Effect of low nickel substitution on structure, morphology,
and electrical transport of La$_{0.7}$Sr$_{0.2}$Ba$_{0.1}$Mn$_{1-x}$Ni$_{x}$O$_3$ (x=0.02 and 0.05)

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Abstract. The effect of low nickel substitution at Mn-site on structure, microstructure and electrical transport properties of La$_{0.7}$Sr$_{0.2}$Ba$_{0.1}$Mn$_{1-x}$Ni$_{x}$O$_3$ (x = 0.02 and 0.05) were investigated. Samples were prepared by sol-gel method. From Rietveld refinement result, crystal structure of both samples were found to be Rhombohedral with R-3c (167) space group. Low nickel substitution at Mn-site shows that the Mn-O-Mn bond angle decreases and the Mn-O bond length increases which can link to Jahn-Teller distortion and double exchange. Scanning electron microscope (SEM) result reveals that nickel substitution leads to smaller grain size. Temperature-dependent resistivity $\rho(T)$ has been measured at 15-285 K with zero field cooling. The experimental resistivity data were fitted by Percolation model. Percolation model can describe the electrical behavior of both samples based on electron-electron, electron-magnon, and electron-phonon scattering, and Kondo-like spin-dependent scattering at low temperature and adiabatic small polaron hopping at high temperature. It was found that nickel substitution decreases the metal-insulator transition temperature ($T_{MI}$) from around 304 to 272 K, and Curie temperature ($T_c$) from around 330 to 310 K.

1. Introduction
The discovery of colossal magnetoresistance (CMR) has renewed interest in studying magneto-transport in a family of mix valence lanthanum manganite La$_{1-x}$AE$_x$Mn$_{1-y}$TM$_y$O$_3$ (AE = alkaline earth element and TM = transition metal element). The substitution at the La site exhibit the mix valence state of manganese ions (Mn$^{3+}$/Mn$^{4+}$) and lattice distortion [1-3]. The ratio of Mn$^{3+}$/Mn$^{4+}$ is playing vital factor to influence the physical properties. Moreover, the properties of mix valence manganites are explained by double exchange (DE) interaction between Mn$^{3+}$ and Mn$^{4+}$ via the 2p orbitals of O$^{2-}$ [2,3]. The hoping of an $e_g$ electron from Mn$^{3+}$ to Mn$^{4+}$ in the Mn$^{3+}$–O$^{2-}$–Mn$^{4+}$ bonds are leading to ferromagnetic interaction. Meanwhile, the substitution of Mn site in perovskite manganites with other transition metal ions is important. It modifies the Mn$^{3+}$–O$^{2-}$–Mn$^{4+}$ network and brings many new exchange interactions between the Mn ions [2-5].

Usually, mix valence manganite reveals a metal-insulator transition accompanied by a Ferromagnetic (FM)-Paramagnetic (PM) transition near the Curie temperature [6-8]. The transport properties behavior in the entire temperature range successfully described with a theoretical percolation model, proposed by Li et al. [7] Taking into account assuming that competition between ferromagnetic...
and paramagnetic regions is important in the formation of the CMR effect. The transport mechanism is explained by Kondo-like mechanism, localization, electron-electron and electron-phonon scattering at the metallic region, while in the semiconductor region is governed by 3D Mott’s variable range hopping (VRH) model, small polaron hopping (SPH) model and by the adiabatic small polaron hopping (ASPH) [7-10].

The Parental compound La$_{0.7}$Sr$_{0.2}$Ba$_{0.1}$Mn$_{1-x}$Ni$_x$O$_3$ with nickel substitution 10% ($x = 0.1$) has been studied in our previous work [11,12]. The Curie temperature are around 349 K for La$_{0.7}$Sr$_{0.2}$Ba$_{0.1}$MnO$_3$ and around 275K La$_{0.7}$Sr$_{0.2}$Ba$_{0.1}$Mn$_{0.9}Ni_{0.1}$O$_3$ [12]. In order to this compound the possibility of application of technology in the spintronics field at room temperature. In this work, we substitute a smaller concentration of nickel to reach the Curie temperature near room temperature. The objective of this work was to synthesize polycrystalline samples of La$_{0.7}$Sr$_{0.2}$Ba$_{0.1}$Mn$_{1-x}$Ni$_x$O$_3$ with an extended low nickel substitution levels ($x = 0.02$ and $0.05$) and study the correlation between structure, microstructure, and electrical transport behavior.

