A study on magnetic and spin polarized electric transport properties of cation doped LaCaMnO$_3$ perovskite ceramic system

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Abstract. The poly-crystalline La$_{0.5}$Nd$_{0.15}$Ca$_{0.35}$MnO$_3$ has been synthesized by a conventional solid reaction method through the cation doping in LaCaMnO$_3$. The analysis of the powder XRD of the composites revealed the formation of an orthorhombic structure in Pbnm space group. The cell parameters of the formed system has obtained and confirmed through Reitveld analysis and it is found to be $a=5.4505,b=5.4457,c=7.6876$. The lattice parameters and the spin ordering temperature $T_C$ of this system are decreasing due to Nd substitution. The ac and dc magnetization studies and resistivity measurements in ZFC and FC mode gives good understanding to the magnetic and electric transport properties of the doped system. The magnetization studies show a paramagnetic to ferromagnetic transition at a temperature below the critical temperature $T_C$. The resistivity measurements reveals semiconducting to metallic transition below the temperature $T_{MS}$. The temperature dependent transport nature shown in this system is one type of the correlated polaron hopping mechanism and it can be modeled by an adiabatic small polaron hopping (SPH) mechanism.

1. Introduction

The compounds with perovskite structure and its usefulness in applied fields of science and technology has been intensively investigating since 1940 [1-3]. These applications includes ferroelectricity, magnetism, ionic conductivity and superconductivity, etc. The atomic ordering in perovskite structure plays an important role in structure formation, in order to achieve thermodynamic stability in these systems. There are evidence in literature about the modification of physical properties of systems due to this atomic ordering [4,5]. The variation in the structure may vary degree of short and far range orders which may significantly affect magnetic, electronic, dielectric, ferroelectric, ionic and other useful properties of these systems[6].

The discovery of colossal magneto resistance in perovskite systems, initiated an organized effort in scientific community to investigate the interplay between crystal structure, magnetic and electric properties of these systems[7,8]. More over most of the complex oxides represent by these structures with ABX$_3$ stoichoimetry. The ideal type of this sort of structures are known as aristotype perovskite structures and it has Pm3m space group symmetry. The B cations form the octahedral framework with X anions, and these octahedra shares corners of a 3-dimensional network while A cations usually sits in 12 the coordinates of the cubo-octahedral cavities of this three dimensional framework [9,10]. Distortions from the aristotopic structures may produce significant changes in physical, magnetic, electric, and optical properties of these compounds. Moreover in 80-90% of all perovskites...
compounds, an octahedral tilting distortion present if A cation is too small in its octahedral cavities[11-15]. The distortions of similar nature also change the conduction bandwidth and strength of magnetic super exchange interactions, which intern helps to fine-tune the magnetic and electric properties for potential applications.[16-17].

In addition to the structural flexibility, these composites posses compositional flexibility[10].Chemical substitutions are possible in all the three sites of these perovskite structures. Oxytitanates and oxyfluorides, etc. are examples for chemical substitution in anions. Cation substitution may lead to an ordered or disordered structural arrangement, which has profound effects on the properties of these compounds. The rare phenomenon of ferromagnetism in ordered perovskite La2MnMO6(where M=Ni,Co) due to B cation ordering and the dependence ionic conductivity of Li3La2/3,TiO3 on A cation ordering, etc. are examples for effect of cationic substitution in perovskite structures[17-19].The present study is interested to investigate the ordered or random cationic ordering in the structural framework to engineer new materials of usefull properties. Cation ordering may be realized with either A or B site cations and there are significant differences in their ordering mechanism[10-16]. In comparison with B cation ordering, A cation ordering is less explored [10-20] and the novel properties of A cation ordering is the focus of present study.

The appearance of colossal magneto resistance in the compound LaCaMnO3[21,22] is the motivating criteria to study the magnetic and electric transport properties of this compound as the effect of cationic ordering . The other excitement in this investigation is that while going deep into this study , one may encounter different interrelated phenomena such as insulator-metal transition, orbital ordering, charge ordering, double exchange, lattice, and magnetic polaron and so on.[23]. The problem of the interplay of magnetic, structural, and electric transport properties is an old one[24,25], but the discovery of high-temperature superconductivity brought it once again at the forefront. High Tc compounds usually have antiferromagnetic magnetic ordering while CMR compounds usually prefers ferromagnetic magnetic ordering[23-25].There are many reports about the doping of metal ions in manganites and its consequences of potential fluctuations of electrons in σ* bond, due to the larger difference in valance between La3+ and doped metal ions.[26,27]. Therefore the study of doped perovskite manganites may lead to the discovery of new compounds that demonstrates interesting magnetic and electric transport properties. In this paper, we study the electric and magnetic transport properties of the cation doped sample.

