Structure, microstructure, electrical transport mechanism and magnetoresistance in La$_{0.8}$Ag$_{0.2}$MnO$_3$

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Abstract. Bulk polycrystalline sample of La$_{0.8}$Ag$_{0.2}$MnO$_3$ has been successfully synthesized by the sol gel method. Structural, morphology, electrical properties and magnetoresistance has been investigated. Refinement results from XRD at room temperature showed a single-phase material with a rhombohedral crystal structure and R-3c space group. Electrical transport showed by comparison of experimental data with theoretical model, the sample undergo a metal-insulator transition at TM-I accompanying the ferromagnetic-paramagnetic transition. Data for temperature dependence of resistivity has been fitted using the formula \( \rho(T) = \rho_{FM}f + (1 - f)\rho_{PM} \), \( \rho_{FM} \) is resistivity of the ferromagnetic region, \( \rho_{PM} \) is resistivity of the paramagnetic region and \( f \) is the volume fraction of ferromagnetic phase. Result of fitted data is in good agreement with experimental data. MR measurements in the range of magnetic field 0-1 T, measurements were carried out at temperatures of 15 K, 100 K, 200 K and 285 K, the results showed a decrease in resistivity.

1. Introduction
Perovskite manganites of RE$_{1-x}$AE$_x$MnO$_3$ (RE is trivalent rare earth and AE is divalent alkaline earth ions) have been studied widely due to physical properties such as magnetoresistance and magnetocaloric effect [1-3]. Colossal magnetoresistance (CMR) is the kind of magnetoresistance occur at perovskite manganites, consists of intrinsic CMR and extrinsic CMR. The intrinsic CMR is caused by double exchange mechanism and the extrinsic CMR is related to grain boundaries, explained by spin polarized tunnelling [4]. Perovskite manganites undergo a metal-insulator transition at TM-I accompanying the transition ferromagnetic to paramagnetic occur near Tc. [5] In this research electrical transport mechanism is explained using a 3D Mott’s variable range hopping (VRH) model, a small polaron hopping (SPH) model and adiabatic small polaron hopping ASPH mechanism in insulator region. In the metal region electrical transport mechanism governed by the contribution of single magnon’s scattering, the mechanism of electron-magnon scattering, the electron-electron scattering and electron-phonon scattering process [3,4].

Element of alkaline earth metal doped (Ag, Na, K etc.) has the valence is +1, the substitution of this elements to parental compound affects the ratio of Mn$^{3+}$ and Mn$^{4+}$ ions which is the place where the double exchange mechanism occurs and can give rise to different interplays among spin, lattice degree of freedom and charge [6,7].
2. Experimental
The ceramic sample of $\text{La}_{0.8}\text{Ag}_{0.2}\text{MnO}_3$ was synthesized by sol-gel method, the stoichiometric amount of $\text{La}_2\text{O}_3$ diluted in nitric acid 65 % and double distilled water, $\text{Ag} (\text{NO})_3$, $\text{Mn} (\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ and C$_6$H$_8$O$_7$ diluted in double distilled water. All precursor mixed and the solution was then heated on hot magnetic plate till temperature 80°C with constant rotation. The pH value was adjusted to 7 using ammonium solution 25%, obtaining transparent solution. Then the solution heated with continues stirring till gel formed. The sample calcined at 500°C for 5 h to eliminate the organic material and the yield was pressed being pellet then sintered at 800°C for 24 h. the phase and crystal structure of sample confirmed by X-ray diffraction (PANalytical:X’Pert Pro) using Cu kα ($\lambda = 1.541$ Å) radiation at room temperature. Scanning Electron Microscopy equipped with EDS measurement was done by a FEI Quanta 650 to investigate the morphology and composition of the sample. The resistivity and magnetoresistance measurement were using cryogenic magnetometer (Oxford Teslatron instrument) in the range of temperature 10 until 300 K.

