PREFACE

Oxides comprise a wide class of materials exhibiting rich crystal structures and physical properties that make them ideal candidates for a plethora of applications. There has been a recent resurgence of interest in oxides in general and complex oxides in particular due to their piezoelectric, ferroelectric, ferromagnetic, ferrimagnetic, multiferroic and superconducting properties as well as, in many cases, large dielectric constants (imperative for scaled Si metal-oxide-semiconductor field effect transistors [MOSFET]). Among all these many oxide materials, manganites and new oxypnictide superconductors are important not only from application point of view but also due to the rich physics behind their unusual properties. This thesis deals with synthesis, characterization of these two particular types of oxide materials and to tailor the properties of these materials by doping/admixing so as to make it amenable for device purposes. First the brief introduction of manganites is described followed by basics about oxypnictide superconductors.

In 1993 Jin et al. observed about thousand-fold change in resistance in epitaxial thin film of perovskite La$_{2/3}$Ca$_{1/3}$MnO$_3$ at a high magnetic field of 6 Tesla and, christened it as Colossal Magnetoresistance (CMR). The growth of interest in their properties stems in large part, from the prospect of creating metal oxide devices whose performance exceeds GMR devices. In addition, it is now recognized that the large magnetoresistivity in these oxides is the result of a unique type of metal–insulator transition, the understanding of which complements the drive for applications. The compounds which have been the focus of the majority of studies are the manganite perovskites A$_{1-x}$B$_x$MnO$_3$ where A is a trivalent lanthanide cation (e.g. La) and B is a divalent, e.g. alkaline-earth (e.g. Ca, Sr, Ba), cation. For the end members of the series, LaMnO$_3$ and CaMnO$_3$, the ground state is antiferromagnetic (AF), as expected for spins interacting via the superexchange interaction when the metal–oxygen–metal bond angle is close to 180°. In a certain range of doping, $x \sim 0.2–0.4$, the ground state is ferromagnetic (FM), and the paramagnetic-to-ferromagnetic transition is accompanied by a sharp drop in resistivity $\rho(T)$. This phenomenon has been known to exist since 1950. Recently, interest in these materials has been renewed by the realization that (i) the magnetoresistance (MR) associated with this correlation between magnetization ($M$) and resistivity ($\rho$) can be very large, and (ii) the basic interaction responsible for the $\rho$–$M$ correlation, the double-exchange (DE) interaction between heterovalent (Mn$^{3+}$, Mn$^{4+}$) neighbours, is by itself not sufficient to explain this MR. Both the large resistance and the associated MR are now thought to be related to the formation of small lattice polarons in the
paramagnetic state. The large MR resulting from the transition has been called ‘colossal magnetoresistance’, mainly to distinguish it as a phenomenon distinct from GMR. In addition to the renewed interest in the FM state, much attention has been given to another type of collective state, charge order (CO), typically observed for $x > 0.3$. At these doping levels CO can compete with the FM ground state, leading to complex electronic phase behaviour as chemical formula is varied. Large MR over a wide temperature range and at relatively smaller external magnetic fields ($\sim \text{mT}$) is of prime importance from the point of view of application of manganites is concerned and this has been observed in randomly oriented polycrystalline bulk as well as thin films. The present investigation has been carried out with a view to optimize the synthesis and formation of some doped LaMnO$_3$ manganites in bulk as well as in film form and also to study their low field magnetotransport characteristics and to bring out structure/microstructure-property (CMR) correlations. We have studied the magnetotransport characteristics i.e. $T_{IM}$ (insulator-metal transition), $T_C$ (paramagnetic-ferromagnetic transition) and LFMR (Low field magnetoresistance) of doped LaMnO$_3$ samples and have attempted to correlate these with their structural/microstructural characteristics.

