Study of structural, electronic and magneto transport properties of La$_{0.7}$Ca$_{0.2-x}$Sr$_x$Ag$_{0.1}$MnO$_3$

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Abstract. Structural, electrical and magneto transport properties of Lanthanum based manganites La$_{0.7}$Ca$_{0.2-x}$Sr$_x$Ag$_{0.1}$MnO$_3$ ($x=0$ & 0.1) synthesized by low temperature nitrate route is studied systematically. The X-ray Diffraction patterns confirm the presence of orthorhombic structure with Pnma space group. The temperature dependence of MR (-35\%) from 233 -272K for $x=0$ and an MR (-26\%) from 281 -309K for $x=0.1$ composition with an overall variation of 1\% is very much advantageous for device application. Interestingly, in low temperature regime, the MR value of -47\% obtained in $x=0.1$ composition at 10T around 5K is 20\% higher than the MR obtained at 10T around the metal insulator transition. Significant changes happening in the low temperature MR measurements is discussed in the light of electron-electron interactions and weak localization mechanisms while the additional broad hump responsible for flat MR is attributed to the intrinsic electronic in homogeneity driven phase competition created due to the presence of mono valent Ag ions. The complex localization mechanism associated with insulating regime is in accordance with Variable range hopping of small polarons.

1. Introduction

Research and development of high density magnetic storage devices requires materials with large magnetoresistivity (MR) at room temperature. In this context, manganites appear to be promising materials due to their colossal magnetoresistivity (CMR) property. The attempts of synthesis and characterization of manganite systems of different compositions are accordingly on the rise in recent years to produce large MR at room temperature. It is known that the physics of manganites is challenging due to the strong interplay between charge, spin, and lattice degrees of freedom [1]. Specifically the electronic transport properties and the CMR effect are understood in terms of Zener’s double exchange (DE) mechanism, strong electron-phonon interaction, charge and orbital ordering, average size of A-site cations ($\langle r_A \rangle$), oxygen stoichiometry and so on[2]. One of the main challenges in CMR property is that the MR reaches a peak at metal to insulator transition temperature and hence shows a strong dependence of temperature. A temperature independent MR that too around the room temperature is very much preferable for device applications. Among the different types of manganites, Lanthanum based manganites of type La$_{1-x}$A$_x$MnO$_3$, ($A = \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}, \text{etc.}$) have been extensively studied and the ground state is found to be ferromagnetic metallic due to the creation of mixed valence of manganese ions (Mn$^{3+}$ & Mn$^{4+}$). A metal–insulator transition is also found to occur close to Curie temperature ($T_C$) accompanied with a very large magneto-resistivity. Similarly, the substitution
of mono valent cations such as Na⁺, Ag⁺, etc., partly in the place of trivalent lanthanum La³⁺ ions also creates mobile carriers to form a ferromagnetic metallic ground state. Among the monovalent manganites, the silver (Ag) doped lanthanum manganites exhibit significantly lower resistivity and 25% MR is reported at room temperature [3]. In the present paper, the structural, electronic and magneto resistive transport properties of silver doped manganites La₀.⁷Ca₀.₂₋ₓSrₓAg₀.₁MnO₃ (LCSAMO) are investigated systematically. Creation of intrinsic chemical inhomogeneity is utilized as a tool to realize the temperature independent MR in these manganite systems.

2. Experimental
The synthesis of La₀.⁷Ca₀.₂₋ₓSrₓAg₀.₁MnO₃ (x=0 & 0.1) manganites is carried out through the low temperature nitrate route [4]. The phase purity of the samples is checked using Philips X-ray diffractometer (XRD) with Cu-kα radiation (λ=1.5406 Å) and XRD patterns are recorded in angular steps of 0.02°. The temperature dependent electrical resistivity and magneto resistivity of the samples are measured using Quantum design Physical Property Measurement System (PPMS) down to a temperature of 2K and upto a magnetic field of 10T.

