The complex interaction between spin, charge, orbital and phase separation degree of freedom and their roles on magnetic state and phase transition behavior of doped rare-earth perovskite manganites ($R_{1-x}A_xMnO_3$; R = rare-earth trivalent cations and A = divalent alkaline earth cations) have made them very fascinating for researchers from several decades.[1-4] Recently, crystallite size and Mn-site doping have been shown to be two other important factors which can affect the magnetic state and phase transition behaviors of these manganites[5,6]. It is currently reported in doped rare-earth manganites that when the particle size is reduced to nanoscale, the low-temperature charge and orbitally ordered insulating phase is destabilized with suppression of charge ordering transition and stabilization of high-temperature ferromagnetic metallic state.[7,8] From last few years researchers are more attracted towards working on the Mn-site doped manganites systems. Ganguly et al. studied effects of substitution of chromium and ruthenium for manganese on the magnetic and transport properties of electron-doped manganite $Ca_{0.9}Ce_{0.1}MnO_3$, with d_z^2 orbital-order and the associated antiferromagnetic (AFM) characters.[9] They reported that the substitution of chromium and ruthenium suppresses AFM transition. Dho et al. also studied effect of chromium doping on magnetic properties of $La_{0.46}Sr_{0.54}Mn_{1-x}Cr_xO_3$ ($0 \leq x \leq 0.08$) and found that FM to AFM transition vanished for x = 0.08 due to appearance of FM double-exchange interaction between Mn^{3+} and Cr^{3+} ions.[10] The effect of non-magnetic Ti^{4+}-ions on structure, magnetic and transport behaviors of $La_{0.7}Sr_{0.3}Mn_{1-x}Ti_xO_3$ ($0 \leq x \leq 0.5$;

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LSMTO) films prepared by chemical solution deposition was studied by Zhu et al.[11] They found that lattice constant increases with increasing Ti^{4+} concentrations up to x = 0.3 due to replacement of Mn^{4+}-ions (0.530 Å) by Ti^{4+}-ions (0.605 Å) and after that it starts decreasing due to substitution of Mn^{3+}-ions (0.645 Å) by Ti^{4+}-ions (0.605 Å) in the lattice. The magnetic study of LSMTO shows that FM component decreases and AFM contribution increases with enhancing Ti-doping concentration. Magnetoresistance (MR) study reveals that MR increases near Curie-temperature on the increase of Ti^{4+} concentration at Mn-site. The importance of the doping of Ti^{4+}-ion at Mn-site is that its ionic radius (0.605 Å) lies between the radii of Mn^{4+}-ion (0.530 Å) and Mn^{3+}-ion (0.645 Å) and non-magnetic behavior. So, Ti^{4+}-ions can replace Mn^{4+}-ions as well as Mn^{3+}-ions present in the mixed-valence manganites without disturbing crystal structure of the host system. The non-magnetic nature of the Ti^{4+}-ion doesn't affect the magnetic properties directly of the parent system.[11-14] Further, there are several other perovskite manganite systems on which researchers are working at Mn-site doping and studied different properties, such as $TbMn_{1-x}(Co;Fe)_xO_3$ (x = 0.1 and 0.2)[15], $Gd_{0.7}Sr_{0.3}Mn_{1-x}Ti_xO_3$ (x = 0, 0.1 and 0.15)[16], $La_{0.7}Sr_{0.3}Mn_{1-x}Ni_xO_3$ (x = 0.0-0.1)[17], $La_{0.7}Ca_{0.3}Mn_{0.8}Cr_{0.2}O_3$[18], $Nd_{0.67}Sr_{0.33}Mn_{1-x}(Cr; Fe; Co)_xO_3$[19], $Nd_{0.67}Ba_{0.33}Mn_{1-x}(Fe; Cu)_xO_3$[21], etc.

