Effect of Silver Substitution on Electrical Transport and Magnetoresistance of La$_{0.8}$Ca$_{0.2}$MnO$_3$

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Abstract. In this work, we have investigated the effect of silver substitution on electrical transport behavior and magnetoresistance of La$_{0.8-x}$Ag$_x$Ca$_{0.2}$MnO$_3$ ($x = 0$ and $0.05$). Preparation and study of structural and microstructure of both samples have been reported on previous work. Temperature-dependent resistivity has been measured at temperature range of 15-285 K with zero field cooling. Magnetoresistance effect has been measured at 15, 100, and 285 K with magnetic field up to 1 T. The electrical transport behavior of both samples are quite well described by a theory based on the Percolation model. The electrical conduction mechanism at low temperature can be explained by a theory based on Kondo-like spin-dependent scattering, electron-electron, electron–magnon, and electron-phonon scattering. It was found that silver substitution increases the metal-insulator transition temperature ($T_{M-I}$) from 197.55 to 277.56 K, and Curie temperature ($T_{C\text{Mod}}$) from 217.25 to 278.65 K. Moreover, the maximum magnetoresistance value of both samples was obtained at 15 K.

1. Introduction

In the last decade, lanthanum manganite (LMO) based materials, which have been substituted by monovalent or divalent metals, have attracted the interest of many researchers due to their fascinating physical properties such as unique conduction mechanism and low field magnetoresistance (LFMR) [1, 2]. Moreover, several studies have mentioned that there are many factors that could affect the performance of a substituted LMO based materials. Some of the well-known example of the factors which could affect the magnetoresistance properties of a substituted LMO based materials are Mn$^{3+}$/Mn$^{4+}$ ratio, average ionic radius, and the width of electronic bandwidth in the compound [3-5]. However, several studies have shown that these factors, which usually viewed in double exchange framework, are not enough to explain the unique conduction mechanism and LFMR properties of a substituted LMO based materials.

One of the most studied examples of a substituted LMO based materials are calcium doped lanthanum mangnites with general formula of La$_{1-x}$Ca$_x$MnO$_3$ (LCMO). This type of compound was found to have high MR% value. However, it was also observed that the high MR% value of LCMO compounds can only be achieved at a temperature below room temperature. Several attempts have been implemented to improve the temperature which corresponds to the high MR% value into a higher value. One of the ways
was to substitute lanthanum or calcium ions with monovalent metals such as potassium, sodium, and silver. Several studies have shown that substitution with monovalent ions on a substituted LMO based materials can increase the curie temperature of the materials. Increasing curie temperature of a substituted LMO based materials are important as it usually coincides with the temperature which the maximum MR% value was found.

Recently, the effect of silver substitution on structural and morphological properties of La_{0.8-x}Ag_{x}Ca_{0.2}MnO_3 (x = 0 and 0.05) have been investigated [6]. It was observed that the material crystallizes in the orthorhombic structure with Pbnm space group. To carry on with the previous investigation, in this work, the effect silver substitution on the electrical transport and magnetoresistance properties of La_{0.8-x}Ag_{x}Ca_{0.2}MnO_3 (x = 0 and 0.05) were studied. Furthermore, to overcome the shortcoming of double exchange framework, the electrical properties of the sample were analysed using percolation model.

2. Experimental

Bulk polycrystalline La_{0.8-x}Ag_{x}Ca_{0.2}MnO_3 (x = 0 and 0.05) was synthesized by sol-gel method. The details regarding sample preparation have been reported elsewhere [6]. Both samples were sintered at 1000 °C for 24 hours. The resistivity measurements of bulk samples were carried out over a range of 10–285 K with Cryogenic Magnetometer by a standard four-probe method. Magnetoresistance of both samples measured at 15, 100, and 285 K with external magnetic field up to 1 T.

3. Result and Discussion

Temperature dependent of resistivity of both samples is shown in Figure 1. It is observed that the resistivity decreases upon silver substitution. As reported in many papers, silver substitution in lanthanum manganite causes a decrease in the overall resistivity [7, 8]. Silver substitution at La-site on mixed valance manganite increase the amount of Mn^{4+} ions so that increase the coupling magnetic Mn^{3+}-O-Mn^{4+} ratio which enhances the number of charge carriers in e_g band [8]. In this particular work, the result of increasing Mn^{3+}-O-Mn^{4+} ratio manifests in the increasing metal-insulator transition temperature (T_{mi}).

![Figure 1](image.png)

Figure 1. Temperature dependent of resistivity for La_{0.8-x}Ag_{x}Ca_{0.2}MnO_3 (black: x = 0; red: x = 0.05).

