Electrical Transport and magnetoresistance properties of \( \text{La}_{0.8}\text{Ca}_{0.2-x}\text{Ag}_{x}\text{MnO}_3 \) \((x = 0 \text{ and } 0.05)\)

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Abstract. A systematic investigation of electrical transport and magnetoresistance properties of polycrystalline \( \text{La}_{0.8}\text{Ca}_{0.2-x}\text{Ag}_{x}\text{MnO}_3 \) \((x = 0 \text{ and } 0.05)\) is reported in this work. According to the resistivity data measured from 40 to 250 K, transition from metallic to insulator behavior upon heating were observed in both samples. Additionally, 5\% silver substitution shifts the metal-semiconductor transition into a higher temperature. Furthermore, silver substitution also decreases the overall temperature compared to the original compound. In this work, this result can be well described using electron-electron, electron-phonon, and the interaction between electron, phonon, and magnon. Resistivity measurements under magnetic field influence shows that silver substitution improves the magnetoresistance properties compared to the original compound. The maximum ratio of magnetoresistance at 285 K was found to be 3.3\% and 4.7\% for \( x = 0 \) and 0.05, respectively.

1. Introduction

Substituted perovskite manganite system have been the subject of many researches in recent years due to its remarkable electrical and magnetic properties \([1-3]\). The remarkable properties of these materials hold a high significance as it can be applied for spintronic devices which are useful in daily life. One of the most studied properties of a substituted perovskite manganite is magnetoresistance property. This property enables a material to exhibit a reduction in the resistivity under the influence of external magnetic field. Understanding this property is essential in order to enhance the potential of this material to be applied in daily life.

During the last decade, \( \text{La}_{1-x}\text{Ca}_x\text{MnO}_3 \) (LCMO), as one of the most studied example of substituted perovskite manganite, have been extensively studied due to its colossal magnetoresistance property which could reach up to 1000\% for its MR ratio \([1]\). Although there have been numerous studies about LCMO material, there is still much to explore regarding the physical properties of this material. Recent study has shown that double exchange framework alone does not enough to fully understand the fundamental of electrical transport and magnetic properties of a substituted LMO based material \([4]\). Thus, it is important to deploy another framework to analyze the electrical properties and magnetic properties of these type of material.

Earlier studies have shown that substitution by monovalent on an LMO based material can enhance the \( \Delta S_m \), MR\%, and RCP values of a substituted LMO based material \([5, 6]\). Thus, in this work, the
electrical transport and magnetoresistance properties of La$_{0.8}$Ca$_{0.2}$Ag$_{x}$MnO$_3$ ($x = 0$ and 0.05) are reported. Furthermore, the electrical properties of the material were analyzed using percolation model. This model was used as it can explain the resistivity behavior of a LaMnO$_3$ (LMO) based compound through whole temperature range.

2. Experimental

Polycrystalline sample of La$_{0.8}$Ca$_{0.2}$MnO$_3$ (LCMO) and La$_{0.8}$Ca$_{0.15}$Ag$_{0.05}$MnO$_3$ (LCAMO-05) were prepared using sol-gel method which have been reported previously [7]. Furthermore, both samples were calcined at 500 °C for 5 hours and sintered at 1000 °C for 24 hours. The resistivity of both samples were measured by standard four points probe method using cryogenic magnetometer in a temperature range from 10 to 290 K with a variation of magnetic field from 0 to 1T.

3. Result and Discussion

The temperature dependence resistivity of LCMO and LCAMO-05 samples without the influence of external magnetic field can be seen from Figure 1. It was observed that silver substitution decreases the overall resistivity of the sample. This can be addressed to the enhancement in the double exchange mechanism as silver ions substitute calcium ions [5, 6]. This argument can be investigated by calculating the amount of Mn$^{3+}$ and Mn$^{4+}$ ions inside the sample. Similar study by Lakshmi et al. have mentioned that in silver substituted La$_{1-x}$Ca$_x$MnO$_3$ compound, the amount of Mn$^{4+}$ ions will increase as many as the number of calcium ions added with the amount of silver ions [8]. The ionic stability of the present compound is given by La$_{0.8}$Ca$_{0.2}$xAg$_{x}$Mn$^{3+}$$_{(1-(0.2+x))}$Mn$^{4+}$$_{(0.2+x)}$O$_3$. Based on this chemical formula, for every x amount of silver ion, there will be (0.2+x) amount of Mn$^{4+}$ ions. In particular case, without silver ions the amount of Mn$^{4+}$ ions are 0.2 while the amount of Mn$^{4+}$ ions after 5% silver ions was substituted increases to 0.25. It has been commonly known that the best magnetic and electrical properties of a substituted LMO based compound was achieved when the amount of Mn$^{4+}$ ions approaches 30 to 33% [9, 10]. Thus, in this work, silver substitution leads to the increase of Mn$^{4+}$ ions which also improve the conductivity of the sample.