3. Results and analysis
3.1 Structural properties
The XRD patterns of all the samples are recorded at room temperature in the angular range of 10-80°. The XRD patterns are analyzed with Rietveld’s method using FULLPROF program which confirms orthorhombic crystal structure with Pnma space group as shown in figure 1 for x=0. The average crystallite size is calculated using Scherrer’s formula and is found to be in the range of 22 to 27 nm.

3.2 Electronic Transport
The electrical resistivity of samples is measured as the function of temperature from 2 to 380 K and the magnetic field is varied up to 10 T. The zero field resistivity as a function of temperature shown in figure 2 reveals two transition peaks at T_p₁ and T_p₂ as the temperature is lowered from 380 K. The peak appearing at T_p₁ (290K for x=0) is found to decrease as the percentage of Sr is increased (313 K for x=0.1) at the expense of Calcium and systematic shifting of these two peaks due to Sr doping is in accordance with the literature [7].

The temperature dependent electrical resistivity of samples for different magnetic field strengths is shown in figure 3 and figure 4. The first peak at T_p₁ is found to disappear for all the samples as the magnetic field is increased. The hump observed at T_p₂ of the samples however is observed to shift to higher temperatures with the increase of magnetic field. With the increase of magnetic field strength, ρ (T) is found to decrease significantly as e_g carriers suffer less scattering during hopping process due to favourable alignment of spins at t₂g orbitals of Mn sites.

Figure 1. Rietveld fits for XRD patterns of La₀.⁷Ca₀.₂₋ₓSrₓAg₀.₁MnO₃ (x=0).

Figure 2. Temperature dependent resistivity of LCSAMO (x=0 & 0.1).
Decrease of electrical resistivity is observed with the increase of magnetic field strength. This negative magneto resistivity is usually calculated by the following formula.

$$\text{MR} = \frac{\rho(T, H) - \rho(T, H = 0)}{\rho(T, H = 0)} \times 100\%$$

Where $\rho (T, H)$ and $\rho (T, H=0)$ are the resistivity of samples measured in applied and zero magnetic field respectively. MR as a function of temperature for different magnetic fields is shown in right axis of figure 3 and figure 4. It is clear from the figure that the MR increases significantly with the increase of magnetic field around MIT. MR around the MIT reaches a maximum value of 40% for $x=0$ and 26% for $x=0.1$ composition in an applied magnetic field of 10T. Interestingly a weak temperature dependence of MR (-35%) from 233-272K for $x=0$ and an MR (-26%) from 281-309K for $x=0.1$ composition is observed respectively with an overall variation of 1% as given by highlighted region in figure 3 and figure 4. This is advantageous for memory device applications. Only few reports using either hetero structures or by composites are available in literature, which addresses the issue of broadening the temperature dependence of MR [8]. In lower temperature regime a maximum MR of 48% for $x=0$ and 47% for $x=0.1$ is observed respectively in an applied magnetic field of 10T. In order to understand the interesting features observed in MR, different models are used to fit the temperature dependent resistivity measurements.

The electronic transport behaviour specifically in the low temperature range is usually explained using various models [9-11] that combine various mechanisms including weak localization and electron–electron scattering. The resistivity of the sample is fitted using the following equation (1) in the temperature $T<T_P$.

$$\rho(T) = \rho_0 - \rho_1 T^{1/2} + \rho_2 T^2 \quad (1)$$

The fitting graphs of $\rho (T)$ for zero field and magnetic field strength of 10 T are shown in figure 5 and figure 6. The fitting data shows reduction in $\rho_0$ from $3.38 \times 10^{-4}$ to $1.62 \times 10^{-4}$ for $x=0$ and $3.28 \times 10^{-4}$ to $1.66 \times 10^{-4}$ for $x=0.1$ sample. The behaviour of $\rho_2$ for the increase of magnetic field strength is observed to be similar [12].

