

# Abstract

For the last few decades, the physics of doped perovskite manganite's ( $RMnO_3$ ) has been an area of intense research due to their interesting physical and electronic properties. Various exciting phenomena such as, colossal magnetoresistance, multiferroicity, ferroelectricity, near room temperature ferromagnetism, etc., have made these systems more fascinating in terms of underlying fundamental physics as well as technological applications. The electronic and magnetic properties of these systems are determined by the competition between different interactions such as antiferromagnetic interaction between the Mn spins, electron phonon coupling, electronic repulsion, and kinetic energy of the carriers, etc. By careful selection of dopant and control of the doping concentration at *A* and *B*-sites, these parameters can be fine-tuned and different phases with diverging properties can be experimentally realized. In this thesis, half doping effect at *A* and *B*-sites of two selected  $RMnO_3$  ( $R = Tb$  and  $Y$ ) systems are studied in detail. *A*-site is hole doped with Sr while *B*-site is doped with Ni and Fe. *B*-site half doped material can be considered as double perovskite ( $R_2BB'O_6$ ) where *B*-site occupants order alternately. *A*-site half doping makes the system glassy while the *B*-site half doped systems show FM behaviour at low temperature. The thesis is organized in eight chapters and a brief summary of each is given below.

*Chapter 1* begins with an introduction to the perovskite and double perovskite structures. Origin of lattice distortions, different magnetic interactions, glassy magnetic phase, and basics of dielectric and impedance spectroscopy techniques, etc. are also discussed. This chapter concludes with a note on the motivation behind the thesis work.

*Chapter 2* discusses the crystal growth techniques and experimental methods used in the present work. The basic working principles of these are briefly explained in this chapter.

*Chapter 3* focuses on the magnetic, dielectric, impedance and pyro current properties of double perovskite  $Y_2NiMnO_6$ . This material crystallizes in monoclinic  $P2_1/n$  space group and shows ferromagnetic transition at 81 K. The ferromagnetic order at low temperature is confirmed by the saturation value of magnetization ( $M_s$ ). Critical behaviour studies conducted across the ferromagnetic transition yield critical exponents. The calculated exponents do not satisfy any of the standard theoretical model explicitly. Analyses of frequency dependent dielectric constant and equivalent circuit of impedance data consider the bulk contribution to total dielectric constant and reveals an anomaly which coincides with the ferromagnetic transition temperature ( $T_c$ ). Pyro current measurements register a current flow near  $T_c$  and a peak at 57 K that shifts with temperature ramp rate. The extrinsic nature of the observed pyro current is established by employing a special measurement protocol. It is conceived that the origin of pyro current is due to re-orientation of electric dipoles created by free charge carriers and not by spontaneous electric polarization.

*Chapter 4* provides a detailed account of magnetic and Raman scattering studies on double perovskite  $\text{Tb}_2\text{NiMnO}_6$ .  $\text{Tb}_2\text{NiMnO}_6$  is synthesized via conventional solid-state synthesis route and crystallizes in monoclinic  $P2_1/n$  space group. DC and AC magnetization data reveal a FM transition at 111 K ( $T_c$ ). Negative deviation from ideal Curie-Weiss law ( $1/c(T)$  curves) and less than unity susceptibility exponents (power-law analysis of inverse susceptibility) are reminiscent of Griffiths phase. Arrott plots derived from magnetization isotherms support the inhomogeneous nature of magnetism in this material. These effects result from antiferromagnetic interactions that originate from inherent antisite disorder in the system. Raman scattering data do not reveal magnetic-order-induced phonon renormalization below  $T_c$  in  $\text{Tb}_2\text{NiMnO}_6$ . This is different from other  $\text{R}_2\text{NiMnO}_6$  double perovskites and may be attributed to the small size of the rare earth ion. The temperature evolution of full-width-at-half-maximum for the stretching mode at  $645 \text{ cm}^{-1}$  presents an anomaly that coincides with the magnetic transition temperature and signals a correlation between magnetism and lattice in this material.

