Density Functional Theory Study of Colossal Magnetoresistance Material $La_{0.67}Sr_{0.33}Mn_{1-x}Fe_xO_3$ Prepared Using Two Different Routes

Synopsis for Ph.D.

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The history of magnetism dates back to earlier than 600 a.c. but it is only the twentieth century that scientists have began to understand it, and develop technologies based on this understanding. The ancient Greeks were the first known to have used this Mineral, which they called a magnet because of its ability to attract other piece of the same material and ion. The curiosity of humans about magnets goes parallel with the expansion of human civilization.

Over the past few years, the science of magnetic materials has been attracting great attention due to its vast technological applications with the help of new processing techniques and ideas and has been in the centre of interest for the materials science community [1-6]. In very recent years, the human life is discriminatory by the development of storage devices like digital magnetic storage, reading magnetic strip and magnetic recording in computers [7-9]. The present information age relies on the development of soft, smart and smaller magnetic materials for storage memories, processing and probing. The development of many technologies that make our existence so comfortable has been intimately associated with the accessibility of suitable materials. These magnetic materials can be divided into the categories depending on their origin, nature and its applications. One important example is the transition metal oxide (TMO) having ideal chemical formula ABO_3in perovskite type structure which from an important class of materials from applications point of view [10]. In many of these materials the resistance changes drastically by application of magnetic field. These materials are called colossal magneto-resistance (CMR) [11, 12].This outstanding property has attracted wide attention in the past decades, as it was believed that the CMR effect could be the key to a new generation of magnetic field sensors or transistors [4, 13]. Even if its application is not as wide as previously expected, CMR is still playing an important role in material science. Modern theoretical and experimental methods have been used to study the materials which have been fabricated in earlier times and new or doped materials [14-15]. This is due to richness of physics they have but there potential to offer the incredible applications.

Manganites are the materials which compose of manganese. These manganites which have very rich phase diagram show complex electronic and magnetic properties. Almost all the degree of freedom known in solid state physics such as charge ordering, localized spins, electronic orbitals and lattice vibration are important in this class of materials to decide their properties. They are interesting compounds and important from the technological point of view because of colossal magnetoresistance (CMR) effect as it is quite interesting in single crystals

[16], films [17] nanostructures [18] and ceramic compounds [19, 20]. However, a fully quantitative understanding of CMR effect has been elusive and it is still the subject of current research activities. Early prospects of great opportunities for the development of new technologies have not yet come to fruition [21].

Microstructural effects have also been investigated for polycrystalline samples and it has been found that the magnetoresistance is often dominated by the tunneling of spin polarized electrons between grains, giving rise to intrinsic grain-size dependence to the magnetoresistance [22, 23]. The CMR manganites are currently being investigated by sizable fraction of the condensed matter and materials scientists following the discovery of the high T_C superconductivity cuprates in the late eighties which provided the platform for rethinking about the use of mixed oxides for variety of applications involving many interesting properties exhibited by them [24]. These systems offer a degree of chemical flexibility which permits the relation between structural, electronic and magnetic properties of these oxides to be examined in a different way.

Over the last two decades, the doped rare-earth mixed valent perovskite manganites that are chemically represented by $RE_{1-x}AE_xMnO_3$ (where RE is the rare-earth La, Nd, Pr, etc. and AE is alkaline earth elements Ca, Ba, Sr, etc) provide a unique opportunity to study the structure property interconnection due to interplay among charge carriers, structure distortion and many striking electronic properties of these systems arising from the strong coupling of electrons to the dynamical lattice distortion [25]. In addition, these materials have been investigated since long for their electronic transport, charge ordering and spin dependent transport properties [1, 3, 4, 26-28].

