Synopsis

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Thesis Title: **Investigation of Microstructural, Electronic-Transport, Magneto-Transport and Magnetic Properties of Nanostructured Spintronic Colossal Magneto-Resistive Manganites.**

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In **chapter 1**, we have presented introductory discussion on basic research interest, several intriguing properties, and overview of physics of manganite systems. Brief discussions on literature survey, motivation behind our present dissertation work and finally organization of thesis have also been presented.

A number of different compounds having general formula $R_{1-x}A_xMnO_3$ ($0 \leq x \leq 1$, R = La^{3+}, Nd^{3+}, Pr^{3+}, Sm^{3+} etc., A = Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+} etc.), such as those derived from $RMnO_3$, have been undergoing a great research interest, enormous imagination and close scrutiny during last decade due to their Colossal Magneto-resistive (CMR) response to applied magnetic fields. This CMR effect and the correlated degrees of freedom of magnetic structure, crystallographic structure and electrical resistivity in CMR materials, in addition to being of fundamental scientific interest, appears to provide some scope for engineering more sensitive magneto-resistive response. This CMR

materials display a fascinating diversity of behaviors including several forms of magnetic, orbital and charge ordering. The materials also exhibit dramatic variations of physical properties with frequency, temperature, chemical composition and applied strain. It should also be remembered that the manganites belong to the class of materials where electron correlations are deemed important - a problem that has challenged the condensed matter physics community for over 50 years.

A huge amount of studies of CMR, electronic-transport, magnetic property etc. have been carried out in this class of materials in case of single crystal, thin film and ceramic CMR materials. In addition, in case of polycrystalline CMR materials a key feature observed is a large negative magneto-resistance (MR) at very low fields followed by a slower varying negative MR at comparatively high fields, at temperatures far below their ferromagnetic Curie temperature. Although this low field MR seems to have potentiality for possible sensor applications, all previously reported experimental results showed that the effect is very much pronounced only at low temperatures and drops sharply with increasing temperature. Thus from technological perspective, because of several difficulties, both CMR and low field spin polarized tunneling MR are not found to be suitable for real field sensing device applications. It is well known that finite-size effects play a central role in physics. It is generally believed that a high value of surface to volume ratio with large fraction of atoms residing at the grain boundaries is what differentiates them from the bulk materials in their properties. Several works in different nanometric systems indicate the surface effect as responsible for their apparent anomalous behavioral changes with reduced dimension. On this background, our objective was to investigate the effect of nanometric grain size on electronic-transport,

magneto-transport and magnetic properties of nano-dimensional CMR manganites. In the whole frame of work, our motivation encompasses both technological and fundamental aspects. **(a)** Our primary objective is to investigate whether nanometric grain size of polycrystalline manganites, has any effect on the magneto-transport properties, especially on low field MR. In spite of a number of such investigations, there has been no detailed study on the temperature dependent behavior of low field MR of manganite nanoparticles, which is absolutely essential both for practical applications as well as for fundamental study. On this background, we have further shed light on this issue of temperature dependence of low field MR of manganite nanoparticles, prepared through a different 'pyrophoric reaction' technique. **(b)** Our aim is to examine the influence of nanometric particle size on the magnetic, electronic-transport properties and a host of other issues of manganite nanoparticles. Our basic aim comprises the investigation of the role of spin-polarized tunneling mechanism at the enhanced grain surface of manganite nanoparticles. For this purpose, we have chosen two prototype CMR manganites $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) and $La_{0.7}Ca_{0.3}MnO_3$ (LCMO). We have carried out detailed study on electronic-transport, magneto-transport and magnetic properties of structurally characterized LSMO and LCMO nanoparticles, prepared through 'pyrophoric reaction' technique. We have tried to coherently discuss all those experimental results for each system, considering the presence/influence of finite size effect or surface effect or any combination of these effects arising due to the nano-dimension of our samples.

