CHAPTER 6

General Conclusion

In conclusion, the entire work is devoted to magnetic and transport properties of strongly correlated interesting transition metal oxides. Since TMOs are the vast topic to investigate so we have focussed our work to investigate some aspects of few TMO systems. TMOs with pervoskite structure are given special emphasis. A large portion of the thesis is related to effect of size reduction in magnetic properties of the systems. As a consequence exchange bias effect in the nanoparticles of the systems has turned out to be a vital topic to investigate and explain the magnetic properties of the systems. From simple oxide (NiO, Cr$_2$O$_3$) to complex ferrite (La$_{1/3}$Sr$_{2/3}$FeO$_3$...
with different doping) have studied elaborately to explain their detail magnetic properties in nano form. Manganites are also a very important topic of TMOs with a rich diversity in physical properties. The systematic study of magnetic and transport properties of rare earth manganites with alkaline divalent alkaline earth (AE) elements doping at the rare-earth site (RE) with Sm_{0.5}A_{0.5}MnO_3 (A = Ca,Sr) are also a major part of this thesis. To ensure the magnetic interaction type and other detail magnetic properties we have done the critical analysis of the manganite single crystal Pr_{0.52}Sr_{0.48}MnO_3. Summary and conclusions of the results in nutshell is following:

**Evolution of exchange bias in different TMOs due to size effects**

1) NiO & Cr_2O_3 Detailed magnetic measurements were performed in the nanocrystalline NiO and Cr_2O_3 prepared by ball milling. Temperature variation of of ZFC magnetization shows absence of blocking temperature in case of Cr_2O_3 observed in case of NiO around 290 K. A sharp rise was seen in both zfc and fc magnetization, analogous to NiO. In M-H measurements, systematic shifts of the MH loops are convincingly observed for both the cases when the sample was cooled in a 10 kOe cooling field. In case of NiO nanoparticles large coercivity and small lead to larger H_E whiles for Cr_2O_3 small coercivity and large magnetization lead to smaller H_E. This exchange bias effect in Cr_2O_3 and NiO appears due to pinning mechanism at the interface between antiferromagnetic core and weak ferromagnetic components. The results suggest that magnetic behavior of both Cr_2O_3 and NiO is dominated by the ferromagnetic component consisting of uncompensated spins at the crystallite
2) La$_{1/3}$Sr$_{2/3}$FeO$_3$ (LSFO) is a well known charge ordered sample. Its charge ordering temperature ($T_{CO}$) is at 200 K. From M-T curve we see a broad peak around 65 K and a signature of $T_{CO}$ around 200 K for nano. The peak at 65 K which is absent at bulk. Emergence of peak for nano indicates the presence of two magnetic phase. In nanocrystalline LSFO we find suppress of charge ordering and a glassy magnetic behavior at low T. A strong exchange bias effect is observed at low temperature for the nanoparticles ($\approx$ 70 nm) which is absent for the bulk counterpart.

The phase coexistance in nanoparticles is further confirmed from polarized neutron measurements. Polarized neutron measurements show considerable broadening with reduced intensities, this indicates short-range charge and magnetic ordering involving wide distribution of grain size in the range of $\approx$ 40-100 nm. This short-range ordering process is not uniform for all planes. From refinement of neutron data, we get the magnetic moment of Fe$^{3+}$ and Fe$^{5+}$ as 3.15 $\mu_B$ and 1.57 $\mu_B$ respectively. These values reduce to 2.70 $\mu_B$ and 0.53 $\mu_B$ for Fe$^{3+}$ and Fe$^{5+}$, respectively for nano. Although CO between Fe$^{3+}$ and Fe$^{5+}$ has been tailored in nano specimen, analysis of Mössbauer spectrum confirms that spin state as well as ratio of Fe$^{3+}$ and Fe$^{5+}$ do not alter compared to the bulk counterpart. To interpret robust EB effect, these crucial results facilitate to propose a phenomenological model displaying possible phase separation scenario in nano specimen where AFM core and disordered glassy magnetic shell in the nanocrystalline compound. This magnetic phase separation leads to the huge exchange bias effect.
3) Detailed studies on magnetic properties were performed on a series of nanoparticles of La\textsubscript{1/3}Sr\textsubscript{2/3}Fe\textsubscript{1−x}Cr\textsubscript{x}O\textsubscript{3} (LSFCO) for x = 0, 0.02, 0.04 and 0.06 to observe the effect of minimal Cr doping in Fe site. Thermal variation of magnetization shows a glassy peak for all compositions. The CO peak is also present for all compositions except x = 0.06. In M-H a constricted double loop was observed for x = 0.02. Exchange bias is observed for the entire doping. The H\textsubscript{E} and M\textsubscript{E} decreases significantly for x = 0.02, 0.04 and 0.06. For x = 0.04 the EB effect emerges below T\textsubscript{CO}, increase sluggishly with lowering of temperature and below T\textsubscript{g}, it increases rapidly. The cooling field dependence exhibits significant increase of H\textsubscript{E} and M\textsubscript{E} for x = 0.04, which is associated with the considerable increase of coercivity. Exchange bias effect has been reduced due to Cr substitution in LSFO. The intricate magnetic phase coexistence consisting of destabilized and short range ordered AFM and FM components leads to a disordered glassy magnetic component at the particle surface and causes modified exchange bias effect in LSFCO.

