Electrical Properties of La$_{0.67}$Sr$_{0.33}$Mn$_{0.8}$Ni$_{0.2}$O$_3$ Synthesized by Sol Gel Method

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Abstract. The previous study of lanthanum manganites showed that physical properties of LaMnO$_3$ compound has changed when Sr doped the La site. La$_{0.67}$Sr$_{0.33}$MnO$_3$ compound give the highest $T_c = 370$ K and showed metal insulator transition. It happens as a result of changed in Mn$^{3+}$/Mn$^{4+}$ ratio. Its indicated that Mn has the most important rule to the physical properties changed. In order to shift $T_c$ of the compound to the near room temperature, Ni doped was given to Mn site of LSMO. In this paper, 20% Mn site was doped by Ni. La$_{0.67}$Sr$_{0.33}$Mn$_{0.8}$Ni$_{0.2}$O$_3$ compound synthesized by sol gel method and characterized using XRD. Then, single phase compound resistivity was measured to see the electrical properties this compound. The XRD result showed that sample have single phase with rhombohedral structure and R-3c space group. Resistivity as a function of temperature graph does not show resistivity peak and metal insulator transition. The resistivity measurement showed that below 300 K, resistivity increased with decreased of temperature that indicates insulator behavior. It caused by decreased of double exchange interaction and increase of superexchange interaction. From this result, we can conclude that Ni doped decreased electrical properties of the sample.

1. Introduction
Lanthanum manganites La$_{1-x}$A$_x$MnO$_3$ (A = Sr, Ba, Ca) have been studied and become subject of research interest because of their magnetic and electrical properties which can be varied and applied in magnetic random access memory, and magnetic sensor [1,2]. Doping in La site would change structure and electrical properties of material. The previous study of lanthanum manganites showed that physical properties of LaMnO$_3$ compound has changed when Sr doped the La site. La$_{0.67}$Sr$_{0.33}$MnO$_3$ compound give the highest $T_c = 370$ K and showed metal insulator transition [3]. It happens as a result of changed in Mn$^{3+}$/Mn$^{4+}$ ratio. Its indicated that Mn has the most important rule to the physical properties changed.

In order to shift $T_c$ of the compound to the near room temperature, Ni doped was given to Mn site of LSMO. In this paper, 20% Mn site was doped by Ni. La$_{0.67}$Sr$_{0.33}$Mn$_{0.8}$Ni$_{0.2}$O$_3$ compound was synthesized by sol gel method. Sample was characterized using XRD and the resistivity was measured using cryogenic magnetometer.

2. Experimental Details
La$_{0.67}$Sr$_{0.33}$Mn$_{0.8}$Ni$_{0.2}$O$_3$ sample was synthesized using a sol gel method. Suitable proportions of La$_2$O$_3$, Sr(NO$_3$)$_2$, Mn(NO$_3$)$_2$.4H$_2$O, and Ni(NO$_3$)$_2$.6H$_2$O were used as starting materials. Each starting material solved in aquabidest, while La$_2$O$_3$ precursor was solved in diluted HNO$_3$. The resulting solution of each
starting material mixed and stirred at 80°C. Ammonia solution was added to the mixed solution to adjust pH until reached 5.6. Then, the solution was stirred and dried it at 120°C for 2 h until sol gel formed. The gel then calcined at 500°C, grinded, and re-calcined at 850°C. The re-calcined sample was pressed into pellet and sintered at 1200°C for 2 h. The sample then characterized using XRD, while the resistivity was measured using cryogenic magnetometer.

3. Result and Discussion

3.1. Structure Characterization

Structure of sample is characterized using X-Ray Diffraction (XRD), and the result shows in figure 1. The figure 1 shows that sample has single phase with no impurity.

