Transport Properties and Magnetoresistance of La$_{0.8}$Ca$_{0.13}$Ag$_{0.07}$MnO$_3$ Perovskite Manganite Synthesized by Sol-Gel Method

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Abstract. In this paper, we investigate the transport properties and magnetoresistance effect of La$_{0.8}$Ca$_{0.13}$Ag$_{0.07}$MnO$_3$ perovskite manganite synthesized by sol-gel method. The XRD pattern of the sample shows a rhombohedral perovskite structure with space group $R3c$. The EDX analysis confirms that the sample contains all expected chemical elements without any additional impurity. The temperature dependence of electrical resistivity was measured using a cryogenic magnetometer. The results show a metal-insulator transition temperature ($T_{MI}$) at 280 K. The resistivity of the sample increases with an increase of temperature below $T_{MI}$. Theoretical analyses of the temperature dependence of resistivity suggest that the resistivity due to electron-electron scattering is predominant below $T_{MI}$. The resistivity of the sample decreases when applied magnetic field 1 T at a temperature range of 10 K to 300 K. The magnetoresistance of La$_{0.8}$Ca$_{0.13}$Ag$_{0.07}$MnO$_3$ emanates from spin-polarized tunneling process at the grain boundary.

Keyword. Magnetometer, manganite, perovskite, sol-gel method, and transport properties.

1. Introduction

Perovskite manganite materials with general formula ABO$_3$ (A = La, B = Mn) are an antiferromagnetic and insulator material [1]. Mangan and oxygen ions in perovskite lanthanum manganite form MnO$_6$ octahedral geometry [2]. Partial substitution in A site with divalent or monovalent ions leads to distorting MnO$_6$ geometry and oxidize Mn$^{3+}$ to Mn$^{4+}$ which influence the magnetic and transport properties [1, 3–6]. Zener double exchange interaction qualitatively explained correlation among structural, magnetic and transport properties, transfer electrons from Mn$^{3+}$ to Mn$^{4+}$ through O$^{2-}$ [7]. Hence, mixed valence Mn$^{3+}$/Mn$^{4+}$ ions play an essential role in the electric and magnetic properties of lanthanum manganite [8].

Skini et al reported that the perovskite manganite La$_{0.8}$Ca$_{0.2}$MnO$_3$ exhibits high magnetoresistance (MR) with a metal-insulator transition temperature ($T_{MI}$) below room temperature [9]. Guo et al also reported that the perovskite manganite La$_{0.8}$Ca$_{0.2}$MnO$_3$ possess high magnetocaloric effect (MCE) with Curie temperature ($T_C$) below room temperature [10]. Magnetoresistance effect in perovskite
manganite emanates to two contributions. First, the intrinsic MR originates from suppression of spin fluctuation when the magnetic field is applied [11]. The intrinsic MR reaches a maximum around the paramagnetic-ferromagnetic transition temperature [12]. Second, extrinsic MR emanates from spin-polarized tunneling process at grain boundary which is dominant at low temperature [11, 12]. For wide application at room temperature, metal-insulator transition temperature and Curie temperature need to increase near room temperature. Pi et al reported that substitutions La site with Ag in perovskite lanthanum manganite increase the $T_{MI}$ and $T_C$ [13]. In this present work, the authors partially substitute Ca site with Ag to form perovskite manganite La$_{0.8}$Ca$_{0.13}$Ag$_{0.07}$MnO$_3$ and investigate the structural and transport properties of that perovskite material.

2. Materials and methods
The material La$_{0.8}$Ca$_{0.13}$Ag$_{0.07}$MnO$_3$ was synthesized by sol-gel method using La$_2$O$_3$, Ca(NO$_3$)$_2$.4H$_2$O, AgNO$_3$, Mn(NO$_3$)$_2$.4H$_2$O as precursor materials. La$_2$O$_3$ was dissolved in nitric acid solution. Then, lanthanum nitrate solution was mixed with other metal nitrate solution. Citric acid was added to the solution with a molar ratio of 1.2 between citric acid and metal nitrate. The pH value of the solution was adjusted to 7 by adding ammonia solution while stirring the solution at a temperature of 80 °C until the gel was formed. The gel was heated at 120 °C for dehydration. It was calcined at 600 °C for 5 h to remove produced organic materials. The materials obtained from this process were ground by using an agate mortar. The powders were pressed into pellets and then heated at 900 °C for 24 h.

The crystal structure of the sample was determined by X-ray diffractometer (XRD) using monochromatic CuKα radiation. The composition of elements was analyzed using energy dispersive X-ray spectroscopy (EDX). The measurement of resistivity versus temperature was determined by cryogenic magnetometer.

3. Results and discussion
The structural properties of the sample were determined by XRD at room temperature. The XRD pattern of the sample is shown in Figure 1.a. The refinement result using Rietveld method indicates that the sample has a rhombohedral structure with space group of $R_3\overline{3}c$. The quality of refinement was determined by the value of goodness of fit ($\chi^2$) [14]–[16]. Lattice parameters, unit cell volume, $R_p$, $R_{wp}$ and the value of $\chi^2$ are summarized in table 1. The EDX analysis result shown in Figure 1.b exhibits La, Ca, Ag, Mn and O peaks corresponding to elements of the sample. The single phase of XRD result and EDX result indicate the successful substitution of Ca site with Ag.