11. X.B. Zhu, Y.P. Sun, R. Ang, B.C. Zhao and W.H. Song; J. Phys. D: Appl. Phys. ***39****, 625-630 (2006); 12. A. Gasmi, M. Boudard, S. Zemni, F. Hippert and M. Oumezzine; J. Phys. D: Appl. Phys.* ***42****, 225408-225414 (2009); 13. V. Dayal, V.P. Kumar, R.L. Hadimani and D.C. Jiles; J. Appl. Phys.* ***115****, 17E111-17E113 (2014); 14. D. Kumar and A.K. Singh, J. Magn. Magn. Mater.* ***469****, 264-273 (2019); 15. A. Das, S. De, S. Bandyopadhyay, S. Chatterjee, D. Das; J. Alloys Compd.* ***778****, 839-847 (2019); 16. A. Anand, R.K. Veena, M. Manjuladevi, V.S. Veena, Y.S. Koshkidko, S. Sagar; J. Magn. Magn. Mater.* ***471****, 537-543 (2019); 17. T.D. Thanh, P.D.H. Yen, K.X. Hau, N.T. Dung, L.V. Nhan, L.T. Huong, L.V. Bau, L.T.A. Thu, B.T. Cong, N.X. Nghia, L.H. Khiem and S.C. Yu; J. Electro. Mater.* ***48****, 1353-1362 (2019); 18. N.D. Sharma, A. Mahajan, M.K. Verma, N. Choudhary, S. Sharma and D. Singh; Ionics* ***25****, 1271-1279 (2019); 19. B. Arun, M.V. Suneesh, B. Sudakshina, V.R. Akshay, K.D. Chandrasekhar and M. Vasundhara; J. Phys. Chem. Solids* ***123****, 327-335 (2018); 20. P. Thamilmaran, M. Arunachalam, S. Sankarrajan, K. Sakthipandi, E. James J. Samuel and M. Sivabharathy; J. Magn. Magn. Mater. 443, 29-35 (2017); 21. B. Sudakshina, B. Arun, K.D. Chandrasekhar, H.D. Yang and M. Vasundhara; Physica B: Condens. Matter* ***539****, 14-20 (2018).*

In view of the above, we selected to investigate the "Structural and Magnetic Phase Transitions Studies on Ti-doped $R_{1-y}Ba_yMn_{1-x}Ti_xO_3$ (R = La, Nd) Perovskite Manganites for the Ph.D. thesis. Our detailed investigations on these materials have resulted in several new important findings not reported by earlier authors. The important findings resulting from the present thesis work is briefly described below:

Important Findings of the Present Work:

(i) Evolution of Structure and Magnetic Properties of Ti-doped $Nd_{0.7}Ba_{0.3}Mn_{1-x}Ti_xO_3$ ($0 \leq x \leq 0.30$) Manganites

The phase pure $Nd_{0.7}Ba_{0.3}Mn_{1-x}Ti_xO_3$ perovskites manganites with nominal compositions ($0 \leq x \leq 0.30$) were synthesized by combustion synthesis method followed by the calcination at 1200°C for 6 hrs. The effect of doping of Ti^{4+}-ion on structural and magnetic behaviours of these samples were examined by X-ray diffraction, scanning electron microscopy, energy dispersive X-ray spectroscopy, and magnetization measurements as a function of temperature and magnetic field. The Rietveld analysis of XRD data reveals that the manganites with compositions $x < 0.30$, crystallized into single phase orthorhombic structure with *Imma* space group, while, for the composition with x = 0.30 two phases of tetragonal structure with *I*4/*mcm* and *P*4*mm* space groups coexist. This shows a structural phase transition from orthorhombic structure to tetragonal structure in the vicinity of the composition $x \sim 0.3$. The unit cell volume for *Imma* space group increases from 235.10(5) $Å^3$ for x = 0 to 238.51(4) $Å^3$ for x = 0.25 with increasing doping concentration of Ti^{4+}-ion due to replacement of Mn^{4+}-ions by Ti^{4+}-ions. The temperature dependent magnetization measurement reveals that all samples exhibit PM to FM phase transition at Curie-temperature T_C. The value of T_C reduces exponentially from 140 K for x = 0 to 39 K for x = 0.30 with increasing doping content of Ti^{4+}-ion. The magnetic saturation is not reached even after the application of

a magnetic field up to 60 kOe which can be related to a threshold in the diminution of Mn^{4+}/Mn^{3+} ratio. The decrease in T_C with Ti^{4+} doping is connected with the weakening of double exchange FM interaction and strengthening of the superexchange AFM interaction resulting due to the reduction of the Mn^{4+}/Mn^{3+} ratio. The field dependent magnetization M(H) shows the co-existence of two magnetic ordering FM and AFM. The bifurcation between ZFC and FC magnetization measurements indicates the possible existence of a spin glass cluster. Analysis of the isothermal M^2 vs. H/M Arrott's plots exhibits that all samples show first order magnetic transition irrespective of Ti-doping. Temperature-dependent ac-susceptibility measurement confirms the spin glass cluster nature. The ac-susceptibility measurements study reveals that on Ti-doping systems undergo from one type of spin glass character to a different kind of spin glass nature.

