Tunnelling mafnetoresistance of (1 – \(x\))La\(_{0.7}Ca_{0.3}\)MnO\(_3\) +\(x\)Ag composites

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Abstract. Magnetization and transport of (1 – \(x\))La\(_{0.7}Ca_{0.3}\)MnO\(_3\) +\(x\)Ag (\(x\) = 0, 0.1, 0.2, 0.3, 0.4 and 0.5) composites has been reported in this paper. Low Field Magnetoresistance (LFMR), conductivity (\(\sigma\)) and metal – insulator transition temperature (\(T_p\)) increases with increasing content of Ag. Due to the presence of nomagnetic Ag in the ferromagnetic La\(_{0.7}Ca_{0.3}\)MnO\(_3\) material, dc magnetization decreases but the corresponding \(T_p\) increases. Based on the spin polarized transport of conduction electrons at the grains boundaries, we find that our experimental data (\(MR – H\)) agree quite well with the dependence of temperature on tunneling magnetoresistance (TMR) described by an expression of Hwang et al.

Keywords: CMR manganite, low-field magnetoresistance, nanomanganite composites, tunnelling magnetoresistance, low-temperature resistivity.

1. Introduction
The discovery of the colossal magnetoresistance (CMR) effect in manganites \(^{[1, 2]}\) has caused a renewed interest in these perovskites, which have been known for more than 50 years \(^{[3, 4]}\). Much research has been done on the manganites Re\(_{1-x}A_x\)MnO\(_3\) (Re = rare earth, A = Ca, Sr, Ba). So far, two CMR effects have been found in these manganites, the intrinsic CMR and extrinsic CMR. The intrinsic CMR \(^{[5]}\) is caused by the double exchange (DE) mechanism. The DE mechanism, which was proposed by Zener in 1951 \(^{[6]}\), is useful to explain the CMR phenomena observed near Curie temperature (\(T_C\)) at a relatively high magnetic field (up to several kOe). The extrinsic CMR, which is related to the grain boundaries \(^{[7]}\), can be explained by spin polarized tunneling \(^{[5]}\) or spin dependent scattering \(^{[7]}\). Unfortunately, as temperature increases, the low field grain boundary magnetoresistance decreases rapidly, hindering the utilization of this effect in sensor application.

Recently, experiments have indicated that the Ag-doped manganites can exhibit an improved \(T_C\), metal – insulator transition temperature (\(T_p\)), temperature coefficient of resistance (TCR) and an enhanced extrinsic MR effect \(^{[8-12]}\). All the above mentioned results indicate that Ag-doped samples have improved MR effect and a significant low field magnetoresistance (LFMR) as compared with the undoped counterpart. In addition, these Ag-doped samples, in most cases, are two phase composites, in which the Ag metal phase occurs in the form of the second phase at grain boundaries and interfaces.
In this paper we investigate the effects of Ag concentration on the LFMR of the bulk polycrystalline $(1-x)\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 + x\text{Ag}$ samples. Significant enhancements in $T_p$, dramatic reduction in resistivity, and also an improved LFMR are observed.

2. Experimental

$(1-x)\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 + x\text{Ag}$ (LCMO/Ag) with $x = 0, 0.1, 0.2, 0.3, 0.4$ and $0.5$ samples were prepared by two steps. Firstly, the LMCO powder was prepared by the sol–gel process. Secondly, appropriate amounts of LMCO and Ag$_2$O powders were mixed according to the desired molar ratio. Then the mixtures were ground and pressed into pellets. The pellets were finally sintered at 900°C in air for 2 h, and then slowly furnace-cooled to room temperature. The crystalline structure of the samples was characterized by the X-ray diffraction. Magnetic properties were measured by a vibrating sample magnetometer (VSM) in the temperature range 100–300 K and in a field up to 5 kOe. The resistivity and the magnetoresistance ($MR – H$) of all the composites were examined by the PPMS (Physical Property Measurement Systems) in a magnetic field from 0 to 3 kOe at a temperature range from 5 to 300 K.