Doped perovskite manganites, with the general formula $La_{0.7-x}R_xA_{0.3}MnO_3$ (where R = smaller rare earth (RE) ions, A = divalent alkaline earth ions such as Sr^{2+}, Ca^{2+}, Ba^{2+}, Pb^{2+}), have been undergoing a great research interest due to exotic modulation

of electronic and magnetic properties with the doping of smaller RE ions on La site, while maintaining the optimum A^{2+} doping level of 0.3. Heavy RE doped manganite system induces a special flavour to the problem for its much smaller ionic radius and high magnetic moment over that of light RE doped system. Apart from having smaller ionic radius (1.107 Å) of Gd^{3+} than La^{3+} (1.216 Å) and large magnetic moment (7/2 ħ), progressive substitution of La^{3+} for heavy RE Gd^{3+} is a particular favourable case among other heavy REs, since Gd^{3+} ion has orbital angular momentum L = 0 and therefore no complications will be caused by the crystalline field. Doping of Gd on La sites besides introducing lattice disorder, promotes random character of distribution of A site cations (La^{3+}, Sr^{2+}, Gd^{3+}). As a result, there is random distribution of hopping of conduction electrons as well as exchange between localized spins that induces random disorder in the magnetic lattice of the system. Additionally, due to large local moment of Gd there exist an antiferromagnetic (AFM) exchange coupling between Gd and Mn moments, resulting in Gd^{3+} spins being polarized antiparallel to the ferromagnetic (FM) Mn sublattice. This competing AFM coupling between Gd and Mn moments would also contribute to the random disorder in the FM host of Gd doped manganite systems. It is well known that the ordered state or the phase behaviour of different condensed matter systems is unstable against arbitrarily small defects and impurities, which is basically one of many examples of sensitivity of materials properties to perturbations. Interestingly, this sensitivity of material properties may be useful, or inconvenient, or both. Thus examination of this effect of random disorder on the physical properties of materials is critical for understanding and controlling this phenomenon. Nanometer-sized magnetic particles have generated growing interest for their novel magnetic behaviour and enormous

potential in technological applications, e.g., in high-density magnetic storage media, hard magnets and biomedicine. The combination of finite size and surface effects of magnetic nanoparticles induce a magnetic behaviour, which strongly differ in several aspects from those observed in conventional bulk magnetic materials. Likewise, it is highly expected that the response of a nanometric system towards random disorder in its magnetic host and the resulting magnetic behavior would also be different from its bulk counterpart. Since any real system has several non-ideal effects, the basic understanding of the effect of random disorder on magnetic properties of nanometer sized magnetic particles is critical for meaningful interpretation of experimental results and their probable technological implementation. Gd doped $La_{0.5}Gd_{0.2}Sr_{0.3}MnO_3$ is a relevant system for the study of this nature for the reasons explained above. In order to address this problem, initially, we have attempted to carry out magnetic study, using same experimental probe, on the bulk counterpart of almost same compositional sample. In this attempt our objective is two fold: first, to establish the magnetic phase of bulk system; second, to investigate the effect of random disorder on magnetic ordering of it. We have discussed the magnetic studies on bulk and nanometric $La_{0.5}Gd_{0.2}Sr_{0.3}MnO_3$ system. This study has enabled us to effectively separate out the effect of random magnetic disorder on magnetic ordering of bulk and nanoparticles of a manganites having almost similar composition. In our next attempt, we have carried out similar magnetic study for $La_{0.4}Gd_{0.3}Sr_{0.3}MnO_3$ nanoparticles, where our underlying objective was to study the effect of increasing random disorder on magnetic ordering of manganite nanoparticles.

Multifunctional materials that combine spontaneous magnetization (M_S) with ferroelectric polarization (P_S) are of tremendous technological and fundamental interest.

The strong coupling between M_S and P_S would allow ferroelectric (FE) data storage combined with a magnetic read and the ability to tune the magnetic properties with an electric field and vice versa. Moreover, coexistence of high dielectric permittivity and magnetic permeability could have potential to replace capacitor and inductor in resonant circuits with a single component thus promises miniaturizing portable cellular technologies. In this aim a large amount of research work has been undergoing a great research interest during last few years. However, it has been found that FE ferromagnets in a single phase materials with large and robust M_S and P_S are rare. In fact, the coexistence of ferroelectricity and ferromagnetism is difficult to achieve. In order to address this problem our approach is to prepare and study a different kind of multiferroics with composite character. In an earlier report Park *et al.* [Phys. Rev. Lett. **92**, 167206 (2004)] proposed unprecedentedly of such a multiferroic composite, where they have studied percolative electrical conduction. Composite materials are subject of continuous research interest as they promises to combine diversified physical properties. Basically, they are multi-phase materials obtained by artificial combination of different materials, so as to attain properties that the individual components by themselves cannot attain. In this attempt to produce and study a multiferroic composite, following recent research trend, we have considered the FE component as hexagonal manganites, whereas for its ferromagnetic (FM) counterpart we have considered extensively studied colossal magneto-resistive manganite LSMO. As already discussed, LSMO crystallizes in the rhombohedral structure with an optimal para-ferromagnetic Curie temperature (T_C) ~ 370 K. On the other hand, it is well known that hexagonal manganites $RMnO_3$ (where, R = heavy rare earth) show ferroelectricity below Curie temperatures between 590 and