2. Experimental
2.1. Sample and its preparation
The poly crystalline powder sample La0.5Nd0.15Ca0.35MnO3 has been prepared using widely known ceramic technique called solid-state reaction method. The raw materials of high reagent graded (99.9%) purity chemicals wiz. lanthanum oxide (La2O3), calcium carbonate (CaCO3), neodymium oxide(Nd2O3), and manganese oxide(Mn2O3) were used as starting precursors. These high purity precursors were weighed in stoichiometric amounts and allowed for ball milling for a period of 48 hours. Thereafter the powder was mixed physically with an agate mortar and pestle in a medium of cyclohexane for a period of one week in order to achieve the required homogeneity. The pellet of this powder sample was then prepared under high pressure and it was again allowed for calcinations at 1100° C repeatedly with intermittent grindings to obtain sample of high crystalline in nature.

The room temperature powder X-ray diffraction pattern of the sample was collected with Bruker advanced diffractometer using Cu Ka radiation. The measurements were done in 10 to 100 range of 2θ with a step size of 0.02. The Reitveld refinement of this pattern was done with help of Fullprof software package. The AC and DC magnetic susceptibility of the sample was measured against temperature for a range of 10-300K using the SQUID Magnetometer. The resistivity of the sample were also taken with the help of superconducting magnets and four-probe arrangements.
3. RESULTS AND DISCUSSIONS

3.1 X-ray Analysis

The sharp and intense peak in the XRD pattern of the sample La$_{0.5}$Nd$_{0.15}$Ca$_{0.35}$MnO$_3$ is an indication of good crystallinity of the sample within the sensitivity limit of the diffractometer and it is corresponding to the perovskite structure. Fullprof software package was used to perform structural refinement. In the comparison of the observed pattern of the structure with the perovskite structure of existing manganites, it is possible to the conclude that this observed pattern is similar to the structure with ICDD card no.1521126 [27,28]. The refinement of the observed pattern given in figure: 1 indicate that it has an orthorhombic structure with Pbnm space group symmetry. The cell parameters thus obtained are $a=5.4505$, $b=5.4457$, $c=7.6876$. No secondary phase was observed in the sample, which strongly confirms the formation of a pure phase. The parameters used for the Rietveld refinement are a sixth-order Chebychev polynomial function for the background, Pseudo-vogit profile function, lattice parameters and atomic coordinates, etc. A good fit was obtained between the observed and calculated patterns. The fit parameters Rwp, Rp, and $\chi^2$ represented a good fit.

![Rietveld refined powder XRD pattern of La$_{0.5}$Nd$_{0.15}$Ca$_{0.35}$MnO$_3$](image)

3.2 Magnetic properties

The AC and DC magnetization measurements have been conducted in Zero magnetic field(ZFC mode) and in the presence of magnetic field(FC mode). The variation of magnetic susceptibility with variation of temperature was measured in these modes. This variation of DC and AC magnetization with temperature are shown in figure 2 and 3. The AC magnetization measurement shown figure 3 indicate a Paramagnetic to Ferromagnetic transition with decrease of temperature as this increases during decreasing of temperature and this transition occurs below a temperature called Curie temperature $T_C$. The cation doping may introduce the mixed valency in Mn as result a sufficient change may happen the Mn$^{3+}$/Mn$^{4+}$ ratio. The mixed valency of Mn may result in double exchange which is believed to one of the reasons for ferromagnetism in manganites [29,30]. The curie temperature can be obtained from the AC magnetization graph shown in figure 4 and it is found to be 206.3K. The observed Curie temperature $T_C$ is below that of the parent compound and this result is similar that observed in the compound La$_{0.7}$Sr$_{0.3-x}$Ag$_x$MnO$_3$,[31]. This is due to the super exchange interactions which become dominant over double exchange when Mn$^{4+}$ concentration becomes more than 30% in total value Mn ions. The ferromagnetic material obeys Curie –Weiss law shown by equation(1), where the sample shows spontaneous magnetization below $T_C$ and it behaves as a paramagnetic at temperature above $T_C$.

$$\chi = \frac{N g^2 \mu_B^2}{k_B T} \frac{1}{T - T_C}$$
\( \chi_m = \frac{C}{T-\Theta} \)  \hspace{1cm} (1)

Figure 3 demonstrates the variation of \(1/\chi_m\) versus temperature \(T\). The high temperature region of graph above \(T_C\) is linear, which is clear indication of Curie-Weiss behavior of sample. The constant \(C\) in equation (1) can be obtained from the \(1/\chi_m\) versus temperature \(T\) graph and it is found to be related to effective magnetic moment as

\[ \mu_{\text{eff}} = 2.828\sqrt{C} \] \hspace{1cm} (2)

