The effect of partial substitution of monovalent ion on divalent ion of La$_{0.8}$Ca$_{0.2}$Ag$_x$MnO$_3$ (x=0 and x=0.05) compounds in structure, morphology, and purity by sol-gel method

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Abstract. La$_{0.8}$Ca$_{0.2}$Ag$_x$MnO$_3$ ceramics with x = 0 and 0.05 has been synthesized using the sol-gel method. These materials are one member of perovskite manganites materials which has the general formula RE$_x$AE$_{1-x}$MnO$_3$. Material LaCaMnO$_3$ and La$_{0.8}$Ca$_{0.2}$Ag$_x$MnO$_3$ was characterized by X-ray Diffractometer (XRD), and Scanning Electron Microscopy-Dispersion Spectroscopy (SEM-EDS). According to X-Ray Diffractometer characterization and high score refinement showed that the crystal structure for both materials are orthorhombic. Partial substitution of the Ag in Ca did not change the structure of the material but there are changes in lattice parameters. Both materials have a high homogeneity with the larger crystal size when doped by Ag, it is seen from the morphology of Scanning Electron Microscope (SEM). EDX characterization using point analysis confirms that in samples with x = 0.05 (La$_{0.8}$Ca$_{0.2}$Ag$_x$MnO$_3$), the Ag ion have been successfully substituted. The result of the measurement of the composition of the two materials is not much different from the calculation, so it can be concluded that both materials have a good compositional purity.

1. Introduction

In recent years, many researchers have studied the manganite perovskite with the general formula RE$_x$AE$_{1-x}$MnO$_3$, where R is a trivalent rare earth element (Nd, La, Pr, etc.), and A is a divalent alkaline earth metal (Ba, Sr, Ca, etc.) as a result of their rich properties. Partial substitution of divalent ions to trivalent ions can produce a mixture of Mn$^2$-/Mn$^4$ valence, which will give unique phenomena, including metal-insulator transition (T$_m$), colossal magnetoresistance effects, ferromagnetic-paramagnetic transition (T$_c$), etc. [1]. The interactions between Mn$^2$ and Mn$^4$ ions are described in the double exchange mechanism, which was first proposed by Zener [2]. A simply, double exchange mechanism is the simultaneous exchange of electrons from Mn$^2$ to Mn$^4$ ions through the oxygen atom to keep the electric charge remains neutral, so the changes in the length and angle of Mn–O–Mn bonds can affect the double exchange interaction [2,3]. Based on literature, modification perovskite manganite material by replacing different dopant elements can affect the microstructure, which results in magnetic and electrical properties [4]. Therefore, the structure of this material is very important to be discussed further.

Recently, engineering of manganite perovskite structures has been carried out by substituting some monovalent ions into divalent ions, which can affect the ratio of Mn$^2$ and Mn$^4$, shortening the bond distance between Mn–O–Mn and increasing the angle of Mn–O–Mn bond that will affect the double exchange interaction and have an impact on the nature of the magnetotransport of the material [4]. So, in this research, we investigated the effect of partial substitution of Ag on Ca-site of the La$_{0.8}$Ca$_{0.2}$Ag$_x$MnO$_3$ (x = 0 and 0.05) compounds in structure, morphology and purity.
**Table 1.** Data Ionic Radii

| Ion   | Ionic radius (nm) |
|-------|-------------------|
| La³⁺  | 1.36              |
| Ca²⁺  | 1.26              |
| Ag⁺   | 1.28              |
| O²⁻   | 1.40              |
| Mn³⁺  | 0.65              |

**Figure 1.** XRD patterns of La₈₀Ca₂₀MnO₃ and La₈₀Ca₁₅Ag₅₀₅MnO₃.

**Figure 2.** Local XRD patterns around the strongest diffraction peak (121)

### 2. Experimental

Materials La₈₀CaₓAgₓMnO₃ (x = 0 and x = 0.05) were prepared by a solgel method using the nitrate form of the raw materials. The raw materials are La₂O₃, Ca(NO₃)₂.6H₂O, AgNO₃, Mn(NO₃)₂.4H₂O, and citric acid were weighed according to stoichiometric calculations. All raw materials, except La₂O₃, were dissolved using aquabidest. La₂O₃ was dissolved in aquabidest and nitric acid while stirred using a magnetic stirrer to form lanthanum nitrate. After that, the solution of the other raw materials were poured into lanthanum nitrate while continuing to stir and heated with a magnetic stirrer at 80 °C. Then the pH of the mixture solution is adjusted to reach pH of 7 with the addition of ammonium solution. Afterwards, leave the solution of mixture for a few moments until gel is formed. Then the gel was dried for 3 h at 120 °C, then calcined for 5 h at 500 °C. The calcined material is then formed into a pellet with pressure and then sintered for 24 h at 800 °C.