2. Experimental
The La$_{0.7}$Sr$_{0.2}$Ba$_{0.1}$Mn$_{1-x}$Ni$_x$O$_3$ ($x = 0.02$ and 0.05) manganite have been prepared via sol-gel auto combustion method. The details of the synthesized were reported in previous work [15]. The pelletized samples sintered at 1200 °C for 6 hours. The structural were measuring using X-ray diffractometer (XRD) with Cu-Kα ($\lambda = 1.5406$ Å) at room temperature the morphology samples and elemental distribution the samples were characterized using a scanning electron microscope (SEM) and energy dispersive spectrometer (EDS). The resistivity measurements of bulk samples were carried out over a temperature range of 15–285 K four-point probe method with Cryogenic Magnet.

3. Result and discussion
Figure 1 presents the XRD pattern of La$_{0.7}$Sr$_{0.2}$Ba$_{0.1}$Mn$_{1-x}$Ni$_x$O$_3$ ($x = 0.02$ and 0.05). The results Rietveld refinement of XRD indicate that both samples are single-phase with Rhombohedral structure with R-3c (167) space group. The results of refinement are listed in Table 1. Nickel substitution changes the lattice parameters and unit cell volume. The decreasing in lattice parameter and the unit cell volume can be related to the smaller ionic radius Ni$^{2+}$ ion (radius 0.56 Å) replaces Mn$^{3+}$ ion (radius 0.65 Å) by having the bigger ionic radius, which causes increasing the ratio of Mn$^{4+}$ (radius 0.53 Å) to cause a decrease in lattice parameters [2,3].

![Figure 1](image1.png)

**Figure 1.** XRD pattern rietveld refinement of La$_{0.7}$Sr$_{0.2}$Ba$_{0.1}$Mn$_{1-x}$Ni$_x$O$_3$: (a) $x = 0.02$ and (b) $x = 0.05$.

The average crystallite size ($D_c$) both samples were determined using Scherrer formula follow as:
\[ D_s = \frac{0.9 \lambda}{\beta_{HKL} \cos \theta} \]  

where \( \lambda \) is the wavelength of the radiation used for XRD (\( \lambda_{Cu} = 1.5406 \text{ Å} \)), \( \beta_{HKL} \) is full-width at half maximum (FWHM) of the strongest intensity diffraction peak and \( \theta \) is the Bragg’s angle [4]. The result of the average crystallite size given Table 1.

| Structural parameter from Rietveld analysis for both samples. |
|-------------------------------------------------------------|
| **Lattice Parameter** | **Nickel concentration (x)** |
| | 0.02 | 0.05 |
| \( a = b \) (Å) | 5.5191 | 5.5153 |
| \( c \) (Å) | 13.4145 | 13.4006 |
| \( V(\text{Å}^3) \) | 353.862 | 352.739 |
| \( d_{\text{Mn-O}} \) (Å) | 1.957 | 1.962 |
| \( \langle \text{Mn-O-Mn} \rangle \) (degrees) | 168.021 | 163.829 |
| average crystallite size (nm) | 84.765 | 70.688 |
| \( W(10^{-3}) \) | 9.485 | 9.474 |

Figure 2 reveals SEM images of both samples. The grain size decreases with increasing Nickel substitution. The grain size from SEM image reveals several larger than those calculated by XRD because each grain observed by SEM consists of several crystalline grains [4].

![SEM images](image)

**Figure 2.** SEM images of La\(_{0.7}\)Sr\(_{0.2}\)Ba\(_{0.1}\)Mn\(_{1-x}\)Ni\(_x\)O\(_3\); (a) \( x = 0.02 \) and (b) \( x = 0.05 \).