1000 K and antiferromagnetic transitions below 100 K. We have considered hexagonal manganites $ErMnO_3$ (EMO) as the FE component of the composite, as the difference in ionic radii of Er^{3+} and La^{3+} are appreciably large thus promising almost complete immiscibility within the mixture of two compounds of LSMO and EMO having nearly identical chemical formula. We have carried out detailed study on magnetic and dielectric properties of structurally characterized multiferroic composites x LSMO - (1-x) EMO (where, x = 0, 0.1, 0.2, 1), prepared through chemical 'pyrophoric reaction' technique. Synthesis, structural, magnetic, dielectric and complex impedance spectroscopy studies of x LSMO - (1-x) EMO (where, x = 0, 0.1, 0.2, 1) composites have been discussed.

In **chapter 2**, we have discussed about the fabrication of a low cost ferroelectric loop tracer employing Sawyer-Tower circuit, dc resistivity set – up (actively involved during fabrication) and complex impedance measurement set – up (actively involved during fabrication), in our laboratory. We have discussed about some characterization techniques, such as x - ray diffraction (XRD), transmission electron microscopy (TEM), high-resolution field emission scanning electron microscopy (FE-SEM) and energy dispersive x-ray analysis (EDAX), involved in characterizing our samples, prepared through chemical pyrophoric reaction technique. We have also presented magnetic measurement techniques, such as vibrating sample magnetometer (VSM), low field ac susceptibility (χ_{ac}) measurement and transport (electronic- and magneto-transport) measurement techniques, employed for studying magnetic, as well as electronic- and magneto-transport properties of our structurally well characterized samples.

In **chapter 3**, we have discussed synthesis, structural, electronic-transport, magneto-transport and magnetic studies of LSMO and LCMO nanoparticles through low temperature chemical "pyrophoric reaction process". Our chemical synthesis technique confirms high purity, small particles sizes, good compositional control and chemical homogeneity with good particle-size distributions of the final products, i.e., nanosized ceramic powders. Structural characterizations through XRD, TEM, FE-SEM and EDAX confirm the formation of pure single cubic perovskite phase of our $La_{0.7}A_{0.3}MnO_3$ nanoparticles, having grain size in the nanometric regime (14 – 36 nm), where increase in calcination temperatures, i.e., T_{Cal} leads to an increase in average grain size from 14 to 36 nm. We have carried out detailed studies on electronic-transport, magneto-transport and magnetic properties of this structurally characterized LSMO and LCMO nanoparticles, having grain size of the order of few tens of nanometer. Based upon spin polarized tunneling mechanism, we have proposed a phenomenological model to analyze certain aspects of nanosize effect on electronic-transport behavior of manganite nanoparticles, those are a) the huge increase in resistivity over the whole temperature range studied with decrease in grain size b) steady drop of metal-insulator transition temperature (T_P) with decrease in grain size with T_C does not follow the drop of T_P c) steeper low temperature (~ 40 K) resistivity upturn for smaller grain size sample than that of larger grain size sample. Most interestingly, MR measurements show that low field MR (LFMR), as well as high field MR (HFMR) remains constant up to sufficiently high temperature and then drops sharply with temperature. This effect gets enhanced with the decrease in particle size and is not common in other polycrystalline bulk, as well as in nanometric manganite samples. We have analyzed our experimental MR data following a phenomenological

model to separate out the MR arising from spin polarized transport (MR_{SPT}), from the intrinsic contribution in our nanosize granular manganites. We have observed that the magnitude of MR_{SPT} remains constant up to sufficiently high temperature and then drops rapidly with temperature, which is an appreciable improvement over previous work. This strange temperature dependence of MR is found to be decided predominantly by the nature of the temperature response of surface magnetization (M_S). The strong freezing of Mn spins into a distorted state, due to random exchange interactions or random anisotropies at the surface causes such a remarkable temperature dependent behavior of MR in these granular nanometric manganites. Though our temperature dependent MR results are far from optimal, they seem to suggest that nanosize modulation of manganite grains may lead to technologically important advances through tuning of temperature dependent behavior of LFMR. Furthermore, considering the immense technological relevance we have undertaken close scrutiny only on the room temperature LFMR property of prototype CMR manganites $La_{0.7}Sr_{0.3}MnO_3$ having $T_C > 300$ K and investigated thoroughly whether nanosize modulation of manganite grains has any effect on room temperature LFMR. Our study reveals that grain size modulation of nanometric manganites can tune room temperature LFMR with a pronounced crossover of LFMR value with particle size. It appears that with decrease in particle size room temperature LFMR increases till the nanoparticles remain magnetically multi domain (MD), but as soon as it falls in single domain (SD) regime LFMR immediately starts diminishing. Our study explores that for MD nanoparticles room temperature LFMR is decided only by surface spin susceptibility (χ_b), whereas for SD nanoparticles LFMR arises as a result of a sensitive balance between χ_b and thermal effect. It is obvious that for effective tuning of