The pellets were characterized using X-Ray Diffractometer from a Rigaku SmartLab with Cu Kα radiation (λ = 1.54178 Å) to determine the crystal structure of the materials. The 2θ range used was 0°–90° and scan rate was 0.02° per second. The XRD pattern was analyzed by Rietveld refinement using high score. The crystallite size D was calculated using the Debye–Scherrer’s equation (D = 0.94 λ/β cosθ) with θ and β are the position and the FWHM of highest diffraction peak, respectively and λ is the wavelength of the Cu Kα XRD source. The morphology of the sample surface was characterized by Scanning Electron Microscopy Hitachi SU-3500 with the accelerating voltage used was 20000 Volt and magnification used was 20000 times. SEM observations are carried out by placing a test sample in the form of a pellet above the holder that has been given carbon-type material. The result of EDX characterization were obtained together with SEM measurements using point analysis.

### 3. Results and discussion

Based on Takehira’s research, one of the requirements of successful doping is the dopant ion radius, which is relatively equal to the ion radius to be doped [5]. Table 1 shows the data of ionic radius, which is based on the Shannon research [6]. From the table, it can be seen that the difference of radius of Ca ion and the radius of Ag ion is relatively small (less than ± 5%). It can be confirmed that the silver ion can substitute the Ca ion. The substitution effect on the crystallographic parameter is shown in figure 1 and table 2.
Table 2. Rietveld refinement results from XRD data.

| Compound | La$_{0.8}$Ca$_{0.2}$MnO$_3$ | La$_{0.8}$Ca$_{0.15}$Ag$_{0.05}$MnO$_3$ |
|----------|----------------------------|--------------------------------------|
| Crystal Structure | Orthorombic | Orthorombic |
| Space Group | Pnma | Pnma |
| a (Å) | 5.483 | 5.458 |
| b (Å) | 7.760 | 7.745 |
| c (Å) | 5.455 | 5.501 |
| V (Å$^3$) | 232.15 | 232.61 |
| $<D>$ | 22 | 24 |
| $<\text{Mn-O}>$ | 1.969 | 1.966 |
| $<\text{Mn-O-Mn}>$ | 154.84 | 156.08 |
| $\chi^2$ | 1.06 | 1.09 |

Table 3. Atomic position, Wyckoff position and occupancy for La$_{0.8}$Ca$_{0.2}$MnO$_3$.

| Atom | Wyckoff position | Occupancy | x | y | z |
|------|-----------------|-----------|---|---|---|
| La   | 4c              | 0.8       | 0.482 | 0.25 | 0.003 |
| Ca   | 4c              | 0.2       | 0.482 | 0.25 | 0.003 |
| Mn   | 4a              | 1         | 0    | 0   | 0   |
| O1   | 8d              | 1         | 0.226 | 0.032 | 0.269 |
| O2   | 4c              | 1         | 0.502 | 0.25 | 0.564 |

Table 4. Atomic position, Wyckoff position and occupancy for La$_{0.8}$Ca$_{0.15}$Ag$_{0.05}$MnO$_3$.

| Atom | Wyckoff position | Occupancy | x | y | z |
|------|-----------------|-----------|---|---|---|
| La   | 4c              | 0.8       | 0.482 | 0.25 | 0.003 |
| Ca   | 4c              | 0.15      | 0.482 | 0.25 | 0.003 |
| Ag   | 4c              | 0.05      | 0.482 | 0.25 | 0.003 |
| Mn   | 4a              | 1         | 0    | 0   | 0   |
| O1   | 8d              | 1         | 0.226 | 0.032 | 0.269 |
| O2   | 4c              | 1         | 0.502 | 0.25 | 0.564 |

Figure 1 shows the XRD diffraction pattern of the La$_{0.8}$Ca$_{0.2}$MnO$_3$ and La$_{0.8}$Ca$_{0.15}$Ag$_{0.05}$MnO$_3$ samples sintered at 800 °C. The strongest peaks (121) for both samples are shown in Figure 2. In the XRD results, both samples have the same diffraction pattern. There is no change in crystal structure when La$_{0.8}$Ca$_{0.2}$MnO$_3$ is doped with monovalent Ag ion. There is no change in structure after doping is indicated by the unchanged position of the wyckoff when the material La$_{0.8}$Ca$_{0.2}$MnO$_3$ is doped by Ag ions (we can see details in table 3 and table 4). From the result of XRD data processing using the Rietveld refinement method, it is known that both samples La$_{0.8}$Ca$_{0.2}$MnO$_3$ and La$_{0.8}$Ca$_{0.15}$Ag$_{0.05}$MnO$_3$ having an orthorombic structure with the position of each atom is shown in table 2. Detailed images of the structure of these two materials are shown in figure 3 and figure 4.