(ii) Investigation of Structural, Magnetic and Dielectric Properties of $Nd_{0.7}Ba_{0.3}Mn_{1-x}Ti_xO_3$ (x = 0.40 and 0.50) Manganites

The polycrystalline samples of $Nd_{0.7}Ba_{0.3}Mn_{1-x}Ti_xO_3$ (x = 0.40 and 0.50) perovskite manganites have been synthesized using auto-combustion method. The structural, magnetic and dielectric properties of these manganites were investigated in detail using X-ray diffraction, magnetic measurements, and impedance measurements, respectively. HR-SEM and EDS were used to study microstructures and elemental compositions. Analysis of the HR-SEM micrographs reveals that the samples with x = 0.40 and 0.50 exhibit microflakes and microrods in microstructures, respectively. The Rietveld structure refinement using X-ray diffraction patterns confirms the coexistence of two crystallographic phases of tetragonal structures with *I*4/*mcm* and *P*4*mm* space groups, in both the compositions. The temperature dependent magnetization measurement reveals that these samples exhibit paramagnetic to ferromagnetic phase

transition at characteristic Curie temperature (T_C). The value of T_C reduces with increasing doping level of Ti^{4+}-ions as a result of deteriorating double exchange interaction. The zero field cooled, and field cooled magnetization plots at lower temperatures deviate from each other. The significant difference between these curves shows the possibility of the existence of non-equilibrium spin-glass cluster behavior in these manganites. The non-equilibrium low-temperature behavior of the samples was investigated using ac-susceptibility measurements. The ac-susceptibility data analysis reveals that these samples are not showing conventional spin glass behavior but they are exhibiting reentrant spin glass (RSG) state. The field dependent magnetization measurements show the coexistence of ferromagnetic and antiferromagnetic components for both the systems. The impedance spectroscopy measurements reveals that the resistivity of the manganites increases and dielectric loss decreases with increasing Ti^{4+}-ions concentration and they display very high dielectric constant of the order of 10^5.

(iii) Size-dependent Structural and Magnetic Properties of $Nd_{0.7}Ba_{0.3}Mn_{1-x}Ti_xO_3$ (x = 0.10) Manganites

Pure perovskite phase nanocrystalline samples of 10 mol% Ti-doped $Nd_{0.7}Ba_{0.3}MnO_3$ manganites have been successfully prepared by the auto-combustion method following calcination at 800 (C8), 900 (C9), 1000 (C10), 1100 (C11) and 1300°C (C13). The Rietveld structure refinement of the XRD data confirms that the synthesized samples with different crystallite sizes have orthorhombic crystal structure with *Imma* space group. The values of crystallite size and particle size increase with increasing calcination temperature. However, the value of lattice strain decreases with rising calcination temperature. The unit cell volume of the samples expanded with increasing calcination temperature and enhancement in particle size. All the

nanocrystalline samples of $Nd_{0.7}Ba_{0.3}Mn_{0.9}Ti_{0.1}O_3$ perovskite exhibit PM to FM phase transition at characteristic Curie temperature T_C, which shows a maximum value of 106 K for the sample C10. All the samples exhibit greater experimental effective paramagnetic moment than the theoretical value, which may be due to the existence of short-range FM ordering within the PM state. Each sample contains FM and AFM components in the low-temperature region (10 K) in which the sample C10 has a maximum percentage of FM and minimum percentage of AFM components. Shift in the field cooled magnetic hysteresis loops reveals the exchange bias effect however this effect is very small. The study of frequency dependence of magnetic ac susceptibility reveals that all the samples are exhibiting metallic spin-glass. The Rietveld structure refinement of the XRD patterns at high temperatures of bulk sample reveals no structural phase transition.

(iv) Quenching of Spin-Orbital Coupling in $La_{0.6}Ba_{0.4}MnO_3$ Mixed-valence Manganite

The nano and bulk samples of LBMO-40 manganite were synthesized via combustion synthesis process. The Rietveld refinement of the XRD patterns for nano and bulk samples of LBMO-40 reveals that LBMO-40 crystallizes into cubic crystal structure having $Pm\bar{3}m$ space group. The refined lattice parameter "a" and unit cell volume "V" decrease with increasing particle size from a = 3.9120(2) Å and V = 59.869(4) $Å^3$ for nano sample to a = 3.9097(1) Å and V = 59.764(1) $Å^3$ for bulk sample. Temperature dependent magnetization M(T) measurements for nano and bulk samples clearly demonstrates paramagnetic to ferromagnetic phase transition at Curie temperature T_C, which decreases with decreasing particles size from 330 K for bulk to 315 K for nano. A signature of Griffiths phase singularity is observed in nano sample. The percentage of FM fraction within the sample increases with increasing particle size

(from nano to bulk) and decreasing measurement temperature (from RT to 10 K). Spontaneous magnetization M_0 of the ferromagnetic sample increases with lowering temperature (from RT to 10 K) and increasing crystallite size (from nano to bulk). A spin-orbital coupling was observed in the bulk sample of LBMO-40 manganite at low temperature (10 K), however, the nano sample does not exhibit spin-orbital coupling. Thus, the spin-orbital coupling is quenched by reducing particle size of the LBMO-40 manganite. According to the Banerjee's criterion, analysis of the Arrott's plots reveals that nano and bulk samples exhibit first and second order magnetic phase transition in the low magnetic field region, respectively. The behavior of the $\chi'(T)$ curves for nano and bulk samples are similar to their respective M_{ZFC} curves.