It is found that the substitution of lanthanum or manganese by another ion in manganites directly modifies their characteristic properties due to new interactions in the La-O and Mn-O networks [29].The substitution of other transition elements at the Mn site of $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) significantly influences the properties of these manganites particularly the Curie temperature (T_C) due to the changes in the average electron concentration and the shifts in the position of the e_g and t_g sub-bands [30]. In this regard the substitution of Fe ions is of particular interest as they do not only replace Mn ions extensively but also serve to fine tune the DE mechanism by breaking of the DE chain, which further weakens in strength with Fe concentration [31]. Furthermore, the significance of the Fe doped LSMO manganites is that the

almost similar ionic radii of Fe and Mn helps in studying the local electronic structure without any lattice distortion. The doping by Fe^{3+} also seems appropriate as Fe^{3+} is magnetic and does not give rise the JT effect and participate in DE mechanism [32]. The 10% Fe doping results a marked decrease in T_C and a continuous decrease in magnetic moment with Fe [29]. The replacement of Mn by Fe favours insulating character and antiferromagnetism opposing the effects of double exchange. The neutron diffraction study shows the existence of antiferromagnetic and ferromagnetic short range ordered regions within the samples of 20% Fe doping [29]. In addition, the modifications in the Mn^{3+}–O–Mn^{4+} network, responsible for the double exchange, can also be brought by doping at the Mn site itself [33]. The Fe doping modifies the Mn^{3+}–O–Mn^{4+} network and increases the resistivity by not participating in the DE and shows magnetic nature for LSMO samples [29].

Further, it is an established fact that the size reduction down to nanoscale modifies the magnetic and electronic properties of a material such as superparamagnetism, large coercivities, low saturation magnetization and spin glass. Therefore, it will be interesting to study the magnanites with particle size comparable to magnetic domain size and develop better understanding of the mechanism of colossal magnetoresistance. It is found that the ferromagnetism (FM) weakens at nano scale and Curie temperature decreases with decreasing size. The cell volume and anisotropy of the unit cell of orthorhombic $La_{0.67}Ca_{0.33}MnO_3$ powders of 30 nm size reduce in comparison to their bulk counterpart [29]. Prellier et al [34] have shown that the manganites of different size exhibit different evolution trends for lattice parameters at room temperature. The increase in the number of grain boundaries and defects at the grain surface significantly modifies the transparent behavior of nano scale manganites. Furthermore, in the case of nanocrystalline samples, the surface contribution to MR increases with the reduction of grain size in the temperature range between 77 K to 300 K at 1000 Oe magnetic field [35].

The present work proposed in the thesis mainly deals with the (LSMO) synthesized of Fe doped $La_{1-x}Sr_xMnO_3$ using two methods. The aim of the present study is may fold:

1) To synthesize Fe doped LSMO using ball mill route and sol –gel method.
2) To study the effect of iron doping on the structural, magnetic, vibrational and electronic properties of LSMO.

3) To perform the density functional theory (DFT) calculations of experimentally obtained LSMFO samples for understanding the properties at atomic calculation.
4) To Compare and understand the properties obtained in point 2 for samples obtained using both synthesis methods and DFT and draw a conclusion for better method to obtain LSMFO samples.

The thesis contains six chapters. A brief outline of the chapters is presented below:

Chapter [I]

The **chapter-I,** gives a brief and up-to-date introduction to the state of the art of manganite polycrystalline material. Here, we present a very brief description of introduction chapter.The history of magnetism and magnetic materials play a great role in improving the living standards of human life and therefore, search for new magnetic materials have been a constant attraction for human beings and it's followed by metal oxides and the physical feeling in the family of perovskite oxides i.e. rare – earth manganites having cubic crystal structures. The concept of the magnetoresistance is elaborated along with its classification based on the nature of the MR and origin in different physical aspects such as anisotropic magnetoresistance (AMR) or negative magentoresistance, tunnel magnetoresistance (TMR), giant magnetoresistance (GMR) and colossal magnetoresistance (CMR). In managnites, negative MR is as large as 100% and hence termed colossal magneto resistance (CMR). Several materials, metals, metallic alloys, semiconductors, magnetic materials and their multilayers exhibit MR properties but the origin of MR effect in these materials phenomenological differs from one to another. In multicomponent and multilayer systems, GMR where trilayer junctions of two ferromagnetic layers separated by a non magnetic space layer are formed [36]. The strength of MR observed in many similar polycrystalline compounds as high as 90% under a few Tesla led the scientists to coin a new term CMR [37].