3. Result and discussion

The phases of samples were characterized by X-ray diffraction (XRD) with Cu Kα radiation. Figure 1 shows the XRD patterns of LCMO/Ag composite samples with $x = 0$ and 0.5. The XRD patterns of the composites with $x = 0.1 \div 0.5$ show two different sets of diffraction peaks, corresponding to orthorhombic LCMO perovskite and cubic Ag phases, respectively, which clearly indicates the coexistence of LCMO and Ag phases. The pure LCMO sample has an orthorhombic unit cell with lattice parameters: $a = 5.462$ Å; $b = 7.720$ Å; $c = 5.478$ Å. The lattice parameters of LCMO in the LCMO/Ag composite do not change within the accuracy of diffractometer. This shows that LCMO maintains its identity and there is no reaction between LCMO and Ag is introduced as second phase and on the surfaces of the LCMO grains. The direct evidence of the coexistence of two phases also comes from SEM micrographs. The representative SEM micrographs of $(1-x)\text{LCMO}/x\text{Ag}$ composites are shown in figure 2. The interfaces between Ag and LCMO can be distinguished clearly. Moreover, energy dispersive X-ray (EDX) spectra of the doped composite for $x = 0$ and $x = 0.5$ shows the silver peak along with La, Ca, Mn and O peaks, which also supports the presence of Ag in the doped composites.

![Figure 1. XRD patterns of $(1-x)\text{LCMO} + x\text{Ag}$ composite.](image-url)
The temperature dependence of magnetization at 5 kOe for LCMO/Ag composites is shown in figure 3. The value of magnetization ($M$) at 100 K can be seen in figure 4, and it is clear that the decrease in $M$ is due only to the silver percentage present in the sample, which leads us to take into account the extra magnetic disorder caused by Ag in the composites. This extra magnetic spin disorder is induced by grain boundaries in the composites and suggests the suppression of DE mechanism resulting suppression of the ferromagnetic alignment of Mn ions. Since the Ag is not incorporated into the LCMO lattice, and it segregates into the grain boundaries or interfacial regions, which blocks the Mn spins at grain boundaries and increases the anisotropy in the interfacial regions and misalignment of the magnetic moments of the neighboring FM domains [13]. Therefore, despite the nonmagnetic character of Ag, it is expected to increase the magnetic disorder by disrupting the Mn-O-Mn bonds in
the interfacial regions and hence suppression of the long range FM order. Moreover, the paramagnetic (PM) to ferromagnetic (FM) phase transition temperature ($T_C$) determined from the peak of $dM/dT$ is almost independent of Ag content and is $\sim 260$ K for all the samples. This is due to the fact that the PM-FM phase transition is an intrinsic and intragrain property. The observed constancy of $T_C$ also indicates that stoichiometry of LCMO phase within the grains remains essentially unchanged as Ag is not accommodated within the perovskite structure and it sits only at the grain boundaries and on the surfaces of LCMO grains.

Figure 5 shows the temperature dependence of zero field resistivity ($\rho$) for the composites measured in the temperature region from 5 to 300 K. Results show that: (i) $\rho$ decrease with Ag addition; (ii) adding Ag in LCMO sharpens the $\rho$ peak and shifts the peak temperature of $\rho$, $T_p$, to higher temperature.

