small ferromagnetic component. However, $\text{C}(\text{NH}_2)_3\text{Cu}(\text{HCOO})_3$ bears the signature of low-dimensional magnetism. It crystallizes in non-polar space group $P2_1nm$ and is a potential choice of room temperature ferroelectric material. Preliminary data reveal PE hysteresis loops related to ferroelectric behaviour.

Chapter 7 concludes the thesis highlighting major observations made in different chapters. Future prospects of the work are briefly outlined.