The discovery of the CMR in the mixed manganese oxides has been a subject of attention in the recent year. The origin of CMR effect is often thought to be based on the double exchange (DE) mechanism and Jahn Teller (JT) distortion [38, 39]. CMR is a property of some material, mostly manganese-based perovskite oxides, that enables them to dramatically change their electrical resistance in the presence of a magnetic field [40, 41]. This is used in practice as recording & reading heads, solid electrolytes of fuel cells, catalysts of chemical reactions and

high sensitive magnetic field pickups [42-47]. However the double exchange model did not adequately explain the high-insulating like resistivity above the transition temperature [48].

In the CMR materials spin, charge and lattice degree of freedom produce a dramatic and fascinating effect such as the transition from a paramagnetic insulator at high temperature to a ferromagnetic metal at low temperature. The discovery of CMR effect in manganites and its relation to various electronic and magnetic properties revived the research interest in similar compounds. The structure and grain boundaries depend on how the material was prepared. Magnetoresistance properties of manganites can be tailored by the grain morphology specifically grain boundaries in polycrystalline bulk, thin films, nanomanganites and device. In this series, Fe was chosen as the dopant because Mn^{3+} and Fe^{3+} have ionic radii that are close to each other, and hence the crystal structure of the material remains almost unaltered.

Chapter [II]

Due to existing properties of the colossal magneto resistance (CMR) materials and it's applications in fields, there is a huge demand to optimize the parameters of synthesis of such materials of perovskite group. From the various experimental techniques, we have used planetary ball milling and sol – gel reactions to prepare the CMR manganite materials in the present study and their details are described in this chapter. The structure property relation is key to decide the utility of any material. The various characterization techniques are used to investigate the different properties of prepared CMR manganite systems. Structure, morphology and compositional elemental analysis of prepared samples have been studied using X-ray diffraction (XRD), Scanning electron microscope (SEM) and energy dispersive analysis of x-ray (EDAX) respectively. For the study of magnetic properties, we explored vibrating sample magnetometer PPMS-Quantum Design using a commercial magnetic properties measurement system. The vibrational characterization of the LSMFO samples with various iron concentration is done using Raman spectroscopy at low as well as room temperature. This helps us to know the possible phase transition through the evolution of phonon modes with temperature and concentration. Resistivity measurements up to 0.5 T magnetic field was done using a PPMS-Quantum Design setup and high magnetic field (7T) was carried out by using commercial physical properties measurement system.

Chapter [III]

Over the past few decades, density functional theory (DFT) has been the most successful, widely used method in condensed-matter physics, computational physics and quantum chemistry to describe properties of condensed matter systems, which include not only standard bulk materials but also complex materials. The main idea of DFT is to describe a many-body interacting system via its particle density and not via its many-body wave function. Its significance is to reduce the 3N degrees of freedom of the N-body system to only three spatial coordinates through its particle density. Its basis is the well-known Hohenberg-Kohn (HK) theorem, which claims that all properties of a system can be considered to be unique functional of its ground state density. Together with the Born-Oppenheimer (BO) approximation and Kohn-Sham (KS) ansatz, practical accurate DFT calculations have been made possible via approximations for the so called exchange-correlation (XC) potential, which describes the effects of the Pauli principle and the Coulomb potential beyond a pure electrostatic interaction of the electrons. Since it is impossible to calculate the exact XC potential (by solving the many-body problem exactly), a common approximation is the so-called local density approximation (LDA) which locally substitutes the XC energy density of an inhomogeneous system by that of a homogeneous electron gas evaluated at the local density.