Attempt is made to fit the electrical resistivity data in the high temperature range to popular models such as small polaron model (SPM) and Mott’s variable range hopping (VRH) model. In the adiabatic regime where the charge carrier motion is faster than the lattice vibrations, the small polaron hopping is described by the following equation.

$$\rho = A \ T \exp \left( \frac{E_a}{k_B T} \right) \quad (2)$$

Where the constant $A$ is linked to scattering by impurities, defects, grain boundaries and domain walls, $E_a$ is the activation energy and $k_B$ is the Boltzmann’s constant. The fitting of resistivity data of samples with the SPM is shown in figure 5 and figure 6. The mechanism of electron hopping between states of nearly equal energy is described by the VRH model as given below.

$$\rho(T) = \rho_0 \exp \left[ \left( \frac{T}{T_0} \right)^{\nu} \right] \quad (3)$$

Where $\rho_0$ is the temperature independent parameter and $T_0$ is the characteristic temperature [13]. The fit of resistivity data with VRH model is shown in figure 5 and figure 6. The characteristic temperature is found to decrease with the increase of $x$ indicating a decrease in effective mass of carriers and
broadening of \( e_g \) electron band width [9]. The further decrease of \( T_o \) with increase of magnetic field shows reduced bending of Mn-O-Mn bond and further broadening of \( e_g \) electron bandwidth [14]. Comparing the performances of the above models in fitting the resistivity data, the VRH model is found to be marginally better than the small polaron model in the high temperature paramagnetic domain. In manganites systems a strong electron phonon coupling due to \( \sigma^2 \) (variation in A site ionic radius) variation is reported to show small polaron conduction mechanism in paramagnetic regime [15]. Localization mechanism which is weak in nature such as disorder or magnetic localization indicates the presence of large spin polarons and the transport is in accordance with VRH model [16].

In our present investigation even though VRH appears more applicable in paramagnetic domain, the resistivity can also be accounted by small polaron model. A recent report in manganites predicts VRH in small polarons especially above the MIT [17].

4. Discussion
The occurrence of MR close to metal to insulator transition (\( T_{MI} \)) reveals the intrinsic contribution of samples. The second broad peak or the hump noticed at \( T_{p2}=280 \) K for \( x=0.1 \) is indicating the phase separation induced by intrinsic chemical inhomogeneity [18]. Substitution of non magnetic \( Ag^+ \) ions is known to give rise to a random distribution of A-site ions and consequentially the \( e_g \) electrons are believed to experience site to site local distortion as they move through the crystal grains. Moreover for every mono valent \( Ag^+ \) ion substituted for the trivalent \( La^{3+} \) ion, two \( Mn^{3+} \) ions oxidized to \( Mn^{4+} \) ions giving rise to individual regions rich in \( Mn^{4+} \) and \( Mn^{3+} \) respectively. This in turn is reported to induce electron inhomogeneity leading to phase separation in ferromagnetic metallic (FMM) phases in the hump region. A strong competition between enhanced double exchange mechanism in FMM region promoted by magnetic field and phase separation created by enhanced \( \sigma^2 \) has led to the weakly temperature dependent magneto resistance in the investigated LCSAMO samples around the MIT transition. This has also reflected in complex localization mechanisms observed as very low temperature as well as at high temperature regime which demand more than a single model to describe the nature of electrical transport.

5. Conclusion
The structural, electrical and magneto transport properties of manganite system \( La_{0.7}Ca_{0.2-x}Sr_xAg_{0.1}MnO_3 \) (\( x=0 \) & 0.1) synthesized through nitrate route are investigated. The temperature dependent electrical resistivity \( \rho(T) \) of samples shows two transition peaks which signifies a significant competition between double exchange mechanism and magnetic phase separation below MIT. The complex insulating nature at the high temperature regime is attributed to the VRH of small polarons. The anomalous low temperature behavior is explained in terms of a model which combines electron-electron scattering and weak localization. The study of magneto transport behavior reveals broad weakly temperature dependent magneto resistance at room temperature which can be exploited for magnetic sensing applications.
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