**Collapse of charge ordering in Sm\textsubscript{1/2}Ca\textsubscript{1/2−x}Sr\textsubscript{x}MnO\textsubscript{3}**

In Sm\textsubscript{1/2}Ca\textsubscript{1/2−x}Sr\textsubscript{x}MnO\textsubscript{3} (x = 0, 1/6, 1/4, 1/3 and 1/2) we have doped Sr in Ca site to investigate the change in magnetic and transport properties in polycrystalline specimen. Sm\textsubscript{1/2}Ca\textsubscript{1/2}MnO\textsubscript{3} is a well known charge ordered sample with charge ordering temperature (T\textsubscript{CO}) ≈ 275 K and with T\textsubscript{CO} = 210 K for Sm\textsubscript{1/2}Sr\textsubscript{1/2}MnO\textsubscript{3}. All compounds belong to Pnma space group. The orthorhombic lattice distortion is larger for the compositions at x = 1/6, 1/4, and 1/3 than the end compositions at x = 0.
and 1/2. At 4 K a magnetic field-induced sharp transition to ferromagnetic metallic state and collapse of charge ordering are observed for \( x = 1/6, 1/4, \) and \( 1/3, \) which is absent up to 100 kOe for end compositions. The field induced transition depends on field sweep rate. The resistivity data showed that magnetoresistance was observed in all the samples except for \( x = 0. \) For intermediate doping we observed magnetic field hysteresis which is indicative of first order transition. MR-H data for \( x = 1/6, 1/4 \) and \( 1/3 \) are in accordance with M-H data. We observed 100% MR around same critical field, indicating the transformation from AFM insulating state to FM metallic state. Since the ionic radius of Sr is greater than the value of Ca, the Sr doping involves the increase of \( \langle r_A \rangle \) and enhances the overlapping of Mn-\( e_g \) and O-2p\( \sigma \) orbitals which results in destabilizing charge ordering and developing ferromagnetism.

**Critical analysis in \( \text{Pr}_{0.52}\text{Sr}_{0.48}\text{MnO}_3 \)**

In this study the critical behavior is investigated across Curie Temperature \( T_C \) in \( \text{Pr}_{0.52}\text{Sr}_{0.48}\text{MnO}_3 \) single crystal. The results emerged from the analysis of bulk magnetization studies point to the second order phase transition from paramagnetic to ferromagnetic (FM) long range ordering close to 275 K. Different techniques like Modified Arrot plot, Kouvel-Fisher plot, and critical isotherm analysis were used to obtain the proper value of critical exponents and finding of the precise the transition temperature. From all studies we found that the critical exponents \( \beta, \gamma \) and \( \delta \) do not follow any universality class. We note that the critical exponents obtained from different methods are close to each other. We have also checked the reliability of data by scaling
hypothesis. The critical constants $\beta$, $\gamma$ and $\delta$ change a bit while direction of magnetic field is applied $\parallel$ and $\perp$ to $\langle110\rangle$ plane. The value of $T_C$ changes considerably from 271.6 K to 273.5 K upon direction of applied magnetic field. To ensure the range of interaction and dimensionality of spin we have done rigorous calculation using renormalization group theory approach. From these results we observed that the direction dependent results are consistent with the long range magnetic interaction following 2D Heisenberg model as evident from renormalization group theory approach.