

Preface

Doped rare-earth manganites with the general formula $T_{1-x}D_xMnO_3$ where ‘T’ is a trivalent rare earth ion, e.g. La^{3+} , Nd^{3+} , Pr^{3+} etc. and ‘D’ is a divalent alkaline earth ion, e.g. Ca^{2+} , Sr^{2+} , Ba^{2+} etc. display various interesting properties. They attracted research attention because of their unique properties and potential applications [1–5]. These materials exhibit exciting properties like CMR (colossal magneto resistance), charge ordering (CO), orbital ordering (OO), ferromagnetism (FM), antiferromagnetism (AFM), phase separation (PS), electron-hole asymmetry, phase complexities, exchange bias effects etc. [1,2,6]. These exciting properties exhibited by manganite system are explained using various interactions taking place in the system like, super exchange (SE), double exchange (DE), Dzyaloshinsky-Moriya interaction (DM interaction), $e_g - e_g$ coulombic interactions, electron-phonon interactions etc. [7–9]. In parent compounds $TMnO_3$ and $DMnO_3$, all Mn ions are in Mn^{3+} and Mn^{4+} states respectively. These parent compounds are governed by SE interaction resulting in AFM insulating phase. On doping with divalent alkaline earth ion in $TMnO_3$, there is a transition from AFM insulating phase to canted AFM phase, then to FM insulating phase and FM conducting phase depending on the ratio of Mn^{3+} and Mn^{4+} ions. Manganites depict principal magnetic and electronic properties across the temperature and composition range. So the phase diagrams of manganites are complex with various phases like AFM insulating, canted AFM, FM insulating, FM metallic, PM, CO, OO etc. These phases are very sensitive to external pressure and magnetic field. Further research in manganites shows that these are complicated systems exhibiting strong correlations between electron, spin, lattice and orbital degrees of freedom.

It is also found that some of the above properties are suppressed when the size of these particles are reduced to nano-scale. For example the CO phase has been observed to suppress/completely disappear depending on the size of the particle [10–12]. Electron-hole asymmetry has also been seen to disappear in nanomanganites [13, 14]. Phase complexities, seen in the bulk [14] particles are observed to disappear. These nanomanganites also display other properties which are not seen in their bulk counterpart, like ferromagnetism, superparamagnetism, exchange-bias, spin-glass state etc. [15]. In nanomanganites, researchers have come up with various theories to explain the properties exhibited by them. Among these core-shell model is generally believed to be most applicable [16].

Our main objective in this thesis was to perform EPR/FMR studies on certain doped rare-earth manganites, in polycrystalline bulk and nano form. In this we study different manganite systems exhibiting unique and interesting properties at certain doping level and try understanding them by performing temperature dependent EPR measurements. These studies are supplemented by DC magnetization studies to characterize the magnetic states of the samples. The thesis is organized into chapters as follows.

Chapter 1

The first chapter contains a brief introduction to the physics of manganites. We explain the crystal and electronic structure of perovskite manganites, different interactions and phenomena they undergo. We also briefly introduce nanomanganites and double perovskite manganites. The chapter also describes the technique of EPR in detail. It describes different EPR parameters and how they enable us to study various phenomena taking place in manganite systems. Further we discuss FMR studies and how FMR enables us to study magnetocrystalline anisotropy in polycrystalline samples. Along with EPR, other techniques which are used for our sample analysis are also discussed.

Chapter 2

The second chapter explores MA in bulk and nanoparticles of $La_{0.85}Sr_{0.15}MnO_3$ (LSMO15) and $La_{0.875}Sr_{0.125}MnO_3$ (LSMO125) via temperature dependent FMR studies. Both bulk and nano LSMO15 samples prepared by us crystallize in rhombohedral crystal structure. Phase diagram of LSMO15 shows that it crystallizes in orthorhombic structure [17]; work done on this composition and other nearby compositions show that it can also crystallize in rhombohedral form [15, 18, 19] depending on the synthesis method and annealing temperature. This is the only composition where the cooperative JT effect takes place below T_c , whereas in other close compositions it takes place above T_c [17]. We observed that at low temperatures the two samples show negative uniaxial anisotropy signals, as the temperature increases there is a switch in MA from negative to positive. This takes place at ~ 200 K for the bulk and at ~ 235 K for the nano LSMO15 sample, much below their T_c at ~ 240 K for the bulk and ~ 280 K for the nano sample. The switch in bulk sample is observed at the temperature where there is a cooperative JT transition according to the phase diagrams. To check if this phenomenon is observed only in LSMO15, we prepared and studied $La_{0.875}Sr_{0.125}MnO_3$ (LSMO125) bulk and nano samples. In here, the nanoparticles crystallize in rhombohedral structure and the bulk crystallizes in orthorhombic structure. These are consistent with earlier reports [19]. FMR measurements show that the nanosamples display negative uniaxial anisotropy signals at low temperatures and show a switch from negative to positive at ~ 240 K, which is below its T_c at ~ 250 K. The bulk sample shows rhombic anisotropy signals and does not show switch in anisotropy. Based on the fact that in bulk LSMO15, the reversal of the sign of MA occurs at the JT transition, we infer that even in the two nano samples, the observed switching temperatures coincide with their respective JT transition temperatures. In conclusion bulk and nano LSMO15 samples and LSMO125 nano sample, all of which crystallize in rhombohedral structure show a switch in MA, at the temperature where the cooperative JT transition takes place. However bulk LSMO15 crystallizes in orthorhombic structure and does not show switch in MA. The results on nano LSMO125 point towards an interesting crossover of T_c above the T_{JT} whereas in