3. Result and discussion
The Figure 1. Shows the experimental and calculation XRD patterns for $\text{La}_{0.8}\text{Ag}_{0.2}\text{MnO}_3$. refinement process using rietveld method, the sample has one phase without impurities and rhombohedral structure of R-3c space group [6-9], in which the (La, Ag) atoms are at 6a (0, 0, ¼) positions, Mn at 6b (0, 0, 0) and O at 18e (x, 0, ¼). This result is consistent with Goldschmidt tolerance factor ($t_G$) value calculated using the formula:

$$t_G = \frac{1(<r_A> + r_o)}{\sqrt{2}(<r_B> + r_o)} \tag{1}$$

Where $<r_A>$, $<r_B>$ are average ionic radii of A, B respectively and $r_o$ is oxygen ion. perovskite manganite compound stable if they have $t_G$ values in the range 0.89 < $t_G$ > 1.02, and for rhombohedral structure has $t_G$ in range 0.96 < $t_G$ > 1[10], the ionic radius of $\text{La}^{3+}$ and $\text{Ag}^{1+}$ are close ($\text{La}^{3+} = 1.18$ Å and $\text{Ag}^{1+} = 1.13$ Å [7].

![Figure 1. Rietveld refined of $\text{La}_{0.8}\text{Ag}_{0.2}\text{MnO}_3$ compound.](image_url)

The Rietveld refinement show excellent agreement between experimental and calculation patterns, the discrepancy factor and structural parameters estimated from the rietveld refinement are given in table 1. The average crystallite size of $\text{La}_{0.8}\text{Ag}_{0.2}\text{MnO}_3$ was calculated using scherrer’s equation given as:

$$D = \frac{K\lambda}{\beta \cos \theta} \tag{2}$$
where \( k \) is shape factor, with the value of about 0.9, \( \lambda \) [11] is the X-ray wavelength (\( \lambda = 1.54056 \) Å), \( \beta \) is full width at half maximum (FWHM) of the diffraction peak and \( \theta \) is bragg position. Crystallite sizes (D) are given in table 1.

**Table 1.** Structural parameters by rietveld refinement for La0.8Ag0.2MnO3 compounds.

| Parameter | La0.8Ag0.2MnO3 |
|-----------|---------------|
| **Structure** | Rhombohedral |
| **Space group** | R-3c |
| \( a = b \) Å | 5.4996 |
| \( c \) Å | 13.3476 |
| \( V \) Å\(^3\) | 349.623 |
| **Average Crystallite size (nm)** | 40.81 |
| **Discrepancy factor** | |
| \( R_{wp} \) (%) | 7.3234 |
| \( R_p \) (%) | 5.7188 |
| GoF | 0.9534 |
| **Bond angle and bond length** | |
| \( \theta_{\text{Mn-O-Mn}} \) (°) | 164.874 |
| \( d_{\text{Mn-O}} \) Å | 1.955 |
| **Factor tolerance** | |
| \( t_0 \) | 0.969 |

The Scanning electron Microscopy of this sample is illustrated in figure 2(a) the particles show by SEM image have a homogeneous distribution. The average of the grain size is 126.12 nm. EDS measurement was carried out to check the atomic composition. The spectra of sample given by figure 2(b), peak of La, Ag, Mn and Oxygen, the atomic ratio is close to the expected for the sample, result and calculation of atomic ratio of this sample given by table 2.

**Figure 2.** (a) SEM images and (b) EDS spectra of La0.8Ag0.2MnO3.

**Table 2.** Atomic ratio of La0.8Ag0.2MnO3.

| Element | EDS measurement (at%) | Calculation (at%) |
|---------|-----------------------|-------------------|
| La      | 16.54                 | 16                |
| Ag      | 3.34                  | 4                 |
| Mn      | 18.33                 | 20                |
| O       | 61.78                 | 60                |
Temperature dependence resistivity without magnetic field of La$_{0.8}$Ag$_{0.2}$MnO$_3$ shown in figure 3(a), this sample show metal-insulator (M-I) transition, temperature transition characterized by a cusp is seen around 180 K which is called by metal-insulator transition temperature (TM-I). We use percolation model to analysed all parameters of the resistivity occur in this material which is given by:

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

\[+ \left[ \rho_\alpha T \exp \left( \frac{E_A}{k_B T} \right) \right] \frac{\exp \left( \frac{-U_0 (1 - T/T\text{mod})}{k_B T} \right)}{1 + \exp \left( \frac{-U_0 (1 - T/T\text{mod})}{k_B T} \right)} \]