Figure 3 shown temperature dependent of resistivity \( \rho(T) \) curves for both samples. Overall resistivity increases with increases in nickel concentration. Generally, the electrical conduction in the
ferromagnetic is usually understood according to DE theory [2,3]. The DE interaction decreases by Nickel substitution at the Mn site. Nickel (Ni\textsuperscript{2+}) substitution causes enhance superexchange interaction coupling between Mn\textsuperscript{3+}-O-Mn\textsuperscript{3+}, Mn\textsuperscript{4+}-O-Mn\textsuperscript{4+}, Ni\textsuperscript{2+}-O-Ni\textsuperscript{2+}, and Ni\textsuperscript{2+}-O-Mn\textsuperscript{3+} which strengthens the antiferromagnetic (AFM) coupling [2,3].

In mix valence manganites, the FM-PM transition at Curie temperature (T\textsubscript{C}) is usually accompanied by a simultaneous metal-insulator (M–I) transition. This transition is characterized by a peak in the resistivity appearing at the temperature (T\textsubscript{M-I}), close to the T\textsubscript{C} [7-9]. In Figure 3 shows peak resistivity for x = 0.02 while for x = 0.05 peak resistivity not yet exhibited because limited the range temperature from equipment. In order to understand electrical behavior and determine T\textsubscript{M-I} and T\textsubscript{C}, we carried out a quantitative analysis for \( \rho (T) \) by percolation model given by an equation:

\[
\rho (T) = \left[ \rho_{0} + \rho_{e} T^{1} - \rho_{s} \ln T + \rho_{p} T^{5} + \rho_{2} T^{2} + \rho_{9} T^{9} \right] \left( \frac{1}{1 + \exp \left( \frac{-U_{0} \left( 1 - \frac{T}{T_{\text{mod}}^{\text{e}}} \right)}{k_{B} T} \right)} \right) \\
+ \left[ \rho_{a} T \exp \left( \frac{E_{a}}{k_{B} T} \right) \right] \left( \frac{\exp \left( \frac{-U_{0} \left( 1 - \frac{T}{T_{\text{mod}}^{\text{a}}} \right)}{k_{B} T} \right)}{1 + \exp \left( \frac{-U_{0} \left( 1 - \frac{T}{T_{\text{mod}}^{\text{e}}} \right)}{k_{B} T} \right)} \right)
\]

which the derivation of full expression explained in many articles in electrical transport research work [7-9]. \( k_{B} \) is the Boltzmann constant, \( T \) is the temperature, \( T_{\text{C}}^{\text{mod}} \) is theoretical Curie temperature, \( U_{0} \) is the energy difference between ferromagnetic metallic and paramagnetic insulating states, and \( E_{a} \) is activation energy. While, \( \rho_{0} \) is the residual resistivity arising from the temperature independent processes such as domain wall, grain boundary and vacancies, \( \rho_{9/2} T^{9/2} \) indicates a combination of electron (e), magnon (m) and phonon (p) scattering processes, \( \rho_{2} T^{2} \) indicates e–e scattering, \( \rho_{p} T^{5} \) indicates e–p interactions, \( \rho_{e} T^{1/2} \) indicates e–e interactions, and \( \rho_{s} \ln T \) is Kondo-like spin dependent scattering [6-9]. The fitting between the experimental data and the percolation model values is quite good, based on the evaluated by comparing the squared coefficient of linear correlation coefficient (R\textsuperscript{2}). The best fit parameters are given in Table 2 and Figure 4 display the simulated (red line) and experimental data results for the \( \rho (T) \) curve obtained for zero field. The fitting has been extended up to 395 K in order to find transition resistivity.

It is mentioned in Table 2, that \( \rho_{0} \) increases with increasing Nickel concentration with decreases grain size as figure 2. It is suggested that resistivity decreases is increasingly influenced by the presence of grain boundaries, which act as regions of enhanced scattering for the conduction of electrons and disorder can be explained by core shell model [9]. The value \( E_{a} \) and \( U_{0} \) increases with increasing nickel substitution, which favors the conduction and charge localization, the electrons hoping requires high energy [7-9]. The values of \( \rho_{e} \), \( \rho_{p} \), \( \rho_{2} \), and \( \rho_{9/2} \) increase as nickel substituted, this result suggests that nickel ions enhance the electron spin fluctuations according to the reduction of double exchange mechanism [7-9]. The \( \rho_{s} \ln T \) value is greater for \( x = 0.05 \), and also in figure 3 it seems that there is a greater upturn resistivity at \( x = 0.05 \). The upturn resistivity in low temperature indicates Kondo like spin-dependant scattering [7-9].
The value of $T_{M-I}$ was determined from the maximum value of the first derivative from the $\rho(T)$ curve obtained after the fitting process ($d\rho/dT = 0$). It was found the $T_{M-I}$ value for $x = 0.02$ and $x = 0.05$ are around 304 K and 272 K respectively, while the value of $T_{c}^{mod}$ which calculated from this model was found around 330 K and 310 K respectively. The $T_{c}^{mod}$ values as a result of this calculation model has been proven to be close to the measurement results [7-9].