Several authors [14-16] attempted to explain the thermal variation of electrical resistivity of Ag doped manganites. In an earlier attempt, Pi et al. [15] computed the total resistivity of $La_{0.67}(Ca_{0.65}Ba_{0.35})_{0.33}MnO_3/Ag_x$ composites assuming metal Ag segregated at the grain surfaces or boundaries improves the atomic disordered structure and magnetic state on the grain surfaces and increases the connectivity between the grains. The change of $\rho$ peak can illuminate the improvement of grain boundaries. Later, Yuan et al. [14] proposed that in Ag doped manganites, there is the existence of high conductive metal Ag among the grains opens a new channel for the electron transport, which also decreases $\rho$ of the samples. Li et al [16] reported that the increased oxygen content released from Ag$_2$O in the sintering process not only improves the magnetic inhomogeneity of the samples and decreases the microstructure deficiency, but also enhances the concentration and hopping mobility of carriers through a little change of Mn$^{3+}$/Mn$^{4+}$ ratio.

Figure 6 displays the magnetic field dependence at 30 K of the LFMR of LCMO/Ag composites in $H = 3kOe$. It can be observed from this figure that the MR ratio increases significantly with Ag addition, LFMR reaches the maximum when $x = 0.2$ and then decreases. The maximum LFMR for $x = 0.2$ samples is as large as 29%, larger than that of pure LCMO (about 25%).

The great change of the resistivity of the Ag-added samples is not closely related to the grain size as mentioned above. So the enhancement of MR should not closely relate to the grain size. We attribute the large enhancement of LFMR to that the Ag addition improves the crystal structure and magnetic homogeneity of the grains and grain boundaries. These improvements are favorable to the increase in intrinsic properties of the compound, especially to the decrease in $\rho$ dramatically. The $\rho$ decrease is also an important factor inducing MR ratio to increase. The smaller is $\rho$ of the sample, the larger is the relative change of LFMR.
In order to further illuminate the intrinsic property of the MR behavior observed in this Ag-added composite, we survey the field dependence of \( MR \) at various for \( x = 0, 0.2 \) and 0.5. Our primary approach is to separate out the part of the \( MR \) originating from SPT (\( MR_{\text{spt}} \)), from the part of the \( MR \) identified by the suppression of spin fluctuation (\( MR_{\text{int}} \)), and mainly to inspect their respective temperature dependencies. For this purpose, we have used the model as proposed by Raychaudhuri et al. [17] and Dey et al. [18], based on SPT transport of conduction electrons at the grain boundaries with attention paid to the magnetic domain wall motion at grain boundaries under the application of a magnetic field. According to this model we following expression for \( MR \)

\[
MR = -A \int_{0}^{H} f(k)dk - JH - KH^3. \tag{1}
\]

Within the approximation of the model, in zero field, the domain boundaries are pinned at the grain boundary pinning centers having pinning strengths \( k \). The grain boundaries have a distribution of pinning strengths (defined as the minimum field needed to overcome a particular pinning barrier) given by \( f(k) \), expressed as:

\[
f(k) = A \exp(-Bk^2) + CK^2 \exp(-Dk^2). \tag{2}
\]

All adjustable fitting parameters, \( A, B, C, D \) are required to known from a nonlinear least square fitting to calculate \( MR_{\text{spt}} \), which is defined as:

\[
MR_{\text{spt}} = - \int_{0}^{H} f(k)dk. \tag{3}
\]

Differentiating equation (1) with respect to \( H \) and using equation (2), we obtain

\[
\frac{d(MR)}{dH} = A \exp(-BH^2) + CH^2 \exp(-DH^2) - J - 3kH^2. \tag{4}
\]

Figure 7. a) Derivative of the experimental (MR-H) curve (dot) and the fitted curve (line) using equation (5) at 30 K in the magnetic field range of \( (1 - 3 \text{kOe}) \) for sample with \( x = 0, 0.2 \) and 0.5. b) Experimental (MR-H) curve (dot) and the fitted curve (line) using equation (2) at various temperatures in the magnetic field range of \( (0 - 3 \text{kOe}) \) for sample with \( x = 0, 0.2 \) and 0.5.