In terms of DE interaction theory, an increase of the electronic bandwidth (W) and the mobility of e_g electrons enhance the electrical conduction and magnetism because of shorter Mn-O average bond length and bigger Mn-O-Mn average angle [9]. The empirical formula of the W for perovskite manganite using tight binding approximation is as follow [10]:

\[ W = \frac{2}{3} \left( \frac{\alpha}{2\pi} \right)^{3/2} \]
\[ W = \cos \frac{1}{2} (\pi - \langle \text{Mn-O-Mn} \rangle) d^{3.5} \langle \text{Mn-O} \rangle \]  

(1)

Based on the author’s previous work in the structural study of LACMO compound, silver substitution resulting in a shorter \( d \langle \text{Mn-O} \rangle \) and bigger of \( \langle \text{Mn-O-Mn} \rangle \) [6]. According to Eq. 1, it can be predicted that the value of \( W \) will increase, which in turn increase the DE interaction due to silver substitution according to decreased resistivity.

With the purpose of understanding the electrical transport behavior mechanism for perovskite manganite. Some attempts have been made to fit the resistivity data, one of them with percolation model. This percolation model is suitable to explain the data over the entire temperature range both above and below Curie Temperature, which determined by the variation volume fractions of the two regions composed of ferromagnetic metal (FM) and paramagnetic insulator (PM) regions [7]. The complete expression describing the temperature dependence of resistivity (\( \rho(T) \)) is written in Equation 2:

\[
\rho(T) = \left[ \rho_0 + \rho_e T^2 - \rho_s \ln T + \rho_p T^5 + \rho_2 T^2 + \rho_9 T^9 \right] \left( \frac{1}{1 + \exp \left( \frac{-U_0 \left( 1 - \frac{T}{T_{c\text{mod}}} \right)}{k_B T} \right)} \right)
\]

\[ + \left[ \rho_a T \exp \left( \frac{E_a}{k_B T} \right) \right] \left( \frac{\exp \left( \frac{-U_0 \left( 1 - \frac{T}{T_{c\text{mod}}} \right)}{k_B T} \right)}{1 + \exp \left( \frac{-U_0 \left( 1 - \frac{T}{T_{c\text{mod}}} \right)}{k_B T} \right)} \right) \]

(2)

Figure 2. Temperature dependence of the resistivity for (a) La\(_{0.8}\)Ca\(_{0.2}\)MnO\(_3\) and (b) La\(_{0.75}\)Ag\(_{0.05}\)Ca\(_{0.2}\)MnO\(_3\). The red solid line is the best fit of experimental data by Eq. 1, Inset is \( d\rho/dT \) dependence temperature.
\( \rho_0 \) is the residual resistivity arising from the temperature independent processes such as domain wall and grain boundary, \( \rho_{9/2} T^{9/2} \) is combination of a electron (e), magnon (m) and phonon (p) scattering processes, \( \rho_2 T^2 \) is \( e-e \) scattering, \( \rho_p T^5 \) e–p interactions, \( \rho_e T^{1/2} \) is \( e-e \) interactions, \( \rho_s \ln T \) is Kondo-like spin dependent scattering. \( U_0 \) is the energy difference between FM and PM at low temperature, \( E_a \) is activation energy and \( k_B \) is Boltzman constant \([11-15]\). Additionally, this model can calculate the theoretical Curie temperature of the material (\( T_c^{\text{mod}} \)) which has been proven near or equal to \( T_C \) from magnetization measurement \([16]\). The fitting results of temperature dependence data using percolation model is shown in Figure 2, and the best fit parameters are listed in Table 1.

It was found that \( \rho_0 \) value decreases when silver ions substitute lanthanum ions. This result indicates that silver ions improve the conduction mechanism in the grain boundaries. The value of \( pe \) and \( ps \) also decreases as silver ions substitute lanthanum ions. This result suggests that silver ions affect the interactions between electrons-electrons and the spin dependent scattering at low temperature. The increase in \( \rho_p \) and \( \rho_2 \) value indicates that silver ions favour the electron-electron scattering and electron phonon interaction process at FM region. The value of \( \rho_{9/2} \) also decreases upon silver substitution. This result suggests that silver substitution decrease the spin fluctuation inside the sample \([17]\). It is interesting to note that silver substitution greatly affects the \( E_a/k_B \) and \( U_0/k_B \) terms. This result suggest that silver ions play a major role in the charge localization mechanism and energy difference between FM and PM phases which coexist in the sample \([18]\).

### Table 1. Fitting parameters of the percolation model for \( \text{La}_{0.8-x}\text{Ag}_x\text{Ca}_{0.2}\text{MnO}_3 \) \((x = 0 \text{ and } 0.05)\).

| Fitting Parameter | Silver Concentration \((x)\) | 0     | 0.05  |
|-------------------|--------------------------------|-------|-------|
| \( \rho_0 \) \((\Omega \text{ cm})\) | 4.212                         | 0.852 |       |
| \( \rho_e \) \((\Omega \text{ cm}/K^{0.5})\) | 0.454                         | 0.064 |       |
| \( \rho_s \) \((\Omega \text{ cm})\) | 1.004                         | 0.071 |       |
| \( \rho_p \) \((\Omega \text{ cm}/K^{1})\) | \(-4.289 \times 10^{-10}\)   | \(-2.793 \times 10^{-11}\) |       |
| \( \rho_2 \) \((\Omega \text{ cm}/K^{2})\) | \(-5.630 \times 10^{-5}\)   | \(-5.034 \times 10^{-5}\) |       |
| \( \rho_{9/2} \) \((\Omega \text{ cm}/K^{9/2})\) | \(6.457 \times 10^{-9}\)    | \(3.730 \times 10^{-10}\) |       |
| \( \rho_e \) \((\Omega \text{ cm})\) | \(1.689 \times 10^{-4}\)    | \(1.920 \times 10^{-10}\) |       |
| \( E_a/k_B \) \((K)\) | 5723.016                      | 1642.105 |       |
| \( U_0/k_B \) \((K)\) | 7013.422                      | 686.468 |       |
| \( T_c^{\text{mod}} \) \((K)\) | 214.248                       | 296.092 |       |
| \( T_{M-I} \) \((K)\) | 197.55                        | 277.56 |       |
| \( R^2 \) \((\%)\) | 99.99                         | 99.96 |       |