Another important field is superconductivity. Since the discovery of superconductivity in mercury, solid state physicists have worked meticulously to attain superconductivity at technically relevant and feasible temperatures. Even a minor increase in the superconducting temperature can greatly ease the practical handling and application of superconductors. This necessity initiated strenuous efforts in developing a superconductor above the BCS limit. The term ‘high temperature superconductor’ (HTS) was first coined for a family of cuprate perovskite ceramic materials, discovered by Muller and Bednorz in 1986. The discovery of superconductivity in an intermetallic MgB$_2$ ($T_c = 39$ K) in 2001 also spurred renewed interest due to its potential in magnetic applications. The superconducting world was reignited when Japanese researchers led by Hideo Hosono discovered a new class of iron based superconducting material having transition temperatures relatively higher than the conventional low temperature superconductors. The team was primarily aiming at the fabrication of transparent oxide semiconductors for flat panel displays. They expected intriguing electromagnetic properties from the two-dimensional electronic structure of the compound LaTMPnO ($TM$-transition metal, Pn-pnictogen), known as oxypnictides. Research on iron based superconductors was taken up seriously only after the discovery in 2006 of superconductivity at 4 K in LaOFeP, a member of this oxypnictide family. The $T_c$ climbed up to 26 K with the replacement of phosphorous by another pnictogen, arsenic and some oxygen atoms with fluorine. The discovery tantalized physicists and materials scientists into a renewed frenzy of
activity, since the compound contained the most familiar ferromagnetic atom ‘iron’ which is incompatible with superconductivity. A great deal of work is in progress to explore the similarities with HTS and thereby to pave the way towards the superconducting mechanism behind the unconventional high temperature superconductors. One of the exciting aspects of these new superconductors is that they belong to a comprehensive class of materials where many chemical substitutions are possible. This versatility has already opened up new research avenues to understand the origin of the superconductivity, and should also enable the superconducting properties to be tailored for commercial technologies.

The present thesis is divided into six chapters and an annexure. The first chapter is an introductory review of the subject and describes the basic structure, phase diagram, various types of ordering and causes of colossal magnetoresistance and oxypnictide superconductors.

The second chapter describes the structural and microstructural characterization techniques employed in the present work. These techniques include X-ray diffraction (XRD) for gross phase identification and scanning electron microscopy (SEM) using secondary electron imaging mode for investigating the microstructure and transmission electron microscopy (TEM) for unraveling the microstructural details and the energy dispersive analysis of X-rays (EDAX) has been used for chemical characterization of materials. X-ray Photoelectron Spectroscopy (XPS) has been used to get information about the valence state of some elements. Different techniques have been used to prepare nano and bulk form of manganite and superconductor such as solid state synthesis route and sol-gel route. The four-probe technique of measuring resistivity and magnetotransport is described.

The third chapter describes the effect of Mm doping at La-site on the structural, electrical and magnetic properties in La$_{0.7}$Ca$_{0.3}$MnO$_3$ perovskite manganite corresponding to La$_{0.7-x}$Mm$_x$Ca$_{0.3}$MnO$_3$ (0 ≤ x ≤ 0.45). A curious result obtained by us for these materials is that for x=0.35, the magnetoresistance is as high as ~61 % under a low applied magnetic field of ~10 kOe. All as grown samples have orthorhombic structure and shows significant colossal magnetoresistance behaviour. With increasing x, corresponding to decreasing the A site average ionic radius (< r$_A$ >) hence increasing the size mismatch at A site ($\sigma^2$ (r$_A$)), results in strong suppression of ferromagnetism and the associated metallicity. Another curious result is that both T$_{IM}$ and T$_C$ decrease with Mm doping. The ferromagnetic transition becomes broader with increasing amount of Mm doping. Two plausible reasons have been put forward for the occurrence of high CMR in these Mm doped manganites. One relates to the presence of Mn$^{2+}$, Mn$^{3+}$ and Mn$^{4+}$. Evidences and arguments based on XPS results have been put forward to suggest that the high CMR in these materials may arise due
to the existence of multivalent ions La and Mm and the resulting presence of Mn$^{2+}$, Mn$^{3+}$ and Mn$^{4+}$. This will cause the simultaneous operation of double exchange mechanism embodying Mn$^{2+}$-O-Mn$^{3+}$ and Mn$^{3+}$-O-Mn$^{4+}$. However, the substitution of Mm also creates inhomogeneities at A-site which produces disorder as evidenced by SAED. The inhomogeneities appear to have more prominent role in enhancing the CMR in these Mm doped LCMO.