The experimental (\( MR-H \)) curves were differentiated and fitted to equation (4) to find the best-fit parameters at several temperatures. Figure 7a shows the differentiated curve and the best-fit function at \( T=30K \) for \( (1-x)\text{LCMO/Ag} \) composite samples. Using the best fit parameters we have fitted equation (1) to our experimental \( MR \) versus \( H \) curves at several temperatures. Figure 7b shows
excellent fit for the experimental curves to equation (2) for samples at several temperatures below $T_C$. We observe that the total magnetoresistance is a nonmonotonic function of temperature with a slow decrease at low temperature followed by the increase as we approach $T_C$. The intrinsic contribution $MR_{\text{int}}$, however, follows the expected DE behavior with a steady increase of temperature. On the other hand $MR_{\text{spt}}$ decreases steadily with temperature. In order to elucidate the basic physics behind temperature dependence of $MR$, Dey et al. [18] believed that the nature of the surface region of nanosize grains plays a very crucial role in electrical transport, magnetic and magneto-transport behavior of nanodimensional systems. When grain size of LCMO are 17 nm and 27 nm, $MR_{\text{spt}}$(H) remains constant up to a high temperature (about $T \sim 200$ K) and then drops sharply with temperature. This effect gets enhanced with the decrease in particle size. This result for nanodimensional manganites is in contrast to the results reported by Hwang et al. [1] for La$_{0.67}$Sr$_{0.33}$MnO$_3$ polycrystalline sample prepared through conventional solid-state reaction process in air and thus have a large grain size ($\sim \mu$m). According to them the part of the MR most clearly identified with spin-polarized tunneling shows a gradual decrease with an increase of temperature. They had observed earlier that the temperature dependence of $MR_{\text{spt}}$ is described quite well by an expression of the type $a + b/(c + T)$, which is a characteristic of spin polarized tunneling in granular ferromagnetic systems.

![Figure 8](image-url)

**Figure 8.** Temperature dependence of various components of magnetoresistance (MR) at 3kOe. (■) is the total MR, (○) is the spin polarized contribution to the magnetoresistance ($MR_{\text{spt}}$), (▲) is the intrinsic contribution $MR_{\text{int}}$. The inset shows the best fit of $MR_{\text{spt}}$ to a function $a + b/(c + T)$ with $x = 0$; $x = 0.2$ and $x = 0.5$.

Figure 8 shows the best fit of $MR_{\text{spt}}$ with the expression $a + b/(c + T)$. The fitted curve matches well with the extracted values of $MR_{\text{spt}}$ from model. However our values of $b$ and $c$ for the best fit are much higher compared to that observed by Hwang et al. although the $T_C$ of our system is much smaller. The reason for this may be related to the structure of the composite. Ag distributed mostly at the grain boundaries can alter the grain behaviour like its size, magnetic and conducting properties. These procedures will significantly influence the tunnel of conduction electrons and hence enhanced $MR$ will be expected. In this context we should note that the intergranular spin polarized tunneling have different temperature dependences for ferromagnetically and superparamagnetically coupled grains [19].

All the samples show the unusual low temperature resistivity minimum at some $T_{\text{min}}$ (figure 5). The reresistivity upturn at $T < T_{\text{min}}$ in polycrystalline manganites is usually attributed to models such as Coulomb blockade (CB) [20], enhanced electron-electron interaction [21], or could be due to the Kondo effect [22, 23]. Here one encounters the phase coherence of two electrons, both becoming localized through elastic impurity scattering. The correction to the electrical conductivity is given by [24, 25]

$$\sigma(T) = \sigma(0) + BT^{1/2},$$

(5)

where $\sigma(0)$ is the residual conductivity contributed by the temperature independent scattering processes and $B$ is proportional to the diffusion constant. However, inelastic scattering, which increases monotonically with temperature, competes with the $e$-$e$ interaction [which decreases with temperature as given in equation (6)] and gives rise to the resistivity minimum. Assuming that all the
temperature dependent scattering processes, like electron-phonon, electron-magnon, and electron-electron, are adequately described by a single power law (\( AT^n \)), one could write
\[
\rho(T) = \frac{1}{\sigma(0) + BT^{1/2} + AT^n},
\]
assuming Mathiessen’s rule [24].

