Study of La_{0.67}Sr_{0.33}MnO_3 structure and resistivity synthesized by using sol gel method

U. Widyaiswari¹, B. Kurniawan¹, A. Imaduddin², S. A. Saptari³

Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Indonesia, Depok 16424, Indonesia
Metallurgical Research Center, Lembaga Ilmu Pengetahuan Indonesia, Puspiptek-Serpong 15314, Indonesia
Faculty of Science and Technologyy, Universitas Islam Negeri Syarif Hidayatullah, Jakarta 15412, Indonesia

E-mail: widyaiswari_utami@yahoo.com

Abstract. In this study a colossal magnetoresistance La_{0.67}Sr_{0.33}MnO_3 material was synthesized by using a sol gel method with different treatment heating process. First sample calcined at 850°C for 10 hours and pelletized, labelled as LSMO1, while another sample calcined at 850°C for 10 hours, pelletized, and sintered at 1200°C for 2 hours, labelled as LSMO2. The aim of this study was to learn a structure and resistivity of this material. The XRD results showed that both samples were single phase with no peak of impurity and formed a rhombohedral structure with space group R-3c. And the result showed that LSMO1 has smaller crystallite size than LSMO2. Result of resistivity measurement showed that LSMO1 has insulator behavior with resistivity several order of magnitude bigger than LSMO2. While LSMO2 had the peak of resistivity that showed a metal-insulator transition.

1. Introduction
During the last decade, lanthanum manganites La_{1-x}A_xMnO_3 (A = Sr, Ba, Ca) have been studied and become subject of research interest because of their magnetic and electrical properties which can be applied in magnetic random access memory, and magnetic sensor [1-2]. Previous study showed that mixed valence manganites have various phase diagram depend on concentration of doping [3]. Doping in La site would change structure and electrical properties of material. Beside the concentration of doping, the difference physical properties caused by different treatment in preparation process that affected the size of particle [3-5].

Yadav et al showed that different annealed temperatur produced the samples with different grain size that caused the different magnetic properties of the samples. The results showed that increased of annealing temperature enhanced the particle size of the samples [5], and increased of particle size leads to increase of magnetic properties indicated by increasing of magnetization saturation of the samples. Another study about the effect of various sintering temperature have been published by Zhang et al and Balcells et al. The results showed that higher sintering temperature increased the grain size and affected the physical properties of samples, such as the resistivity of samples [3], [4]. Smaller particle size gave higher resistivity measurement.
The aim of this study was to learn a structure and resistivity of La$_{0.67}$Sr$_{0.33}$MnO$_3$ material synthesized by sol gel method with different treatment heating process.

2. Experimental details
La$_{0.67}$Sr$_{0.33}$MnO$_3$ perovskite manganites materials were synthesized using a sol gel method. Suitable proportions of La$_2$O$_3$, Sr(NO$_3$)$_2$, and Mn(NO$_3$)$_2$.4H$_2$O were used as starting materials, and citric acid as a fuel. Each starting material solved in aquabidest. La$_2$O$_3$ precursor then 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 7 [6]. Then, the solution mixed and stirred at 70-80°C until the water evaporated and dried it at 120°C for 2 h until sol gel formed. The gel then calcined at 500°C for 5 h, ground, and calcined again at 850°C for 10 h.

The re-calcined samples were divided into two portions. For first portion, sample was pressed into pellet [7] and labelled as LSMO1, while another portion of sample was pressed into pellet, sintered at 1200°C for 2 h, and labelled as LSMO2. Both of sample then characterized using XRD and SEM, while the resistivity were measured using cryogenic magnetometer.

Cryogenic magnetometer using four point probe (FPP) principal include the cryostat system, sehingga resistivity measurement can be done in the various temperature with range of temperature 5-300 K.

3. Results and discussion
Samples that have been synthesized by sol gel method then characterized by XRD and cryogenic magnetometer to learn the structure and transport properties of the samples.

3.1. Structure characterization
The LSMO1 and LSMO2 samples synthesized using sol gel method were characterized using X-ray Diffraction (XRD). Figure 1 shows XRD pattern of both samples. The result shows that samples have single phase with no impurity peak. The data was fitted with Rietvel refinement. The samples have rhombohedral structure with R-3c space group.

