Chapter: VI

Summary of the Present Work and Suggestions for Future Work

Chapter-VI

6.1 Summary of the Present Work

In the present thesis work, crystal structure, phase transition and physical properties of nanocrystalline $R_{0.5}A_{0.5}MnO_3$ (R = La, Nd, Sm and A = Ca, Sr) perovskites have been investigated. The samples were synthesized by chemical combustion and sol-gel methods. The phase purity and crystal structures were characterized by using x-ray powder diffraction in conjugation with Rietveld crystal structure refinement. Microstructure was characterized by scanning electron microscopy and transmission electron microscopy. X-ray photoelectron spectroscopy measurement was carried out to ascertain compositional ratios of Mn^{3+} and Mn^{4+} ions. Nature of phase transitions was investigated by temperature dependent magnetic and x-ray diffraction measurements on samples of different crystallite sizes. M-H measurements were carried out to determine the magnetic state of the samples and verify the suppression of charge ordering transition in nano samples.

The important findings of the present research work are listed below:

(1) We have investigated the origin of suppression of charge ordering transition in nanocrystalline half doped rare earth perovskites manganites by studying crystal structure and magnetic properties of $La_{0.5}Ca_{0.5}MnO_3$, $Nd_{0.5}Ca_{0.5}MnO_3$ and $Pr_{0.5}Ca_{0.5}MnO_3$ samples of various crystallite sizes obtained by calcining at various temperatures. The unit cell volume is enhanced in all the three manganites by crystallite size reduction in the nanocrystalline form which is attributed to increase

e_g - electron bandwidth. Enhanced e_g -electron bandwidth leads to suppression of charge ordering transition and stabilization of ferromagnetic state down to low temperatures in nanocrystalline samples. The crystal structure is orthorhombic in *Pnma* space group for both bulk and nanocrystalline $La_{0.5}Ca_{0.5}MnO_3$, $Nd_{0.5}Ca_{0.5}MnO_3$ and $Pr_{0.5}Ca_{0.5}MnO_3$ samples but the lattice parameters and Mn-O bond lengths are significantly affected by crystallite size reduction in the nanocrystalline samples. A comparative study of sol-gel derived $La_{0.5}Ca_{0.5}MnO_3$, samples suggests that smaller unit cell volume of nanocrystalline samples than the bulk samples, reported by some authors, is linked with the non-stoichiometry of the samples which can also suppress the charge ordering transition and stabilize the ferromagnetic state in nanocrystalline form. The nanocrystalline samples have significant anisotropic strain which may also have significant role on the magnetic and phase transition behavior of these samples.

(2) We have studies structure and magnetic behaviour of bulk and nanocrystalline $Nd_{0.5}Sr_{0.5}MnO_3$ samples of various crystallite sizes. The nanocrystalline samples exhibit ferromagnetic behaviour and absence of charge ordering transition down to low temperatures. The Rietveld structural analysis of the nanocrystalline samples reveals that the structure can be described as a new modulated phase in monoclinic structure with space group (*Pm*) the unit cell of which corresponds to doubled orthorhombic 'a_o' parameter and three times orthorhombic 'c_o' parameter for the structure of bulk sample at room temperature. We have discovered this new modulated phase in $Nd_{0.5}Sr_{0.5}MnO_3$ for the first time. The samples calcined at temperatures $\geq$1000 ^{O}C with bigger crystallite sizes exhibit bulk behaviour and

orthorhombic structure with *Imma* space group. The nanocrystalline samples exhibit Griffith phase like behaviour also, around the paramagnetic to ferromagnetic phase transition. The bulk samples exhibits transition from room temperature orthorhombic *Imma* to monoclinic structure in the $P2_1/m$ space group at lower temperatures. For bulk samples coexistence of the orthorhombic and monoclinic phases are observed in wide temperature range around phase transition below room temperature.

(3) We have investigated 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 the lattice parameters for orthorhombic phase of the bulk sample. The suppression of charge ordering transition is also observed in the nanocrystalline samples.

6.2 Suggestions for Future Work

1. High resolution neutron and synchrotron powder diffraction measurements should be carried out to study the detailed structure of new modulated phases in nanocrystalline $Nd_{0.5}Sr_{0.5}MnO_3$ and $Sm_{0.5}Ca_{0.5}MnO_3$ ceramics.

2. Atomic pair distribution function (PDF) analysis should be carried out to understand the structural details of new modulated phases in nanocrystalline $Nd_{0.5}Sr_{0.5}MnO_3$ and $Sm_{0.5}Ca_{0.5}MnO_3$ ceramics and also in other compositions.

3. First Principles density functional calculations should be carried out to understand the nature of new phases in nanocrystalline $Nd_{0.5}Sr_{0.5}MnO_3$ and $Sm_{0.5}Ca_{0.5}MnO_3$ ceramics and other compositions of these systems.

4. High Resolution Transmission Electron Microscopic studies of new modulated phases in $Nd_{0.5}Sr_{0.5}MnO_3$ and $Sm_{0.5}Ca_{0.5}MnO_3$ should be carried out to verify the modulations about various crystallographic axes.

5. Thin film nanocrystalline samples of these manganites under compressive and tensile strain should be investigated in future to understand the role of strain on the structure and magnetic behaviour of nano samples.