This chapter starts with a brief history and idea interpretation of the Density Functional Theory (DFT), and then explains more detailed about the original thought of Hohenberg and Kohn and their first and second theorem of the DFT. It also introduces a methodology to treat the calculation based on DFT, which is the Kohn-Sham method based on the Local Density Approximation (LDA) and Local spin density approximation (LSDA) treatment for the exchange energy term. In theoretical aspects, we have carried out of all properties by Density Functional Theory using First Principle calculation using Vienna ab-initio simulation package (VASP) is discussed in this present study.

Chapter [IV]

In this chapter, we present experimental and theoretical studies on the effect of Fe doping at Mn site, on the structural, morphological, electronic and vibrational properties of $La_{0.67}Sr_{0.3}MnO_3$ polycrystalline materials. The samples of $La_{0.67}Sr_{0.3}MnO_3$ and $La_{0.67}Sr_{0.33}Mn_{1-x}Fe_xO_3$ (x=0.15, 0.25 and 0.35) have been prepared by ball milling routedifferent calcination temperatures ranging between 800^{o}C to 1100^{o}C for 7 h. The phase purity of these samples has

been confirmed using X-ray diffraction, while compositional analysis is done using EDAX. The morphological analysis done using scanning microscope indicates the agglomeration. The vibrational analysis which is done using Raman scattering and density functional theory (DFT) calculations show a substantial shift in A_{1g} and E_g modes with Fe doping. The E_g modes become broader with Fe doping. The spin polarized density functional calculations show an increase in density of states at Fermi level due to MnO_6octahedra modification and significant magnetism on Fe doping.An analysis of the frequency and peak broadening of Raman modes as a function of calcination and measurement temperature clearly show the temperature effect on the A_{1g} and E_g modes in LSMFO was observed. The shift and broadening of the A_{1g} and E_g modes are discussed in light of oxygen sublattice distortion. Our study shows the reduction in distortion with increased calcinations temperature suggesting the decrease in JT effect. We present the Raman spectroscopic study Fe doped $La_{0.67}Sr_{0.33}Mn_{0.65}Fe_{0.35}O_3$ (LSMFO) at 300 and 80 K. Valence band study is a very informative tool to look into the electronic structure of any material. The valence band spectroscopy measurements on these manganite samples using a synchrotron radiation source, show considerable change in the density of states (DOSs) at the Fermi level with the Fe doping at different calcinations temperature.

Chapter [V]

In this chapter a detailed experimental and theoretical studies are reported for the $La_{0.67}Sr_{0.33}Mn_{1-x}Fe_xO_3$ polycrystalline manganite samples prepared by sol-gel method with different concentration (x=0, 0.15, 0.25 and 0.35) at different calcination temperatures. We have used all characterization techniques discussed in previous chapter to know the structure property relation for these samples. Of particular interest is to know the role of doping concentration of iron and calcination temperature on the samples prepared using sol gel technique. The X-ray diffraction together with the Rietveld analysis show that the samples prepared using sol-gel method has orthorhombic (pnma) and cubic (pm-3m) structure in contrast to the rhombohedral structure (R-3c) found for the samples synthesized using ball mill method. The other variation in the properties is almost on the similar line limited to the structural differences.

Chapter [VI]

This chapter reports the comparative study of the manganite samples $La_{0.67}Sr_{0.33}Mn_{1-x}Fe_xO_3$prepared using two experimental techniques planetary ball mill and sol-gel for different concentration of iron and calcination temperature. We have considered same concentration of

iron doping and calcination temperatures for understanding the technique based synthesis and properties. The structure-properties relation obtained through different characterization techniques has been analyzed and understood at atomistic level using first principles calculations based on density functional theory. The electronic band structures and phonon modes obtained using density functional theory have been used to interpret the valence band spectra, magnetization and Raman spectra obtained from various corresponding experimental techniques. An analysis in the conclusion chapter is put forward to justify the differences in the properties of manganite samples prepared using two different techniques.

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