LFMR for probable technological applications, optimization of those two effects viz. χ_b and thermal effect is essential. Achievement of appreciably large room temperature LFMR has been a continuous effort of scientific community from last decade and we believe that our study will give a new dimension to that effort through the modulation of grain sizes of nanometric manganites. We have performed ac susceptibility measurements in the temperature range of 80 – 300 K for both LSMO and LCMO nanoparticles. It appears that T_C shifts towards lower temperature with decrease in grain size which can be explained in the light of finite size effect. Furthermore, zero-field-cooled (ZFC) and field-cooled (FC) dc magnetization measurements confirm enhanced grain surface effect and role of surface disorder on magnetic properties of LSMO nanoparticles. We have performed ZFC and FC dc magnetization and ZFC relaxation measurements in the temperature range of 1.5 – 300 K and in the magnetic field range of – 5.5 - 0 - + 5.5 T on our LCMO nanoparticles. We have considered core-shell structure of our LCMO nanoparticles, which enable us to coherently analyze all those magnetic results. From the temperature dependence of FC and ZFC dc magnetization, the magnetic properties could be distinguished into two regimes: a relatively high temperature regime $T \geq 40$ K where the broad maximum of ZFC curve (at $T = T_{max}$) is associated with the blocking of core particle moments, whereas the sharp maximum (at $T = T_S$) is related to the freezing of surface (shell) spins. We have observed an unusual shape of low temperature isothermal (T = 1.5 K) magnetic field dependent magnetization M (H) measurements that can be understood in terms of surface spin freezing of LCMO nanoparticles. Additionally, the temperature dependent feature of coercive field and remanent magnetization (M_r) gives strong support of surface spin freezing. Our ZFC

relaxation measurements of magnetization for waiting times (t_w) 10 and 1000 sec at T = 50 K show the relaxation rate S (t) is weakly dependent on t_w. Moreover, the time variation of the logarithmic time derivative of the ZFC magnetization i.e., $dM/d\ln(t)$ is found to follow a logarithmic variation on time. These two features strongly support that the high temperature regime (T > 40 K) is associated with the blocking of core moments of our LCMO nanoparticles. On the other hand, ZFC relaxation measurements at T = 20 K indicates the existence of two different types of relaxation processes in the sample. Importantly, S (t) attains a maximum at the elapsed time very close to the wait time t_w = 1000 sec, which is an unequivocal sign of glassy behavior. Thus this age-dependent effect convincingly point out surface spin freezing of our LCMO nanoparticles associated with a background of SPM phase of core moments. We have also carried out both magnetic field and temperature dependence of FC and ZFC dc magnetization measurements for a comparatively large grain size ($\Phi \sim 27$ nm) LCMO sample. Although, our magnetization study give evidences of surface spin freezing for this $\Phi \sim 27$ nm LCMO sample as well, the effect gets reduced for this comparatively large grain size sample. Thus these comparative analyses between $\Phi \sim 17$ and 27 nm LCMO samples strongly establishes enhanced grain surface on magnetic properties with decreasing grain size of manganite nanoparticles.

In **chapter 4**, we have presented magnetic studies on Gd doped $La_{0.7-x}Gd_xSr_{0.3}MnO_3$ (x = 0.2, 0.3) (LG_xSMO) nanoparticles. We have performed both dc magnetization (DCM) and linear and non-linear ac susceptibility (χ_{ac}) measurements on our samples. Doping of Gd on La sites and its antiferromagnetic (AFM) coupling with