Figure 4. Temperature dependence of the resistivity for (a) $La_{0.7}Sr_{0.2}Ba_{0.1}Mn_{0.98}Ni_{0.02}O_3$ and (b) $La_{0.7}Sr_{0.2}Ba_{0.1}Mn_{0.95}Ni_{0.05}O_3$. The solid red line is the best fit of experimental data by Eq. 1. Inset is $d\rho/dT$ dependence temperature.

Table 2. Fitting parameters of the percolation model for $La_{0.7}Sr_{0.2}Ba_{0.1}Mn_{1-x}Ni_xO_3 (x = 0$ and 0.05).

| Fitting Parameter | Nickel Concentration ($x$) |
|-------------------|---------------------------|
| $\rho_0$ ($\Omega$.cm) | 0.416 | 0.866 |
| $\rho_e$ ($\Omega$.cm/$K^{1/2}$) | 0.029 | 0.349 |
| $\rho_s$ ($\Omega$.cm) | 0.007 | 0.520 |
| $\rho_p$ ($\Omega$.cm/$K^5$) | $1.499 \times 10^{-12}$ | $9.533 \times 10^{-12}$ |
| $\rho_{p2}$ ($\Omega$.cm/$K^2$) | $1.027 \times 10^{-5}$ | $1.187 \times 10^{-4}$ |
| $\rho_{p9/2}$ ($\Omega$.cm/$K^{9/2}$) | $3.045 \times 10^{-11}$ | $1.903 \times 10^{-10}$ |
| $\rho_a$ ($\Omega$.cm) | $2.394 \times 10^{-7}$ | $2.707 \times 10^{-6}$ |
| $E_a/k_B$ (K) | 1011.087 | 2823.259 |
| $U_0/k_B$ (K) | 1028.412 | 2853.274 |
| $T_{c}^{mod}$ (K) | 330.622 | 310.198 |
| $T_{M-I}$ (K) | 304.343 | 272.508 |
| $R^2$ (%) | 99.99 | 99.99 |

The decreases of the $T_c$ with the increase in the Nickel concentration can be explained by considering the reduction of the effective $e_g$ electron bandwidth ($W$) [10]. The following empirical formula has been generally used to describe the electron bandwidth ($W$):

$$W \sim \frac{\cos \frac{1}{2} \left( \pi - <Mn-O-Mn> \right)}{d_{<Mn-O>}^{3.5}}$$

The lattice parameters (average bond length ($d_{<Mn-O>}$) and average bond angle $<Mn-O-Mn>$) and the results of $W$ calculation are given in Table 1. The reduction in the $W$ value reduces the overlap between
the Mn-3d and the O-2p orbitals in the exchange interaction between Mn$^{3+}$-O-Mn$^{4+}$ ions, leading to a reduction in the $T_c$ \[10\].

4. Conclusion
In summary, the structural, microstructure and electrical transport properties of La$_{0.7}$Sr$_{0.2}$Ba$_{0.1}$Mn$_{1-x}$Ni$_x$O$_3$ ($x = 0.02$ and $0.05$) compounds have been investigated. The results show that the $<$Mn-O-Mn$>$ bond angle decreases and the $<$Mn-O$>$ bond length increase with the decrease in grain size. The overall resistivity increases with increases in nickel substitution. Electrical transport behavior has been successfully explaining by the percolation model. It was found that nickel substitution greatly influences the interaction and scattering between electron, phonon, and magnon, which causes reduction of DE interaction. Furthermore, the metal-insulator transition temperature ($T_{MI}$) decreases from 304 to 272 K and Curie Temperature from theoretical calculated ($T_c^{mod}$) from around 330 to 310 K respectively.

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