Structure and microstructure of La$_{0.8}$Ca$_{0.05}$Ag$_{0.15}$MnO$_3$ material synthesized by sol-gel method

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Abstract. The La$_{0.8}$Ca$_{0.05}$Ag$_{0.15}$MnO$_3$ material was prepared by the sol-gel method, sintered at 800°C for 24 hours. The material is derived from the La$_{0.8}$Ca$_{0.2}$MnO$_3$ material substituted by 15% Ag on the Ca-site. The substitution changed the lattice parameters, Mn-O bond length, and Mn-O-Mn bond angle. These can affect the transport of electrons from the material. The XRD data were analyzed using Rietveld refinement technique and show the material has a rhombohedral structure with the lattice parameters $a$, $b$, and $c$ are 5.494, 5.494, and 13.33, respectively. The SEM data with SE mode show La$_{0.8}$Ca$_{0.2}$MnO$_3$ material substituted by 15% Ag seen the existence of agglomeration and porous. Furthermore, the material has a high homogeneity, this is seen in SEM data with BSE mode. The EDX results show that the silver has been successfully substituted into the La$_{0.8}$Ca$_{0.2}$MnO$_3$ matrix with the value at% for each element contained in the material close to value at% calculation.

1. Introduction
Manganite perovskite material with the general formula Re$_{1-x}$Ae$_x$MnO$_3$ (Re = La, Pr, Nd, etc., Ae = Ca, Sr, Ba, etc.) has an interesting phenomenon, that is magnetotransport properties effect [1, 2]. Because of this phenomenon, manganite perovskite materials can be applied as a data storage device, magnetic sensors, magnetic recording device, etc. [2, 3] The magnetotransport effect occurs because of the double exchange interaction, in which introduced by Zener [4]. The double exchange is an electron hopping from Mn$^{3+}$ ion to Mn$^{4+}$ ion through the O atom. The Mn-O bonding distance may affect the electron hopping that will occur [4]. According to J. C. Debnath (2015), the interaction of DE occurs as stronger as the Mn-O-Mn bonding angle increases, in which causing the magnetotransport of the material to be better [5]. In this study, Ca ion in La$_{0.8}$Ca$_{0.2}$MnO$_3$ is substituted by 15% silver ion, wherein according to Y. Kalyana (2010) the magnetotransport effect depends greatly on the doping level of an element to be doped into a material [2]. When an element in a material is doped by another element, which has an average of the different ionic radius will cause the lattice distortion [2]. The distortion can changes the Mn-O bond length and Mn-O-Mn bond angle, thus affecting the magnetotransport of the material [6,7].

2. Experimental
La$_{0.8}$Ca$_{0.05}$Ag$_{0.15}$MnO$_3$ materials were prepared using the sol-gel method. Precursors used include: La$_2$O$_3$, Ca(NO$_3$)$_2$, AgNO$_3$, and Mn(NO$_3$)$_2$. Precursors based on nitrate are dissolved into aquabidest, while precursor based on oxide is dissolved into nitric acid which has been diluted by aquabidest. All dissolved precursors are mixed while stirring using magnetic stirrer until the solution...
becomes a gel. The gel was dehydrated at 120°C for 3 hours. After which, it is calcined at 500°C for 5 hours. Then, the sample was compacted at 4 ton for 3 minutes to form a pellet sample. The pellet was sintered at 800°C for 24 hours. The pellet sample was characterized by X-Ray Diffractometer to see the sample structure. After that, it was characterized by Scanning Electron Microscopy to know the microstructure of the sample and Energy Dispersive Spectroscopy to confirm the purity of the sample.

3. Result and discussion

Figure 1 shows the XRD pattern of La$_{0.8}$Ca$_{0.05}$Ag$_{0.15}$MnO$_3$ material sintered at 800°C for 24 hours. The pattern indicates that La$_{0.8}$Ca$_{0.05}$Ag$_{0.15}$MnO$_3$ material has a single phase, where no other phase is identified (phase of base material or impurities phase). Refinement of XRD data has been done using the Rietveld technique. The technique is used to match the XRD pattern obtained with the XRD pattern present in the database. From the refinement results, it is known that the material has a rhombohedral structure with $Rar{3}C$ space group. Stability of the structure can be determined by Goldschmidt’s tolerance factor ($\tau$). The value of $\tau$ can be calculated by using the equation:

$$\tau = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$

With $r_A$ is ionic radii of each element on site A (La$^{3+}$, Ca$^{2+}$, and Ag$^+$), $r_B$ is ionic radii of the Mn element (Mn$^{3+}$ and Mn$^{4+}$), $r_O$ is ionic radii of O$^2$ [8]. Ye. et al. (2002) revealed the stable condition for the orthorhombic structure on perovskite material at $\tau < 0.96$ and stable condition of the rhombohedral structure at 0.96 < $\tau$ < 1 [8]. From the calculation, the value of La$_{0.8}$Ca$_{0.05}$Ag$_{0.15}$MnO$_3$ material tolerance factor is 0.965 so that the stable condition of the rhombohedral structure is achieved.