the bulk sample of LSMO125 T_{JT} lies above T_c .

Chapter 3

Chapter 3 investigates the effect of size reduction to nanoscale on the electron-hole asymmetry observed in the bulk samples of $Nd_{0.6}Ca_{0.4}MnO_3$ (NCMOH) and $Nd_{0.4}Ca_{0.6}MnO_3$ (NCMOE). The magnetization measurements done on these samples show that the bulk NCMOH undergoes a CO transition at ~ 250 K, AFM transition at ~ 150 K and canted AFM phase/mixed phase transition at ~ 80 K. Bulk NCMOE undergoes a CO transition at ~ 280 K, thus showing an electron-hole asymmetry between the two systems. The nanoparticles of NCMOH and NCMOE behave similar to each other by undergoing only a single FM transition at ~ 100 K, indicating the vanishing of the electron-hole asymmetry in nano samples. Further EPR measurements done on these samples support the behavior seen in the magnetization measurements. Temperature dependent g-value plot has been demonstrated to be a very useful tool in understanding electron-hole asymmetry [6, 13]. The g-value plot for our samples show that there is a huge difference in the g-value behavior throughout the temperature for bulk samples and this difference decreases significantly for nanosamples, there by providing the proof for the vanishing of electron-hole asymmetry in nano samples. Also the complexity seen in the phase diagram of bulk samples is seen to have disappeared in the nano samples.

Chapter 4

Chapter 4 studies the effect of 10% of ‘Cr’ substitution in $Bi_{0.5}Sr_{0.5}MnO_3$ bulk sample. $Bi_{0.5}Sr_{0.5}MnO_3$ undergoes a CO transition at ~ 525 K and T_N at ~ 110 K [20]. It was found that, CO and AFM phases are unaffected by the size reduction of $Bi_{0.5}Sr_{0.5}MnO_3$ sample [21]. Another way of suppressing CO phase is by substituting ‘Cr’ in the ‘Mn’ site [22, 23]. Here we study $Bi_{0.5}Sr_{0.5}Mn_{0.9}Cr_{0.1}O_3$ (BSMCO) composition. Magnetization measurements show that the sample undergoes FM transition at ~ 50 K and is in

PM phase till 400 K. Field cooled M vs. H curve shows that exchange bias is absent in the sample. But the magnetization curve does not saturate even up to 5 T field, this could be due to the existence of PM/AFM phase along with FM phase. EPR measurements show that the signals are symmetric and can fit to a broad Lorentzian lineshape till 80 K from RT. Intensity plot obtained after fitting shows that the sample undergoes an FM transition at around ~ 80 K, indicating the presence of FM clusters above 50 K, which is the magnetization T_c . Both magnetization and EPR measurements do not give any indication of existence/disappearance of AFM phase.

Chapter 5

Chapter 5 deals with magnetization and EPR properties of bulk and nanoparticles of the colossal magnetodielectric La_2NiMnO_6 (LNMO). Nanoparticles of two different sizes were prepared. The nanoparticles of first set were of ~ 17 nm in size (LNMO600) and the other were of ~ 90 nm in size (LNMO800). The bulk is prepared by sintering the nano sample at high temperature. M vs. T measurement done on the LNMO600 sample shows that the sample undergoes FM transition at ~ 160 K; this is according to dM/dT curve. However the onset of T_c for the sample is at ~ 250 K. Bulk LNMO and LNMO800 samples show similar magnetization behavior as both the samples undergo FM transition at ~ 270 K. The EPR measurements done on the samples show that, LNMO600 sample signals are characteristic of uniaxial anisotropy in the FM region. In contrast LNMO800 sample signals are very different from that of LNMO600 sample, and similar to that of bulk LNMO sample. These FMR signals are characteristic of rhombic anisotropy.

Chapter 6

In the sixth and the final chapter, we summarize the main results of the thesis and indicate scope for possible future research work.