![Figure 1. XRD pattern of La_{0.67}Sr_{0.33}MnO_{3} sample [4] and La_{0.67}Sr_{0.33}Mn_{0.8}Ni_{0.2}O_{3} sample.](image)

The result of XRD characterization is analyzed using Rietveld refinement analysis method. The Rietveld refinement results show that sample has Rhombohedral structure with R-3c space group. Refinement result of La_{0.67}Sr_{0.33}Mn_{0.8}Ni_{0.2}O_{3} sample compared with La_{0.67}Sr_{0.33}MnO_{3} sample [4] and summarized in table 1.

| Parameters | La_{0.67}Sr_{0.33}MnO_{3} | La_{0.67}Sr_{0.33}Mn_{0.8}Ni_{0.2}O_{3} |
|------------|---------------------------|----------------------------------------|
| a (Å)      | 5.5005                    | 5.4767                                 |
| a (Å)      | 13.368                    | 13.316                                 |
| Volume (Å³)| 350.26                    | 345.90                                 |
| Crystallite size (Å) | 535.6                    | 572.8                                 |

3.2. Resistivity

The result of resistivity measurement show in figure 2. It show that sample has insulator behavior in temperature range 100-300 K with resistivity value range 0.01-0.34 Ω.m. The insulator behavior is indicated by increasing of resistivity with temperature decreased. The result does not show resistivity peak as shown in La_{0.67}Sr_{0.33}MnO_{3} sample and denote higher resistivity compared with La_{0.67}Sr_{0.33}MnO_{3} sample resistivity value range [4]. When Ni doped Mn site, there are more localization of electron,
because the ratio of Mn$^{3+}$/Mn$^{4+}$ will be decreased and suppress the Double Exchange (DE) interaction [5].

![Figure 2](image2.png)

**Figure 2.** Resistivity of La$_{0.67}$Sr$_{0.33}$Mn$_{0.8}$Ni$_{0.2}$O$_3$ sample in respect of temperature at zero magnetic field.

Resistivity of this sample could be analyzed using Small Polaron Hoping (SPH) model with equation (1) [5,6,7,8].

$$\rho = \rho_0 T \exp \left( \frac{E_A}{k_B T} \right)$$

(1)

Where $E_A$ is the sum of the activation energy required to create free carriers and the energy that activates carriers for hoping [5], $k_B$ is Boltzmann’s constant with value $8.617 \times 10^{-5} \text{eV.K}^{-1}$, and $\rho_0$ is residual resistivity [6,7,8].

![Figure 3](image3.png)

**Figure 3.** Theoretical fit of insulator state resistivity data for La$_{0.67}$Sr$_{0.33}$Mn$_{0.8}$Ni$_{0.2}$O$_3$ using SPH model.
When Ni doped Mn site, DE interaction will be reduced due to decrease of Mn$^{3+}$-O$^2$-Mn$^{4+}$ bond. In the insulator state as shown by La$_{0.67}$Sr$_{0.33}$Mn$_{0.8}$Ni$_{0.2}$O$_3$ sample, many electrons are localized, due to the decrease of Mn$^{3+}$/Mn$^{4+}$ ratio and the coupling between electrons and phonons that form polarons. When given temperature increases, the energy supplied is also getting bigger, and more polaron activated, so that the resistivity decreases. It explain the insulator behavior that showed by decreases of resistivity when temperature increased.

Value of obtained fitting parameters of La$_{0.67}$Sr$_{0.33}$Mn$_{0.8}$Ni$_{0.2}$O$_3$ sample are showed in table 2. Quality of fitting is evaluated by the value of squared linear correlation coefficients ($R^2$) [6]. We obtained $R^2$ value above 99.9%, and it means that the fitting that has been done has a good quality.

| Parameters            | Value |
|-----------------------|-------|
| $\rho_a$ ($\Omega m$) | 0.034 |
| $E_A \times 10^{-7}$ meV | 1.973 |
| $R^2$ (%)             | 99.93 |

4. Conclusion

La$_{0.67}$Sr$_{0.33}$Mn$_{0.8}$Ni$_{0.2}$O$_3$ sample was synthesized by sol gel method. XRD result showed that sample has single phase with no peak of impurity with rombhoedral structure and R-3c space group. The resistivity measurement showed that sample has insulator behavior with resistivity value range 0.01-0.34 $\Omega m$ in temperature range 100-300 K. Analysis of resistivity found that small polaron hoping (SPH) model fit the experimental data with $R^2$ value 99.93%.

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