**Figure 9.** Resistivity (\(\rho\)) vs T plots for (1-x)LCMO/xAg. The solid lines are the best fits to equation (6).

**Figure 10.** The best fitted parameters \(\sigma(0), B, A, n\) [see equation (6) for definition] are plotted with \(x\) for LCMO/Ag. The solid lines are just guides to the eye.

**Figure 11.** \(T_{\text{min}}\) and the depth of the minima are plotted against \(x\) for LCMO/Ag. The solid lines are just guides to the eye.

**Table 1.** Best fit parameters obtained from equation (6).

| (1-x)LCMO/xAg | \(\sigma(0)/(\Omega cm)\) | \(B/(\Omega cmK^{1/2})\) | \(A/(10^{-5} \Omega cm/K^n)\) | \(n\) |
|---------------|-----------------|-----------------|-------------------|----|
| \(x = 0\)    | 0.82            | 0.15            | 22.58             | 1.64 |
| \(x = 0.1\)  | 2.47            | 0.18            | 4.04              | 1.85 |
| \(x = 0.2\)  | 3.65            | 0.21            | 1.83              | 1.94 |
| \(x = 0.3\)  | 4.71            | 0.26            | 1.33              | 1.96 |
| \(x = 0.4\)  | 5.17            | 0.26            | 1.17              | 1.97 |
| \(x = 0.5\)  | 7.30            | 0.36            | 0.66              | 2.03 |
The $\rho(T)$ data for all samples shown in figure 9, are fitted to equation (6). Excellent fits are obtained as shown by the solid lines in figure 9. The coefficients of the fits are given in table 1. The best fitted coefficients $\sigma(0)$, $B$, $A$ and $n$ are plotted against $x$ (is Ag content) in figure 10. The decrease of $A$ with $x$ is understandable in view of the decrease in the depth of minima as shown in figure 11. The inelastic scattering temperature exponent $n$ varies from 1.64 to 2.03 with $x$ increases 0 to 0.5. Tiwari and Rajeev [26] found $n = 2.4$ at $H = 0$ in La$_{0.7}$Ca$_{0.3}$MnO$_3$ were prepared by the conventional solid sate method, while Kumar et al. [24] found $n = 1.9$ at $H = 0$ in La$_{0.7}$Ca$_{0.3}$MnO$_3$ thin film compared to $n = 1.64$ of ours. The $\sigma(0)$ increases with $x$.

4. Conclusion
In summary, $(1 - x)$LCMO/$x$Ag composites were prepared by a sol-gel process. The XRD and SEM results show that no reaction between Ag and LCMO takes place, and most Ag is distributed at the grain boundaries. We have studied the effect of Ag on microstructure and low field magneto transport properties of $(1 - x)$LCMO/$x$Ag. As the Ag content increases, the ferromagnetic-paramagnetic (FM-PM) transition temperature remains almost constant, the metal-insulation transition temperature shift towards higher temperatures. The unusual low temperature upturn in resistivity minimum is seen for all the samples. The observed resistivity minimum is explained very well in terms of the electron-electron interaction. It has been found that LFMR increases as the Ag content increases. This enhanced LFMR is due to increased spin polarized tunneling behavior at lower temperature. We have analyzed our experimental MR data following a phenomenological model to separate out the MR arising from spin polarized transport, from the intrinsic contribution in our nanosize $(1 - x)$LCMO/$x$Ag composite samples. It is found that the temperature dependence of the LFMR displays a Curie-Weiss law-like behavior, i.e. $LFMR(T) = a + b/(c + T)$, and the fitting parameter $c$ increases monotonically when increasing the Ag content. A detailed study on magnetic behavior and magnetoresistance properties is in progress and results will be forthcoming.

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