Preface

Complex interplay between spin, charge, phase separation and orbital degrees of freedom and their role on magnetic state and phase transition behavior of doped rare earth perovskite manganites have made them very fascinating for researchers from several decades[1-4]. Recently crystallite size and hydrostatic pressure have been shown to be two other important factors which can affect the magnetic state and phase transition behavior of these manganites. It is recently reported in several doped rare earth perovskite manganites that when the particle size is reduced to nanoscale, the low temperature charge and orbitally ordered insulating state is destabilized, with suppression of charge ordering transition and stabilization of high temperature ferromagnetic metallic state down to low temperatures[5-8]. In case of $La_{0.5}Ca_{0.5}MnO_3$ [LCMO] it is reported that the charge ordered state is completely absent when the particle size is less than 40 nm[9]. The suppression of charge ordering transition is reported in nanocrystalline form of several other half doped manganites also such as $Pr_{0.5}Ca_{0.5}MnO_3$ [PCMO][10], $Nd_{0.5}Ca_{0.5}MnO_3$ [NCMO][11], $Nd_{0.5}Sr_{0.5}MnO_3$ [NSMO][12], $Pr_{0.5}Sr_{0.5}MnO_3$ [PSMO][13] etc. There is no unanimity on the origin of suppression of this charge ordering transition in half doped rare earth manganites and different authors have made different propositions like core-shell structure, effective excess pressure due to small size of the samples etc. The reason for suppression of charge ordering transition in nanocrystalline form is reported variously by different authors[14–16]. In LCMO and PCMO it is reported that charge ordering transition is suppressed due to the enhanced surface disorder in

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the nano size samples[14, 15]. Similarly in NCMO it is reported that antiferromagnetic phases disappear in the nanoparticles making way for an emergence of ferromagnetic metallic phase[13]. The actual reason of the absence of charge ordering transition in nanocrystalline form of these manganites and origin of FM state is still a controversial issue and matter of great debate.

Further, there are contradictory reports about the effects of particle size reduction on the unit cell volume of the manganites. Since the unit cell volume and orthorhombic strain[10] have great impact on the magnetic state of the doped rare earth perovskite manganites there is a need to unambiguously ascertain the effect of particle size on the unit cell volume. There are some papers which report the lowering of unit cell volume with decreasing particle size in $La_{0.5}Ca_{0.5}MnO_3$[13, 17], $Pr_{0.5}Ca_{0.5}MnO_3$[17 18], while several authors have reported the enhancement of the unit cell volume with decreasing particle size[18-20]. Many authors have reported that there is no significant change in the unit cell volume by changing the particle size in nanocrystalline manganites[6, 18]. Thus the effect of particle size reduction on the unit cell volume of nanocrystalline manganites needs to be settled to arrive at the actual reason of suppression of charge ordering transition. In view of the forgoing we have investigated in detail crystal crystal structure, phase coexistence and phase transitions in several nanocrystalline half doped perovskite manganites to settle these outstanding issues.

The important findings resulting from this Ph. D. work are listed below:

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In the present thesis we have investigated the changes in structure, phase transition and magnetic behavior of nanocrystalline materials as a function of crystallite size. Our detailed investigations on these materials have resulted in several new important findings not reported earlier. The important results obtained by us are listed below.

(i) Origin of Suppression of Charge Ordering Transition in Nanocrystalline $Ln_{0.5}Ca_{0.5}MnO_3$ (Ln=La, Nd, Pr) Ceramics:

The bulk and nanocrystalline samples of half doped, rare earth, perovskite manganites, $Ln_{0.5}Ca_{0.5}MnO_3$ (Ln=La, Nd, Pr) were investigated by x-ray diffraction and magnetic measurements at various temperatures to understand the origin of suppression of charge ordering transitions in nanocrystalline samples of these manganites. The controversial reports regarding the effect of crystallite size reduction on the unit cell volume has been resolved by studying these three manganites prepared by combustion synthesis method. As reported by earlier authors also, reduction of the particle size to nanocrystalline range leads to suppression of charge ordering transition and stabilization of ferromagnetic phase at low temperatures. The unit cell volume is found to systematically increase for all the three manganites with decreasing particle size, which results in increased e_g electron bandwidth and is responsible for suppression of charge ordering transition. Even through the crystal structure of both bulk and nanocrystalline samples is orthorhombic with space group *Pnma*, crystallite size reduction into nanocrystalline form affects the orthorhombic strain, lattice parameter, atomic coordinates and unit cell volume. A comparative study for the $La_{0.5}Ca_{0.5}MnO_3$ samples prepared by sol-gel route is also presented to show that the reduction of the unit cell volume with decreasing crystallite size is linked with non-stoichiometry of the samples, which can also lead to the suppression of the charge ordering transition and stabilization of ferromagnetic state in nanocrystalline form reported by some earlier authors. The role of inherent anisotropic strain in nanocrystalline samples on the magnetic state and phase transitions is also investigated.