The theoretical magnetic moments can be calculated from the following equation [40, 41]

\[ \mu_{\text{cal}} = \sqrt{1.15\mu^2_{\text{Nd}^{3+}} + x\mu^2_{\text{Mn}^{3+}} + y\mu^2_{\text{Mn}^{4+}}} \] \hspace{1cm} (3)

of where \(x\) and \(y\) are fractions of \(\text{Mn}^{3+}\) and \(\text{Mn}^{4+}\). The fractions of \(\text{Mn}^{3+}\) and \(\text{Mn}^{4+}\) present in the sample is found from equation 2 and 3 and this value is an observable indication for preference of super exchange over double exchange. The Curie constant \(C\) can also express as \(C = NPf\mu_B^2/3k_B\), where \(P_f\) is the effective magneton number of the manganese ions of the sample. But the small polaron contributes the electronic and magnetic transport properties of the sample. At a temperature below \(T_C\), the conductivity of the ferromagnetic phase is mainly due to the small polaron. The metal to insulator transition occurs at \(T_{\text{MS}}\), which almost coincide with \(T_C\) is a sharp transition. At temperature below \(T_C\), an ordering of magnetic moment occurs by Frank-Condon transition. This transition arises as the coexistence of parallel spin of the neighbouring sites. In polaron model the electrons move from \(\text{Mn}^{3+}\) ion to \(\text{Mn}^{4+}\) with the exchange of zero point phonons traveling in opposite direction for zero – momentum field transfer, which is the cause of phase coherence in magnetite [32] and it also requires a doubling of effective magneton number. The metallic behaviour of sample at a temperature below \(T_{MS}\) is also due to the mixed valence of \(\text{Mn}\) ion.

**Figure 2.** DC Magnetization curve of \(\text{La}_{0.5}\text{Nd}_{0.15}\text{Ca}_{0.35}\text{MnO}_3\)
Figure 3. Plot of $\chi_m^{-1}$ with the temperature of La$_{0.5}$Nd$_{0.15}$Ca$_{0.35}$MnO$_3$ for $T_C$ calculation

3.3 Electric Transport properties

Figure 4 represents the resistivity of the sample measured against temperature range (10K to 300K) in the presence of field (FC mode) and absence of field (ZFC mode) respectively. The resistivity measurements shown in the graph has good evidence of metal to semiconductor transition. The resistivity of the sample in the high temperature region of $\rho$-$T$ graph shows an increase in resistivity with decrease in temperature, which is a clear indication of its semiconducting behaviour. Such a semiconducting behaviour has reported in many literature.[33,34]. But if we carefully observe resistivity of sample continuously during the decrease of temperature, the temperature coefficient becomes abruptly positive after a particular temperature and it is due to the metallic nature of the sample. This transition temperature is called metal to semiconductor temperature ($T_{MS}$). The magnitude of $T_{MS}$ obtained from the graph is found to be close to $T_C$, which is a strong indication of mutual correlation of magnetic and electric transport properties of the prepared sample. This observations allow us to conclude that the sample is ferromagnetic-metallic at low temperature and paramagnetic-semiconductor at high temperature. The electric conductivity of the these sort of sample is mainly due to the hopping of electrons from the occupied Mn$^{3+}$ site to unoccupied Mn$^{4+}$. The cation doping may change or tilt Mn-O-Mn bond angle and it may increase the hopping of electrons from the occupied Mn$^{3+}$ site to unoccupied Mn$^{4+}$. This eventually might have decreased resistivity at low temperature.

There exist different models of conduction such as Arrhenius model, Small Polaron Hopping model and Mott’s variable Range Hopping model to explain the electrical conductivity mechanism in perovskite structures. Figure 5 shows that the resistivity of prepared sample is very well fitted with Small Polaron Hopping model (SPH) and the equation of resistivity according to this model is $\rho = \rho_0 T \exp \frac{E_P}{k_B T}$, where $E_P$ is the polaron hopping energy, $T$ is the absolute temperature, $k_B$ is the Boltzmann constant and $\rho_0$ is the pre exponential part of resistivity. The polaron hopping energy can be calculated from the slope of the fitting curve between $\log (\rho/T)$ versus $1/T$ and this values found to be good agreement with that of some of the previously reported cases.[34,35].
Figure 4. Resistivity versus temperature curve of $\text{La}_{0.5}\text{Nd}_{0.15}\text{Ca}_{0.35}\text{MnO}_3$

Figure 5. $\log(\rho/T)$ versus $1/T$ curve of $\text{La}_{0.5}\text{Nd}_{0.15}\text{Ca}_{0.35}\text{MnO}_3$
4. CONCLUSION

The conventional solid-state reaction method is used to prepare the cation doped sample La_{0.5}Nd_{0.15}Ca_{0.35}MnO_3. The structural, magnetic and electric transport properties of the sample have been investigated. The refinement of the XRD of sample revealed the formation orthorhombic perovskite structure in Pbnm space group symmetry. The correlated polaron model is used to explain the temperature dependence of the resistivity of the sample. The AC susceptibility and resistivity measurements revealed that the material has ferromagnetic-metallic behavior at low temperature and paramagnetic-semiconducting behavior at high temperature. The sharp decrease of magnetic susceptibility from its maximum value at a temperature $T_C$, is due to the Frank-Condon type of spin transfer of magnons of small order of energy. The charge transfer between Mn$^{3+}$ and Mn$^{4+}$ ions due to the exchange of phonon leads to the polaron type of electronic transport and magnetic order. Small Porelon Hopping model is found to be good to explain the electrical transport properties of the doped sample.

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