![Figure 1](image-url)
Table 1. Lattice parameters, unit cell volume, $R_p$, $R_{wp}$ and goodness of fit ($\chi^2$)

| Parameters       | $La_{0.8}Ca_{0.13}Ag_{0.07}MnO_3$ |
|------------------|-----------------------------------|
| $a$ (Å)          | 5.497                             |
| $b$ (Å)          | 4.497                             |
| $c$ (Å)          | 13.314                            |
| Volume (Å$^3$)   | 348.385                           |
| $R_p$            | 8.279                             |
| $R_{wp}$         | 10.743                            |
| Goodness of fit ($\chi^2$) | 1.154                           |

Figure 2. The temperature dependence of $La_{0.8}Ca_{0.13}Ag_{0.07}MnO_3$ for measurement without magnetic field and with 1 T magnetic field.

The measurement result of resistivity versus temperature of $La_{0.8}Ca_{0.13}Ag_{0.07}MnO_3$ at zero applied a magnetic field and applied magnetic field 1 T is shown in Figure 2. Below 280 K, the resistivity of $La_{0.8}Ca_{0.13}Ag_{0.07}MnO_3$ increases with increment temperature indicating metallic behavior. The transport mechanism at the metallic region was analyzed by fitting the experimental data of $La_{0.8}Ca_{0.13}Ag_{0.07}MnO_3$ using equation [17]–[19]:

$$\rho(T) = \rho_o + \rho_2T^2 + \rho_{4.5}T^{4.5}$$  \hspace{1cm} (1)

Where $\rho_o$, $\rho_2$ and $\rho_{4.5}$ are resistivities due to grain/domain boundary scattering, electron-electron scattering, and combinations of electron-electron, electron-magnon and electron-phonon scattering processes, respectively [17]–[19]. The quality of fitting data was evaluated by the square of linear correlation coefficients $R^2$ [17]. Parameters of fitting data and the value of $R^2$ are summarized in Table 2. Figure 3 shows the fitting result of experimental data using equation 1. The $\rho_2$ higher than that of $\rho_{4.5}$ indicates the resistivity of $La_{0.8}Ca_{0.13}Ag_{0.07}MnO_3$ dominantly originated from electron-electron scattering. The highest value of $\rho_o$ suggests that grain/domain boundary plays a vital role in transport mechanism of $La_{0.8}Ca_{0.13}Ag_{0.07}MnO_3$. 


Table 2. Fitting parameters of electrical resistivity data of polycrystalline La$_{0.8}$Ca$_{0.17}$Ag$_{0.03}$MnO$_3$

| H = 0 | H = 1 |
|-------|-------|
| $\rho_0$ (ohm.m) | 0.047 | 0.019 |
| $\rho_2$ (10$^{-3}$ ohm.m$^{-1}$K$^{-2}$) | 0.223 | 0.054 |
| $\rho_{4.5}$ (10$^{-6}$ ohm.m$^{-1}$K$^{-0.2}$) | 2.116 | 1.252 |
| Adj. R-Square | 99.95% | 99.99% |

Figure 3. Theoretical fitting of resistivity data in the metallic region at (a) zero magnetic field, and (b) applied magnetic field 1 T.

Figure 3 shows that the resistivity of La$_{0.8}$Ca$_{0.13}$Ag$_{0.07}$MnO$_3$ decreases when applied magnetic field 1 T at range temperature of 10 K to 300 K. The value of magnetoresistance of La$_{0.8}$Ca$_{0.13}$Ag$_{0.07}$MnO$_3$ is calculated using Equation (2)

$$MR(\%) = \frac{\rho_0 - \rho_H}{\rho_0} \times 100\%$$  \hspace{1cm} (2)

Where $\rho_0$ and $\rho_H$ are the resistivities without and with 1 T magnetic fields, respectively. Figure 4 shows the magnetoresistance versus temperature of La$_{0.8}$Ca$_{0.13}$Ag$_{0.07}$MnO$_3$. The value of magnetoresistance of La$_{0.8}$Ca$_{0.13}$Ag$_{0.07}$MnO$_3$ decreases with increment temperature indicating that the decrement of resistivity of La$_{0.8}$Ca$_{0.13}$Ag$_{0.07}$MnO$_3$ emanates from spin-polarized tunneling process at the grain boundary. The magnetic spins at grain boundary are randomly oriented [20]. The spins align to the applied magnetic field direction resulting in a decrease of electron scattering by the grain boundary and increase electron tunneling [9, 11].

Figure 4. The magnetoresistance versus temperature of La$_{0.8}$Ca$_{0.13}$Ag$_{0.07}$MnO$_3$. 


4. Conclusions
The transport properties and magnetoresistance of La$_{0.8}$Ca$_{0.13}$Ag$_{0.07}$MnO$_3$ synthesized by sol-gel method were investigated. The XRD analyses exhibit a single phase with rhombohedral structure. The EDX results confirm that the sample contains all expected chemical elements. The temperature dependence of La$_{0.8}$Ca$_{0.13}$Ag$_{0.07}$MnO$_3$ at the metallic region which is originated from electron-electron scattering. The magnetoresistance of La$_{0.8}$Ca$_{0.13}$Ag$_{0.07}$MnO$_3$ emanates from spin-polarized tunneling process at the grain boundary.

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