Additionally, the decrease in overall resistivity also in parallel with the increase in average bond angle ($<$Mn-O-Mn$>$) while reducing the average Mn-O bond length ($<$Mn-O$>$). These results will affect the transport of electron which becomes easier at bigger value of average bond length and smaller value for average bond length [11]. Based from Figure 1, both LCMO and LCAMO-05 samples exhibit the same electrical behavior which is a transition from metallic behavior at low temperature and insulator behavior at high temperature. The transition happened at certain temperature which usually known as metal-insulator transition ($T_{mi}$).

![Figure 1. Temperature dependence of resistivity at zero magnetic field for LCMO and LCAMO-05 samples.](image-url)
In order to understand the transport mechanism of both samples, a theoretical model is used in this work. Several earlier researches have shown that the metallic behavior of a substituted LMO based compound can be well described using mathematical expression written as Equation 1.

\[
\rho(T) = \rho_0 + \rho_2 T^2 + \rho_{9/2} T^{9/2}
\]  

(1)

where \(\rho_0\) term represents resistivity due to grain boundary, \(\rho_2 T^2\) term represents resistivity due to electron-electron scattering, and \(\rho_{9/2} T^{9/2}\) term represents resistivity due to a series of combination between electron-electron, electron-magnon, and electron-phonon scattering. Although Equation 1. can explain metallic behavior of a substituted LMO based compound, it fails to explain the minimum resistivity which often occurred at temperature below 60K. This minimum resistivity usually known as kondo effect [12]. In order to explain the additional kondo effect, Equation 1 needs to be modified into Equation 2.

\[
\rho(T) = \rho_0 + \rho_e T^{1/2} - \rho_s \ln T + \rho_p T^5 + \rho_2 T^2 + \rho_{9/2} T^{9/2}
\]  

(2)

where \(\rho_e T^{1/2}\) term represents resistivity due to electron-electron interaction, \(-\rho_s \ln T\) term represents resistivity due to kondo-like spin dependent scattering, and \(\rho_p T^5\) term represents resistivity due to electron-phonon interaction. According to several researches, the insulator behavior of a substituted LMO based compound at high temperature can be explained using two different theoretical approaches which are Variable Range Hopping (VRH) and Adiabatic Small Polaron Hopping (ASPH) [13, 14]. However, in this work, the data obtained was best fitted with ASPH model written in Equation 3

\[
\rho(T) = \rho_a T \exp \left( \frac{E_a}{k_B T} \right)
\]  

(3)

where \(\rho_a\) represents residual resistivity, \(E_a\) is activation energy for hopping conduction, and \(k_B\) is Boltzmann constant. In order to explain the transport mechanism at low and high temperature simultaneously, percolation model which was proposed by Li et al. can be used. In this model, Li et al. proposed that ferromagnetic metal and paramagnetic insulator phases coexisted in a substituted LMO based compound through the whole range temperature [15]. According to percolation model, the resistivity of a substituted LMO based compound can be expressed as equation 4.

\[
\rho(T) = \rho_{FM} f + \rho_{PI} (1 - f)
\]  

(4)

where \(f\) is volume fraction of ferromagnetic metal phase which follows Boltzmann distribution as written in equation 5.

\[
f = \frac{1}{1 + \exp \left( \frac{-U_0}{k_B T} \left( 1 - \frac{T}{T_{cmod}} \right) \right)}
\]  

(5)

where \(U_0\) represents the energy difference between ferromagnetic metal (FM) phase and paramagnetic insulator (PM) phase at a temperature below its Curie temperature and \(T_{cmod}\) is the theoretical Curie temperature. Combining equation 2 to equation 5, the resistivity of a LMO based manganite through the whole temperature can be explained using equation 6.

\[
\rho(T) = \left[ \rho_0 + \rho_e T^{1/2} - \rho_s \ln T + \rho_p T^5 + \rho_2 T^2 + \rho_{9/2} T^{9/2} \right] \frac{1}{1 + \exp \left( \frac{-U_0}{k_B T} \left( 1 - \frac{T}{T_{cmod}} \right) \right)} + \rho_a T \exp \left( \frac{E_a}{k_B T} \right) \frac{\exp \left( \frac{-U_0}{k_B T} \left( 1 - \frac{T}{T_{cmod}} \right) \right)}{1 + \exp \left( \frac{-U_0}{k_B T} \left( 1 - \frac{T}{T_{cmod}} \right) \right)}
\]  

(6)

The fitting result of both samples using equation 6 can be seen in figure 2 while the best fit parameters are given in table 1. It can be seen from figure 2 that silver ions shift the Tmi and the theoretical Curie temperature (Tcmod) to a higher temperature. This result suggests that the volume fraction of ferromagnetic metal phase increases while the paramagnetic insulator phase decreased over the range...
of temperature from 10 to 290 K. This result is in accordance with the enhancement in double exchange interaction when silver ions substitute calcium ions.