The forth chapter describes the enhanced low field magnetoresistance in broad temperature range (~70 K) in LCMO: ($x\%$) nano-ZnO ($x\% = 0, 1, 3, 5, 7$ and $10$) composites. Nano-ZnO has been synthesized by vapor phase transport technique which then admixed with sol–gel synthesized nano-LCMO that leads to LCMO: nano-ZnO composites. Nano-ZnO admixing does not show any significant change in lattice parameter of the composites. All samples exhibit characteristic insulator–metal ($T_{IM}$) and para-ferromagnetic ($T_C$) transition temperature, which decreases with increase in nano-ZnO content. Higher nano-ZnO ($x \geq 3\%$) leads to dual I–M as well as PM–FM transitions. The first transition occurs close to $T_{IM}$ or $T_C$ of pure LCMO and another at a significantly lower temperature. At $x > 7\%$, the double transitions transforms into a single-broad transition and then finally disappears for $x > 10\%$. The occurrence of dual transition has been explained on the basis of stress induced phase separation due to nanoglobular ZnO structures that result in formation of intragranular and intergranular regions having different transition temperatures. The interesting and important result for the present LCMO: nano-ZnO composites is the observation of improved MR ~13–18% at a moderate magnetic field of 3 and 5 kG in a broad temperature range of 70K (80–150 K). The improved broad range low field magnetoresistance (LFMR) has been explained on the basis of grain boundary tailoring due to coating of polar nature nano-ZnO on the LCMO grains.

The section A of fifth chapter put forward the studies of the effect of silver doping on the structure and magnetotransport properties of La$_{0.7}$Ca$_{0.3-x}$Ag$_x$MnO$_3$ ($x=0, 0.1, 0.15, 0.2, 0.3$) nanocrystalline bulk. La$_{0.7}$Ca$_{0.3-x}$Ag$_x$MnO$_3$ (LCAMO) was prepared by sintering amorphous powders synthesized by soft chemical polymer based sol-gel route at two different temperatures 700°C and 1000°C. Structural characterization reveals that the undoped compounds (LCMO) are single phasic and when doped with Ag, orthorhombic to rhombohedral phase transition occurs for $x \geq 0.15$. The ferromagnetic (FM)–paramagnetic (PM) transition temperature ($T_C$) and metal-insulator transition temperature ($T_{IM}$) both the values increase due to doping. For example, the $T_C$ and $T_{IM}$ values of the samples sintered at 1000°C are 260K and 255 K for $x=0$ which enhances to 310K and 309 for $x=0.30$ respectively. Similar trend is observed for 700°C sintered samples. The transport properties are found to be sensitive to sintering temperature as well. Room temperature magnetoresistance (MR)
values are very high for Ag doped LCMO in comparison to LCMO, e.g. it is only ~1.5% for x=0 while ~10% for x=0.3 at 10kG. The structural phase transition and improved magnetotransport properties have been explained on the basis of disorder induced due to radii and valence fluctuations at La-site and incorporation of nascent oxygen in the perovskite lattice as a consequence of Ag doping.

The section B of fifth chapter deals with the comparative study on the effect of Ag doping and admixing on the structure and magnetotransport properties of nanophasic La_{0.7}Ca_{0.3}MnO_3 (LCMO) manganite to resolve the issue of ambiguous issue of Ag substitution at La-site in LCMO manganite. In this context two sets of samples were synthesized, (a) Ag doped La_{0.7}Ca_{0.3-x}Ag_xMnO_3 (x=0, 0.1, 0.15, 0.2, 0.3) and (b) chemically synthesized Ag nanoparticles admixed La_{0.7}Ca_{0.3}MnO_3 (LCMO + x wt% Ag-NP, x = 0, 10, 15, 20, 30) and were annealed at 700°C in oxygen ambience. XRD study reveals that for Ag doped nanophasic LCMO samples, orthorhombic LCMO transforms to rhombohedral for x ≥ 0.15 while for Ag admixed LCMO no such transformation occurs, rather Ag is present as a secondary phase. Resistivity decreases for both types of samples, In the case of Ag admixed LCMO; it is due to the metallic nature of silver while for Ag doped samples increase in the number of holes as silver being mono valent may be the reason for decrease. Both the insulator-metal (T_{IM}) and ferromagnetic–paramagnetic (T_C) transition temperatures increase with Ag. The corresponding increment in these parameters is ~ 100K and ~50K for 30% Ag doped and for Ag admixed (30%) it is ~60K and ~15K respectively than that of pure LCMO. Room temperature magnetoresistance (MR) values are higher (6.8% for x=0.30) for Ag doped LCMO as compared to undoped LCMO (~ 0.5%).