![Figure 1. XRD Pattern of La$_{0.8}$Ca$_{0.05}$Ag$_{0.15}$MnO$_3$ Material](image)

Table 1 is the result of Rietveld refinement analysis for La$_{0.8}$Ca$_{0.05}$Ag$_{0.15}$MnO$_3$ material. When compared with the literature, when Ca atoms in La$_{0.8}$Ca$_{0.2}$MnO$_3$ material are doped by silver with a concentration of 0.15, lattice parameters and unit cell volume of the material have increased [9]. These changes are caused by the radius of Ag ion is greater than the radius of Ca ion, that is 1.28 Å and 1.12 Å, respectively [10]. In addition, the Mn-O bond length and the Mn-O-Mn bond angle are altered.
Table 1. The results of Rietveld Refinement analysis of XRD data

| Sample | $\text{La}_{0.8}\text{Ca}_{0.05}\text{Ag}_{0.15}\text{MnO}_3$ |
|--------|---------------------------------------------------------|
| a [Å]  | 5.494                                                  |
| b [Å]  | 5.494                                                  |
| c [Å]  | 13.33                                                  |
| V [Å³] | 348.475                                                |
| $d_{\text{Mn}-\sigma}$ | 1.955                                                  |
| $\theta_{\text{Mn}-\sigma-\text{Mn}}$ | 164.297                                                |
| Goodness of fit | 1.115                                                  |

These will have an impact on the transport properties of the $\text{La}_{0.8}\text{Ca}_{0.05}\text{Ag}_{0.15}\text{MnO}_3$ material [7]. According to Manjunatha. et al. (2015), the change in the Mn-O bond length and the Mn-O-Mn bond angle are due to doping on site A of the manganite perovskite structure, in which causes a lattice distortion [11, 12].

To know the surface morphology of $\text{La}_{0.8}\text{Ca}_{0.05}\text{Ag}_{0.15}\text{MnO}_3$ material can be characterized by Scanning Electron Microscopy (SEM). SEM image capture uses two modes; those are the SE (secondary electron) mode and BSE (backscattered electron) mode. Figure 2 is the result of SEM for SE mode on $\text{La}_{0.8}\text{Ca}_{0.05}\text{Ag}_{0.15}\text{MnO}_3$ material. In the micrograph show granular morphology with a presence of axis. The average grain size in the SEM result is larger than Cs from the XRD data using the Debye Scherrer equation [13]. The values of each result are 101 nm and 26.85 nm, respectively. The larger of the average grain size in the SEM result is caused by the agglomeration so that the grain boundary in the material is not visible, it is seen in the micrograph. But the value cannot be compared, because in SEM result only takes the average of 9 points of grain. This result is also shown by Ben Jemaa. et al. (2014) [13]. BSE mode is shown in Figure 3, from the micrograph seen on the entire surface of the $\text{La}_{0.8}\text{Ca}_{0.05}\text{Ag}_{0.15}\text{MnO}_3$ material has an almost uniform color. It is identified that the material has high homogeneity or no grouping of certain elements [11].

![Figure 2. Secondary Electron (SE) Mode Image for the $\text{La}_{0.8}\text{Ca}_{0.05}\text{Ag}_{0.15}\text{MnO}_3$ Material](image1)

![Figure 3. Backscattered Electron (BSE) Mode Image for the $\text{La}_{0.8}\text{Ca}_{0.05}\text{Ag}_{0.15}\text{MnO}_3$ Material](image2)
The result of edx for La₀.⁸Ca₀.⁰₅Ag₀.₁₅MnO₃ material is shown in figure 4. Besides to see the purity of the material, the edx characterization can also confirm whether or not the silver substitutes the calcium element. The spectrum in Figure 3 shows that silver (in the red circle) has entered into the LCMO matrix. This indicates that silver has been successfully performed. Table 2 shows the value at% obtained from EDX results and calculation result. If compared, the value at% for elements La, Ca, Mn, and O obtained from EDX close to the value at% obtained from the calculation, but the value at% Ag is reduced this is caused by silver evaporation during a sintering process. These results are the same as those obtained by Kalyana. et al. (2010) [2].

4. Conclusion
The La₀.⁸Ca₀.⁰₅Ag₀.₁₅MnO₃ material has been successfully synthesized using the sol-gel method. The material was sintered at 800°C for 24 hours. X-ray diffraction (XRD) characterization results show a single-phase material with a rhombohedral crystal structure. The Scanning Electron Microscopy (SEM) characterization with SE mode indicates that La₀.⁸Ca₀.⁰₅Ag₀.₁₅MnO₃ material has granular morphology in the presence of porous and agglomeration. In the SEM result with BSE mode show a uniform color throughout the surface, it identifies that the material has a high homogeneity. Energy Dispersive X-Ray (EDX) characterization result shows that the La₀.⁸Ca₀.⁰₅Ag₀.₁₅MnO₃ material has a high purity with the value at% for each element contained in the material close to value at% calculation.

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