(ii) Emergence of a new modulated phase and Ferromagnetism in nanocrystalline $Nd_{0.5}Sr_{0.5}MnO_3$ ceramic:

In $Nd_{0.5}Sr_{0.5}MnO_3$ ceramic, we report the emergence of a crystallographically modulated phase alongwith the ferromagnetic character in nanocrystalline samples. The Rietveld analysis of the powder x-ray diffraction data reveals that the structure of nanocrystalline $Nd_{0.5}Sr_{0.5}MnO_3$ ceramic can be described as a modulated phase in monoclinic structure with space group (*Pm*) which corresponds to doubled orthorhombic 'a_o' parameter and three times orthorhombic 'c_o' parameter for the structure of bulk sample at room temperature. The modulated monoclinic phase in nanocrystalline $Nd_{0.5}Sr_{0.5}MnO_3$ sample discussed by us is completely new and not known earlier for perovskite manganites. Increasing crystallite size converts the modulated monoclinic structure to orthorhombic structure with *Imma* space group as reported for bulk $Nd_{0.5}Sr_{0.5}MnO_3$ sample. The magnetic measurements on nanocrystalline samples reveal ferromagnetic behaviour and absence of charge ordering transition down to low temperatures. The nanocrystalline samples also exhibit Griffith phase like behaviour around the paramagnetic to ferromagnetic phase transition. In contrast, the bulk sample exhibits transition to monoclinic phase in the $P2_1/m$ space group at lower temperatures and the coexistence of the orthorhombic and monoclinic phases are observed in wide temperature range, as reported by earlier authors.

(iii) Emergence of two new modulated phases and Suppression of charge ordering transition in nanocrystalline $Sm_{0.5}Ca_{0.5}MnO_3$ ceramic:

We have studied the stability of various crystallographic phases with reduction of crystallite size in nanocrystalline $Sm_{0.5}Ca_{0.5}MnO_3$. The orthorhombic structure with space group *Pnma* for the bulk sample transform into coexistence of orthorhombic *Pnma* and monoclinic space group $P2_1/m$ phases with reduction of particle size. Further reduction of crystallite size leads to appearance of a new modulated monoclinic phase with space group Pm having lattice parameters ($2a_o$, b_o, $3c_o$). This again transforms to another modulated monoclinic phase with space group *Pm* having lattice parameters

($5a_o$, b_o, $2c_o$) at further lower crystallite size where a_o, b_o, c_o are lattice parameters for orthorhombic phase of bulk sample. The suppression charge ordering is also observed in the nanocrystalline samples. The Neel temperature vanishes with reduction of particle size bellow ~ 20 nm. Only ferromagnetic phase is found to be present in nano samples with particle size ~ 20 nm and the antiferromagnetic phase transition completely disappears.

These important results are presented in the six chapters of the thesis as summarized below:

Chapter I gives an introduction to some fundamental concepts related to the mixed valence perovskite manganites. A brief review of the existing literature on structure and magnetic behavior of mixed valence perovskite manganites is also presented.

Chapter II describes the details of the sample preparation for pure perovskite phase of nanocrystalline $R_{0.5}A_{0.5}MnO_3$ (R = La, Nd, Sm, Pr and A = Ca, Sr) ceramics.

Chapter III presents the results of our investigation regarding origin of suppression of charge ordering transition in nanocrystalline $Ln_{0.5}Ca_{0.5}MnO_3$ (Ln=La, Nd, Pr) ceramics along with the evolution of crystal structure and magnetic behavior in these samples.

Chapter IV describes the results of our discovery of emergence of a new modulated phase and ferromagnetism in nanocrystalline $Nd_{0.5}Sr_{0.5}MnO_3$ ceramic.

Chapter V presents the results of our investigation on the emergence of two new modulated phases and suppression of charge ordering transition in nanocrystalline $Sm_{0.5}Ca_{0.5}MnO_3$ ceramics.

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