Based on the insets of Figure 2, both samples exhibit a local minimum at temperature below 50K which indicated by a first minimum in the first derivative of resistivity as a function of temperature graph. These local minima suggest that both samples exhibit kondo-effect, thus the use of equation 2 to fit the resistivity behavior at low temperature was correct.

It can be seen that $\rho_0$ value has the biggest value compared to all other parameters. This suggests that the transport mechanism in both samples are strongly correlated with the grain boundary factor. A study by Gadani et al. have shown that in a nano structured LMO based compound, the electron displacement follows the grain boundaries of the samples [16]. This result is in parallel with the $\rho_0$ values obtained from both samples which obtained after fitting process. Additionally, the reduction in $\rho_0$ value also in parallel with the reduction of the average crystallite size of LCAMO-05 sample compared to the parent compound [7].

| Parameters | LCMO   | LCAMO-05 |
|------------|--------|----------|
| $\rho_0$ (Ohm cm) | 117.224 | 0.955    |
| $\rho_e$ (Ohm cm/K$^{0.5}$) | -18.539 | -0.0723  |
| $\rho_s$ (Ohm cm) | -9.678  | -0.0839  |
| $\rho_p$ (Ohm cm/K$^3$) | 9.94 × 10$^{-8}$ | 1.21 × 10$^{-11}$ |
| $\rho_2$ (Ohm cm/K$^2$) | 2.95 × 10$^{-2}$ | 6.32 × 10$^{-5}$ |
| $\rho_{9/2}$ (Ohm cm/K$^{1.5}$) | -1.05 × 10$^{-6}$ | -1.36 × 10$^{-10}$ |
| $\rho_a$ (Ohm cm) | -0.383  | -4 × 10$^{-5}$ |
| $U_0/k_B$ (K) | 1.95 × 10$^3$ | 3.27 × 10$^3$ |
| $E_a/k_B$ (K) | 543.398 | 1.69 × 10$^3$ |
| $T_{c_{mod}}$ | 171.61  | 273.892  |
| $T_{mi}$ | 160.44  | 235.96   |
| $\chi^2$ | 99.96   | 99.99    |
It was observed that substitution changes the \( \rho_e \) and \( \rho_s \) value into several orders. According to the research by Lalita et al., \( \rho_s \) value is mainly decided by the intensity of the spin scattering process while \( \rho_p \) value represents electron-phonon scattering at low temperature region [17]. Additionally, Lee and Ramakrishnan have stated that \( \rho_e \) value represents the electron-electron interaction [18]. Thus, it can be concluded that silver substitution greatly affects the intensity of spin scattering process, electron-phonon scattering and electron-electron interaction in the sample. Moreover, silver substitution also greatly changes the value of \( \rho_p \) and \( \rho_{02} \) by several orders. This result suggests that silver ions in the sample affect the scattering of electron-electron, electron magnon, or magnon-magnon scattering in ferromagnetic metal region [19].

It is also interesting to study the effect of silver substitution on the magnetoresistance properties of the sample. Magnetoresistance value (MR\%) can be calculated using equation (7). The field dependence of magnetoresistance properties of both samples can be seen from Figure 3.

\[
MR\% = \frac{\rho(H) - \rho(0)}{\rho(0)}
\]

(7)

It was observed that maximum MR\% occurred at 5K and bigger external fields tends to increase the MR\% value. This is due to the well-ordered electron spin at low temperature which will ease the electronic transport in the sample. Additionally, silver substitution improves the maximum MR\% value of the sample near room temperature (285K) which are -3.36% and -4.94% for LCMO and LCAMO-05 samples respectively. This result is in parallel with the enhancement in double exchange mechanism due to 5% silver substitution.

![Figure 3. Field dependence of MR properties from (a) LCMO sample and (b) LCAMO-05 sample](image)

4. Conclusion
The electrical transport and magnetoresistance properties of La\(_{0.8}\)Ca\(_{0.2-x}\)Ag\(_x\)MnO\(_3\) (x = 0 and 0.05) compound prepared using sol-gel method have been studied. It was found that silver substitution increases the Mn\(^{4+}\) ions which can be responsible for the decrease in overall resistivity compared to the parent compound. Percolation model has been used in order to understand the electrical transport mechanism of the samples through low and high temperature simultaneously. The model shows that the electrical transport of La\(_{0.8}\)Ca\(_{0.2}\)Ag\(_{0.05}\)MnO\(_3\) (x = 0 and 0.05) are mainly governed by the scattering and interaction between electron, phonon, and magnon. Furthermore, it was found that silver substitution greatly influences the scattering and interaction between electron, phonon and magnon, which can be the reason behind the big difference in the resistivity of the sample with silver ions. It is also noted that MR\% value increases as silver ions substitute some of calcium ions. This study has shown that there is a possibility to improve near room temperature MR property with silver substitution in a substituted LMO based compound.

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