The derivation of this formula has been explained in research about electrical transport [3,4]. Where \(\rho_0\) is resistivity due to grain/domain boundary and point defect scattering, \(\rho_e\) is resistivity due to electron-electron interaction, \(\rho_s\) is scattering of conduction electrons due to magnetic impurities, \(\rho_p\) is electrical resistivity due to electron-phonon interaction, \(\rho_2\) is electrical resistivity due to electron-electron scattering, \(\rho_{9/2}\) is a grouping electron-electron, electron-magnon and electron-phonon scattering processes [12], \(\rho_\alpha = \frac{2k_B}{3ne^2a^2\vartheta}\) is residual resistivity, \(K_B\) is Boltzmann’s constant ~8.617 x 10$^{-5}$ eV K$^{-1}$, \(e\) is electronic charge, \(n\) is the density of charge carriers, \(a\) is the site-to-site hoping distance and \(\vartheta\) is the longitudinal optical phonon frequency, \(E_A\) is polaron activation energy, \(U_0\) is taken as the energy deference for temperature well below \(T_{\text{C mod}}\) \((T_{\text{C mod}}\) is paramagnetic-ferromagnetic transition temperature used in the model. It is near or equal to \(T_c\) [3,4,12].

![Figure 3](image_url)

**Figure 3.** (a) temperature dependence of resistivity without magnetic field (b) percolation model of La$_{0.8}$Ag$_{0.2}$MnO$_3$. Inset is \(d\rho/dT\) dependence temperature.
Figure 3(b) shows fitting using percolation model, with red line is result of fitting and solid dot is result of experimental. Fitting parameters given by table 3. There many factors affect the resistivity of this sample; effect of grains and domain boundary is the most dominant parameter affecting the resistivity. This is occurred because increment of intergrain distance caused electron tunnelling which across grain boundaries become more difficult [4], the larger grain boundary size, value of $\rho_0$ will decrease.

The region around 60 K shows the upturn of resistivity at low temperature that indicate kondo effect arises due to scattering from a magnetic impurity in nonmagnetic lattice. $T_M$ obtained by first derivative of $\rho(T)$ (d$\rho$/dT=0) with value is 179.213 K and the $T_c^{mod}$ is the $T_c$ obtained of the model with value is 274.015 K.

| Fitting Parameter | $La_{0.8}Ag_{0.2}MnO_3$ |
|-------------------|-------------------------|
| $\rho_0$ ($\Omega$.cm) | 6.396                   |
| $\rho_e$ ($\Omega$.cm.K$^{-1/2}$) | 0.712                   |
| $\rho_s$ ($\Omega$.cm) | 2.307                   |
| $\rho_P$ ($\Omega$.cm.K$^{-5}$) | $2.598 \times 10^{-12}$ |
| $\rho_2$ ($\Omega$.cm.K$^{-2}$) | $7.689 \times 10^{-5}$  |
| $\rho_{9/2}$ ($\Omega$.cm.K$^{-9/2}$) | $-8.102 \times 10^{-11}$ |
| $\rho_0$ ($\Omega$.cm) | $-7.352 \times 10^{-7}$ |
| $E_A/k_B$ (K) | 1514.086                |
| $U_0/k_B$ (K) | 1558.633                |
| $T_c^{mod}$ (K) | 274.015                 |
| $T_M-I$ (K) | 179.213                 |
| $R^2$ (%) | 99.99                   |

The percentages of magnetoresistance (MR) of $La_{0.8}Ag_{0.2}MnO_3$ has been calculated using the formula:

$$MR\ (%) = \frac{(\rho(0,T) - \rho(0,H))}{\rho(0,T)} \times 100$$  \hspace{1cm} \text{(4)}$$

Where $\rho(0,T)$ is the resistivity under zero magnetic field and $\rho(0,H)$ is the resistivity under an applied field. Figure 4 shows the Magnetic field dependence of MR ratio at various temperature. The largest MR ratio occur at 15 K, decreasing of resistivity till ~25 %.

Figure 4. Magnetic field dependence of magnetoresistance ratio of $La_{0.8}Ag_{0.2}MnO_3$ at various temperature.
4. Conclusion

The structural, microstructure, electrical transport mechanism and magnetoresistance of La$_{0.8}$Ag$_{0.2}$MnO$_3$ compounds have been investigated. The results show that the sample has rhombohedral structure with R-3c space group, microstructure show small grain size around 126.12 nm. Electrical transport mechanism has been explained using percolation model. There are many that affect the resistivity of this sample which is make electron more difficult to tunnel inter grain boundaries. the metal-insulator transition temperature ($T_{MI}$) is 179.213 K and $T_{Cmod}$ is 274.015 K. Magnetoresistance ratio calculated at various temperature, the largest decreasing occurs at 15 K.

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