Mn sublattice are expected to induce random magnetic disorder in the magnetic lattice of Gd doped manganite systems. In this present study our objective was to investigate the effect of that random magnetic disorder on magnetic properties of LG_xSMO (x = 0.2, 0.3) nanoparticle system. Our experimental results suggest that for $LG_{0.2}SMO$ nanoparticles the resulting magnetic phase is the mixture of long range ordered ferromagnetic (FM) phase and interacting superparamagnetic (SPM) phase, where we suppose the long range ordered phase takes place on relatively larger size particles of the distribution and interacting SPM phase originates from relatively smaller size particles of the distribution. Thus our present study reveals that $LG_{0.2}SMO$ nanoparticles exhibit contrasting magnetic behaviour from that of its bulk counterpart, which was found to show cluster glass (CG) like phase. For bulk $LG_{0.2}SMO$ sample the origin of its CG like phase and the intriguing variation of its freezing temperatures with applied magnetic field have been understood in the light of random magnetic disorder, arising due to Gd doping, influencing its magnetic behavior. This has also supports from previous literatures. We understand that random magnetic disorder that creates 'finite size' virtual magnetic entities, which results in CG magnetic behaviour in an otherwise physically infinite matrix of bulk $LG_{0.2}SMO$ system, does not have similar significant effect when the uniformity of the host matrix reduces to nanosize. On the contrary as revealed from our analysis, in case of nanoparticles the magnetic behavior is determined primarily by its nano-dimension. Our study brings out that both finite size effect and enhanced grain surface effect collectively yields different effect of random magnetic disorder on magnetic properties of bulk and nanoparticles of $LG_{0.2}SMO$ sample. In our next attempt, we have carried out comparative magnetic study between $LG_{0.2}SMO$ and $LG_{0.3}SMO$ nanoparticles, having nearly equal particle sizes and

their distributions, thus confirming almost similar finite size and enhanced grain surface effect. Our experimental results give evidences of the mixing of features of SPM phase and collective particle dynamics on $LG_{0.3}SMO$ nanoparticles, where we consider the respective magnetic phases to take place on relatively larger and smaller size particles of the distribution. We suppose that increase in Gd doping level of x = 0.3 results in an increase in random magnetic disorder in the magnetic lattice of the system, which along with the possible modification in characteristic correlation lengths of random disorder, results in less effective magnetic exchange coupling between neighbouring magnetic entities. This in turn results in isolated system of particles, which eventually, depending on their anisotropy energy barrier (E_b) and interparticle interactions, results in SPM phase or collective particle dynamics. Thus our study seems to suggest two important points. In one hand, the random magnetic disorder in magnetic matrix of a nanoparticle system is strongly dictated by both of its finite size effect and enhanced grain surface effect and yields significantly different response of nanoparticle system than its bulk counterpart. In other hand, it suggests that even if two nanoparticle systems have nearly equal particle sizes and their distributions, they may show disparity in magnetic behavior depending upon different random magnetic disorder introduced in their host magnetic matrix. This in turn indicates the nanoparticle systems are also sensitive to random disorder.

In **chapter 5**, we have studied a different kind of multiferroics with composite character. In this direction, we have carried out detailed studies on magnetic and dielectric properties of structurally characterized multiferroic composites x LSMO - (1-x) EMO (where, x = 0, 0.1, 0.2, 1), prepared through chemical 'pyrophoric reaction' technique.

Our structural and magnetic studies confirm almost complete immiscibility within the mixture of two compounds of LSMO and EMO having nearly identical chemical formula. Arrott-Belov-Kouvel (ABK) plots at 300 K for all those three samples confirm the presence of a finite spontaneous magnetization (M_{SP}), which is a signature of ferromagnetic (FM) phase of the samples. The observed sharp decrease in M_{SP} and enhancement of coercive field of LSMO in the composite with increasing EMO content can be attributed to the increase in grain boundary pinning center of LSMO grains. These features, in turn add an extra flavor to the magnetism of this multiferroic composites ($x = 0.1, 0.2$) with enhanced magnetic hardness from that of pure LSMO. Our dielectric study reveals that both pure EMO and 0.1 LSMO – 0.9 EMO composite exhibit ferroelectric (FE) relaxor behavior, whereas 0.2 LSMO – 0.8 EMO composite is found to be strongly diffusive FE sample. Thus we have optimized the weight percent x in the x LSMO - (1-x) EMO composite ($0 \leq x \leq 1$) to attain sustained simultaneous FM and FE property in a single composite. We have found a heterogeneous multiferroic composite 0.1 LSMO – 0.9 EMO, which conserves the individual characteristic properties such as high spontaneous polarization (P_s) and M_{SP} and explicitly show the M-H and P-E data at room temperature indicating the coexistence of both FM and FE phases in this mixture.

In **chapter 6**, we have discussed the summary of my dissertation work and also the scope of future work, which can be derived from of my thesis.