The section A of sixth chapter describes the superconductivity in a LaOFeAs system. Superconductivity in a LaOFeAs system is known to get introduced by F-doping (LaO_{1-x}F_xFeAs) even under ambient pressure and oxygen deficiency (LaO_{1-x}FeAs) under high pressure conditions. Here unreported, superconductivity in F-free undoped LaOFeAs samples is observed and confirmed for the first time by various characterization tools–resistive ρ(T,B), magnetic M(T,B) and modulated microwave absorption (MMA) measurements. The ρ(T ) at B = 0 shows a clear superconducting transition with an onset at T_{con} ~ 17 K and a tail-like behavior when R goes to zero at T_{c0} ~ 8 K. In the presence of B, the superconducting transition shifts to lower T with a rate ~5.5 and ~1.65 T/K, depending on whether the ρ(T ) has dropped to 90% or 5% of its normal state value, respectively. M(T ) in zero field cooling at B = 10 mT shows diamagnetic downturn below at ~12 K. At T <T_{c0} the change in MMA with B shows a low field (B ~ 1 mT) peak, which vanishes at T >T_{c0}, indicating the presence of weak link superconducting networks in the sample. The
sample shows a complex electrical and magnetic behavior in the normal state. For instance, $\rho(T)$ reveals a weak SDW-like anomaly at $T \sim 132$ K along with a resistivity minimum at $T_{\text{min}} \sim 78$ K. Magnetization measurement also shows the presence of a magnetic anomaly at $T \sim 130$ K. Both below and above $T_{\text{cont}}$, presence of an additional ferromagnetic component is observed in the isothermal $M(B)$ loop measurements. The superconducting and normal state features of our sample are compared with other undoped and doped LaOFeAs systems reported in the literature.

The section B of the sixth chapter investigates the effect of Ag addition (0–30 wt %) on polycrystalline SmO$_{0.8}$F$_{0.2}$FeAs superconductor. Critical current density ($J_c$) is observed to increase with Ag concentration first and it decreases a little on further admixing. The transition temperature $T_c$ decreases for Ag admixed samples. Microstructural study was done to correlate the enhancement in the $J_c$ values. Ag improves the connectivity between grains. An amorphous layer is present in case of silver free SmO$_{0.8}$F$_{0.2}$FeAs which disappears when admixed with Ag. Moreover, Ag nano particles were found at the grain boundaries and within the grains. The silver present at grain boundaries helps in reducing the scattering of charge carriers and also acts as pinning centers when present in the sofa matrix that enhances current density. The improvement of superconducting properties in Ag-added samples is discussed in correlation with microstructure.

The annexure focuses on the effect of chemical pressure on superconducting transition temperature caused by the partial substitution of samarium at the lanthanum site in 15% fluorine doped LaFeAsO$_{0.85}$F$_{0.15}$ compounds. We prepared samples having composition La$_{1-x}$Sm$_x$FeAsO$_{0.85}$F$_{0.15}$ (where $x=0, 0.2, 0.8, 1.0$) by two step solid state synthesis route. Phase purity and substitution of Sm is confirmed by XRD and its Rietveld refinement. Substitution of Sm produces shrinkage of both the $a$- and $c$- lattice parameters owing to the fact that ionic radius (IR) of Sm is 1.04Å (while IR of La is 1.15Å). The chemical pressure provided by the partial substitution with this smaller ion size causes an increase in the superconducting transition temperatures in the doped samples. The maximum transition temperature observed for SmFeAsO$_{0.85}$F$_{0.15}$ is ~53K. For morphological information transmission electron microscopic analysis and for compositional analysis EDAX is done. EDAX confirmed the stoichiometric composition for all the samples.

The above mentioned results forming the subject matter of this PhD thesis constitute the following publications.