Figure 3 shows that magnetic field dependence of MR\% value. The MR\% value can be calculated using Equation 3.

\[
MR\% = \left[ \frac{p(H) - p(0)}{p(0)} \right] \times 100\%
\]

Based on Figure 3, the biggest MR\% values are obtained at low temperature. This is due to the less scattering process at low temperature which result in easier spin alignment, thus greatly reduce the resistivity under the influence of external magnetic field. In order to apply substituted LMO based material to a practical use, the material should have high MR\% value and that value should be obtained at near room temperature. It was observed that maximum MR\% value at 285K decreases upon silver substitution. The obtained MR\% values are 3.12\% and 1.01\% for LCMO and LCAMO, respectively.
4. Conclusion

In conclusion, the effect of silver substitution on the electrical transport and magnetoresistance properties of \( \text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3 \) was studied. It was found that silver substitution decreases the overall resistivity due to the enhancement of double exchange interaction as silver increase the amount of \( \text{Mn}^{4+} \) in the sample. Additionally, silver substitution also increases the metal-insulator transition of the sample. Percolation model have been used in order to understand the electrical properties of the sample. It was observed that silver substitution improves the conduction mechanism in the grain boundaries. Furthermore, silver substitution also affects the resistivity due to scattering and interaction between electron, phonon, and magnon in ferromagnetic metal region. Additionally, it also greatly affects the hopping mechanism in the paramagnetic insulator region. At near room temperature, the maximum MR\% values of the samples are 3.12% and 1.01% for LCMO and LCAMO, respectively.

Acknowledgement

This work was supported by Universitas Indonesia under research grant PITTA B with contract NKB-0619/UN2.R3.1/HKP.05.00/2019.

References

[1] T.M. Tank, V. Shelke, S. Das, D.S. Rana, C.M. Thaker, S.S. Samatham, V. Ganesan, S.P. Sanyal. 2017. J. Magn. Magn. Mater. 432 581.
[2] K. Gadani, M.J. Keshvani, D. Dhruv, H. Boricha, K.N. Rathod, P. Prajapati, A.D. Joshi, D.D. Pandya, N.A. Shah, P.S. Solanki. 2017. J. Alloy. Comp. 719 47.
[3] S.B. Kansara, D. Dhruv, B. Kataria, C.M. Thaker, S. Rayaprol, C.L. Prajapat, M.R. Singh, P.S. Solanki, D.G. Kuberkar, N.A. Shah. 2015. Ceram. Int. 41 7162.
[4] F.L. Tang and X. Zhang. 1996. Phys. Rev. B 54 22.
[5] L.M. Rodriguez-Martinez and J.P. Attfield. 2017. Inter. J. Mod. Phys. B 21 (5) 707.
[6] T. Geng, S. Zhuang. 2010. Phys. Lett. A, 374 1784.
[7] P.G. Radaelli, G. Iannone, M. Marezio, H.Y. Hwang, S.-W. Cheong, J.D. Jorgensen, D.N..
Argyriou. 1997. *Phys. Rev. B* **56** 8265.

[11] A. Urushibara, Y. Moritomo, T. Arima, A. Samitsu, G. Kido, Y. Tokura. 1995. *Phys. Rev. B: Condens. Matter.* **51** 14103.

[12] P.T. Phong, N.V. Khiem, N.V. Dai, D.H. Manh, L.V. Hong, N.X. Phuc. 2009. *J. Magn. Magn. Mater.* **321** 3330.

[13] V. Sen, N. Panwar, G.L. Bhalla, S. K. Aguarwall. 2007. *J. Phys. Chem. Solids* **68** 1685.

[14] M. Ziese. 2003. *Phys. Rev. B: Condens. Matter.* **68** 132411.

[15] A. Dhahri, M. Jemmali, E. Dhahri, E.K. Hill. 2015. *Dalton Trans.* **44** 5620.

[16] S. Mahjoub, M. Baazaoui, R. M’nassri, N.C. Boudjada, M. Oumezzine. 2015. *J. Supercond. Nov. Magn.* **28** (7) 1.

[17] G. Lalitha, P.V. Reddy. 2010. *J. Alloy. Compd.* **494** (1–2) 476.

[18] J.M.D. Coey. 1998. *Phil. Trans. R. Soc. Lond. A* **356** 1519.