*Chapter 5* deals with dielectric and impedance properties of the double perovskite  $\text{Tb}_2\text{NiMnO}_6$ . Real ( $\epsilon'(f, T)$ ) and imaginary ( $\epsilon''(f, T)$ ) parts of dielectric permittivity show three plateaus suggesting that dielectric relaxation originate from bulk, grain boundaries and sample-electrode interfaces, respectively.  $\epsilon'(f, T)$  and  $\epsilon''(f, T)$  are successfully simulated by RC circuit model. Complex plane of impedance ( $Z''-Z'$ ) is simulated using a series network with a resistor and constant phase element. The analysis of  $\epsilon'(f, T)$  using modified Debye model reveals two different relaxation regimes separated by a characteristic temperature,  $T_*$ . The temperature variation of R and C corresponding to the bulk and the parameter  $a$  (modified Debye fit) lend support to this hypothesis. Interestingly, the  $T_*$  of this compound compares well with the Griffiths temperature as observed in magnetic measurements. Although this result cannot be interpreted as due to magneto-electric coupling, the relationship between lattice and magnetism remains distinct.

*Chapter 6* describes the magnetic properties of  $\text{TbMn}_{0.5}\text{Fe}_{0.5}\text{O}_3$ . Orthorhombic single crystals of  $\text{TbMn}_{0.5}\text{Fe}_{0.5}\text{O}_3$  exhibit spin-reorientation, magnetization reversal and weak ferromagnetism. Strong anisotropy effects are evident in the temperature dependent magnetization measurements along three crystallographic axes **a**, **b** and **c**. A broad magnetic transition is visible at 286 K ( $T_{\text{Fe/Mn } N}$ ) due to transformation from paramagnetic to  $A_xG_yC_z$  ordering. A sharp transition is observed at 28 K ( $T_{\text{Fe/Mn } SR}$ ); this is pronounced along **c**-axis as a sharp rise in magnetization in which the spins reorient to  $G_xA_yF_z$  configuration. Negative magnetization observed below  $T_{\text{Fe/Mn } SR}$  along **c**-axis is explained in terms of domain wall pinning. A component of weak ferromagnetism is observed in field-scans along **c**-axis below 28 K. Field induced, step-like transitions are observed in hysteresis measurements along the **b**-axis below 28 K. It is interesting to note that no sign of Tb-ordering is discernible down to 2 K.  $\text{TbMn}_{0.5}\text{Fe}_{0.5}\text{O}_3$  is highlighted as a prospective material that deserves to be investigated for its magneto-dielectric effects across the magnetic transitions.

*Chapter 7* is devoted to the growth and characteristics of  $\text{Tb}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  single crystals. The crystals were grown by float zone method and the material crystallizes in the orthorhombic  $Pnma$  space group. DC magnetic measurements reveal a magnetic anomaly at  $\sim 44$  K which is confirmed as a spin-glass transition through AC susceptibility, magnetic relaxation and memory

experiments. Magnetic moments are not saturated at 5 K even at the applied field of 140 kOe , a result that excludes the possibility of long-range order. Temperature cycling relaxations below the spin- glass transition temperature can be interpreted through Hierarchical model. Large A-site cationic size mismatch together with mixed valency of Mn ions lead to magnetic frustrations and make the system glassy. Dielectric response has a clear frequency dispersion in real and the imaginary parts. Two relaxation regimes are discernible, one below and another above the magnetic anomaly temperature. This is a strong indication of interplay between electronic and magnetic degrees of freedom in the system. The origin of dielectric dispersion is attributed to electron transfer between Mn<sup>3+</sup> and Mn<sup>4+</sup> ions. Transport studies highlight insulating behaviour in the temperature range 60-300 K. The activation energy calculated agrees with that obtained from dielectric data. Specific heat data are obtained in the range 2-300 K and different contributions to the total specific heat have been identified.

*Chapter 8* concludes with general findings pertaining to various observations made in the different chapters. Prospects for future work are briefly outlined in this chapter.