(v) Effect of Ti-doping on Structural and Magnetic Properties of $La_{0.6}Ba_{0.4}Mn_{1-x}Ti_xO_3$ ($0.02 \leq x \leq 0.08$) Manganites

We have investigated the effect of non-magnetic Ti^{4+}-ions doping on structural and magnetic properties of $La_{0.6}Ba_{0.4}Mn_{1-x}Ti_xO_3$ ($0.02 \leq x \leq 0.08$) bulk manganites. The Rietveld refinement of the X-ray diffraction data reveals that all the samples crystallize into the cubic structure with $Pm\bar{3}m$ space group. The lattice parameter of the unit cell increases exponentially with doping content which reveals that Ti^{4+}-ions substitute Mn^{4+}-ions in the lattice. Analysis of the SEM micrographs shows that the particle size of the samples increases with increasing Ti^{4+}-ions concentration. The magnetic properties measurements reveal that these samples undergo PM to FM phase transition at T_C. The value of T_C decreases exponentially with Ti-doping from 309 K for x = 0.02 to 212 K for x = 0.08. The experimental value of effective paramagnetic moment calculated from the slope of inverse susceptibility increases exponentially from 6.10 μ_B for x = 0.02 to 6.52 μ_B for x = 0.08, while theoretical value decreases from 4.48 μ_B for x = 0.02 to 4.38 μ_B for x = 0.08. Deviation of inverse susceptibility from Curie-Weiss law

on lower temperature side for the sample with x = 0.08 reveals the signature of the Griffiths phase. The singularity of the dc inverse susceptibility in Griffiths phase region provides the numerical values of Griffiths temperature (T_G), the critical temperature for random ferromagnet (T_C^R) and the exponent (λ_{GP}) as 325 K, 245 K and 0.95(1), respectively. The irreversibility between zero field cooled, and field cooled magnetization may be due to spin glass behavior of the samples present due to the inhomogeneity of magnetic ordering. The experimental value of the saturation moment at 10 K is larger than the theoretical value of saturation moment which indicates the signature of spin-orbital coupling in low-temperature region. However, the spin-orbital coupling can be quenched by reducing particle size in the nanometer range. Application of Banerjee's criterion and the analysis of the isothermal Arrott's plots (M^2 vs. H/M) confirm that all samples exhibit first order magnetic transition. The temperature and frequency dependent ac susceptibility measurements show several anomalies and needs to be understood properly.

Organization of the Thesis:

Chapter I describes an introduction to some fundamental concepts related to the mixed-valence perovskite manganites. A concise review of the existing literature on the structural and magnetic properties of mixed-valence perovskite manganites is discussed. The effects of magnetic and non-magnetic ions doping at Mn-site on their physical properties have also described.

Chapter II presents the details of the combustion method and procedures for the synthesis of pure phase $R_{1-y}Ba_yMn_{1-x}Ti_xO_3$ (R = La and Nd) perovskite manganites. It also describes experimental techniques used for characterizing the prepared samples.

Chapter III describes the results of our studies of the effects of Ti-doping on structural and magnetic properties of $Nd_{0.7}Ba_{0.3}Mn_{1-x}Ti_xO_3$ $(0 \leq x \leq 0.30)$ perovskite manganites.

Chapter IV presents the results of our investigations on structural, magnetic and dielectric behaviors of $Nd_{0.7}Ba_{0.3}Mn_{1-x}Ti_xO_3$ (x = 0.40 and 0.50) perovskite manganites.

Chapter V describes the results of our particle size and temperature dependent investigations on structural and magnetic properties of $Nd_{0.7}Ba_{0.3}Mn_{1-x}Ti_xO_3$ (x = 0.10) perovskite manganite.

Chapter VI presents the results of our investigations on structural and magnetic behaviors of $La_{0.6}Ba_{0.4}MnO_3$ perovskite manganite as a function of particles size.

Chapter VII describes the results of our investigation on the effect of Ti-doping on structural and magnetic properties of $La_{0.6}Ba_{0.4}Mn_{1-x}Ti_xO_3$ ($0.02 \leq x \leq 0.08$) perovskite manganites.

Chapter VIII summarizes the main findings of the present work and lists a few suggestions for the future investigations.