![Figure 1. XRD pattern of LSMO1, sintered at 850°C [7], and LSMO2, re-sintered at 1200°C](image-url)
Rietveld refined parameters were showed in Table 1. The results show that lattice parameter of LSMO1 is smaller than LSMO2. The crystallite size of LSMO2 is bigger than LSMO1. It is caused by crystal growth at higher temperature better than in low temperature.

| Sample  | a = b (Å) | c (Å) | V (Å³) | Crystallite size (nm) | Structure | Space group |
|---------|-----------|-------|--------|-----------------------|-----------|-------------|
| LSMO1   | 5.4875    | 13.359| 348.38 | 26.01                 | rhombohedral | R-3c        |
| LSMO2   | 5.5005    | 13.368| 350.26 | 53.56                 | rhombohedral | R-3c        |

3.2. Resistivity measurement

Resistivity of samples were measured using cryogenic magnetometer with four point probe work principle. Figure 2 and figure 3 show the results of resistivity measurement as temperature function of LSMO1 and LSMO2 respectively. It is shows that LSMO1 has insulator behavior, it is showed by increased of resistivity with temperature decreased, while LSMO2 has metallic behavior showed by increased of resistivity with temperature increased. In figure 3, resistivity peak of LSMO2 haven’t been seen yet. It is predicted happened above room temperature, 300 K, while the maximum working temperature of cryogenic magnetometer used in this study is 300 K.

Beside the different behavior of LSMO1 and LSMO2, LSMO1 has resistivity several order of magnitude bigger than LSMO2 resistivity. We can stated that sample with smaller crystallite size give higher resistivity than sample with bigger crystallite size. It is related with the content of oxygen. To analyze this phenomena, EDX characterization have been done to observe the element content of LSMO1. In LSMO1, EDX result shows that atomic percent of oxygen element in the amount of 35.15%, half times below the expected value.

The oxygen deficiency indicate the presence of oxygen vacancies [8]. The oxygen vacancies suppresses the Double Exchange (DE) interaction that have a big role in mixed valence manganites transport phenomena. Lakshmi and Reddy showed same result and used same approximation to analyze the decreases of resistivity with increased of grain size. Besides the intrinsic DE interaction between Mn$^{3+}$ and Mn$^{4+}$, extrinsic contribution due to spin-polarized tunneling affect the resistivity [8]. In granular sample, smaller grain size give larger number of grain boundaries in sample and enhance the resistivity due to spin-polarized tunneling [8].
The different behavior and resistivity value of both sample can be related to the crystallite size of samples. LSMO1 have smaller crystallite size than LSMO2, so that there will be more local interface between the grain and the more tunneling process.

4. Conclusions
Temperature of sintering process affect the crystallite size of sample. Higher sintered temperature gives bigger crystallite size. It is related with oxygen content in the sample. Lower temperature gives smaller crystallite size and less oxygen content. This oxygen deficiency affected enhancement of resistivity and different electrical behavior. LSMO1 has insulator behavior with high resistivity, while LSMO2 has metallic behavior with smaller resistivity than LSMO1.

Acknowledgement
We sincerely thank to LPDP, Ministry of Finance, Republic of Indonesia and Universitas Indonesia for partially funding this research through Indonesian Education Scholarship program for thesis and PITTA grant.

References
[1] Myron BS and Marcelo J 2001 Rev. Mod. Phys. 73 583
[2] Danyan Cao, Yuanyuan Z, Wenxia D, Jing Y, Wei B, Ying C, Genshui W, Xianlin D and Xiaodong T 2015 Ceram. Int. 41 381
[3] Ll Balcells, J. Fontcuberta, B. Martinez and X. Obradors 1998 Phys. Rev. B 58 697
[4] Ning Zhang, Weiping D, Wei Z, Dingyu X and Youwei D 1997 Phys. Rev. B 56 8138
[5] P A Yadav, A V Deshmukh, K P Adhi, B B Kale, N Basavaiah, S I Patil 2013 J. Magn. Magn. Mater. 328 86
[6] D T M Hue, T V Manh, L H Anh, L V Hong, M H Phan, P T Huyen and H D Chinh 2014 IEEE Trans. Magn. 50
[7] Would be published in online proceedings of Seminar Nasional Fisika
[8] Y Kalyana Lakshmi and P Venugopal Reddy 2009 J. Alloys Comp. 470 67