Table 2 presents the result of refinement XRD data using High Score Plus. The result showed that if Ca ions are substituted by the Ag ion, there is an increase in lattice parameter and cell volume when the concentration is 0.05. This can also be seen in the diffraction pattern in figure 2. The figure shows the diffraction peak shift to a smaller angle for the dopped sample, which indicates an increase in the lattice parameters. The increase in lattice parameters and cell volume may be due to the radius of the Ag ion which is greater than the radius of Ca ion (see table 1). These results are the same as the results obtained by Lakshmi and Reddy [7]. Changes in lattice parameters also identify distortions in the crystal structure according to what has been obtained from previous study [8].
The presence of distortion in the La,Ca,MnO material is also seen from the FTIR results as previously examined by Shinde et al. [9] and Li et al. [10]. When Ca doped La on La,Ca,MnO material, there was an absorption band at 600 cm\(^{-1}\), which attributed to the metal oxide stretching vibration that can change the length and angle of the Mn–O–Mn bond, but the vibration of these changes are not detected in the FTIR spectrum which usually appears at 200 cm\(^{-1}\). \cite{9,10}. Table 4 shows changes in length and angle of the Mn-O-Mn bonds after being doped by silver. It is possible that there was a change in the absorption band when the La,Ca,MnO material was doped by the Ag ion. However that is only based on the results of the XRD data, so that it cannot be explained in detail.

Changes in bond distance and bond angle of Mn-O-Mn greatly affect the double exchange interaction, which will cause changes in electrical properties of the samples. Based on the bandwidth theory, this interaction has a strong correlation with the conduction bandwidth \(W\) shown in equation (1):

\[
W = \cos\left(\pi \left(\frac{\theta_{\text{Mn–O–Mn}}}{d_{\text{Mn–O–Mn}}}\right)\right)
\]

with \(d_{\text{Mn–O–Mn}}\) represents the length of Mn-O-Mn bond and \(\theta_{\text{Mn–O–Mn}}\) represents the angle of Mn-O-Mn bond \cite{3}. Electron transport will be more difficult with the greater length and angle of the Mn-O-Mn bond, which will affect the weakening of the double exchange interactions \cite{3,8}. From table 2 it can also be seen that when Ca ions are substituted by Ag ions with a concentration of 0.05, the distance of the Mn-O-Mn bond becomes smaller and the bond angle becomes larger (close to 180\(^\circ\)) which results in stronger double exchange interaction so electron transport becomes easier.

The surface morphology of La,Ca,MnO and La,Ca,Ag ,MnO materials are shown in figure 5a and figure 5b. The grain cannot be clearly seen from the S\(\text{E}\)M results of La,Ca,MnO sample because of the limitation of the magnification of the S\(\text{E}\)M used, which is only able to enlarge images up to 20,000 times. However logically, substituting 0.05 Ag to the AE site may cause greater grain growth \cite{7}. Increasing grain size due to doping can reduce pores and defects, which can improve the electrical properties of the samples \cite{11}. The average grain size of La,Ca,MnO, without and with doping monovalent Ag ions is 105.2 nm and 260 nm, respectively.

The success of material engineering can be seen in figure 6, which is the result of EDX analysis for each material, La,Ca,MnO and La,Ca,Ag ,MnO. The EDX analysis results are important to confirm the purity of the material that has been made. The results show that the Ag ion is substituted the perovskite manganite structure (seen in the red circle in figure 6) so that it can be said that Ag successfully entered La,Ca,MnO material. Table 5 shows the composition obtained from EDX analysis and the results of the calculations. The table shows that the composition of the EDX analysis results for both samples is close to the calculation results, with the EDX analysis composition generally smaller than the calculation results because the composition obtained from EDX analysis
Table 5. Composition of La$_{0.8}$Ca$_{0.2}$MnO$_3$ and La$_{0.8}$Ca$_{0.15}$Ag$_{0.05}$MnO$_3$ obtained by EDX analysis and manual calculation.

|                  | At% (EDX analysis) | At% (calculation) |
|------------------|--------------------|--------------------|
|                  | La     | Ca     | Ag | Mn | O   | La     | Ca | Ag | Mn | O   |
| La$_{0.8}$Ca$_{0.2}$MnO$_3$ | 14.08  | 3.37   | 0  | 15.87 | 66.68 | 16     | 4  | 0  | 20 | 60 |
| La$_{0.8}$Ca$_{0.15}$Ag$_{0.05}$MnO$_3$ | 13.72  | 2.68   | 0.71 | 17.53 | 65.36 | 16     | 3  | 1  | 20 | 60 |

Figure 5. Scanning electron microscope image of (a) La$_{0.8}$Ca$_{0.2}$MnO$_3$ and (b) La$_{0.8}$Ca$_{0.15}$Ag$_{0.05}$MnO$_3$.

Figure 6. EDX spectrum of (a) La$_{0.8}$Ca$_{0.2}$MnO$_3$ and (b) La$_{0.8}$Ca$_{0.15}$Ag$_{0.05}$MnO$_3$.

is semiquantitative. The table also shows that when Ag is doped on La$_{0.8}$Ca$_{0.2}$MnO$_3$ material with a concentration of 0.05, the composition of Ag in perovskite material is smaller than the composition of the calculation result. This is due to the possibility that the Ag ion evaporates during the heating processes i.e. calcination process and sintering process. This phenomenon has also been reported before by Lakhsmi and Reddy [7].

4. Conclusions

We have succeeded in synthesizing La$_{0.8}$Ca$_{0.2-x}$Ag$_x$MnO$_3$ with $x = 0$ and 0.05 using the sol-gel method. XRD data processing using Rietveld refinement produced orthorhombic crystal structures for both samples. Substitution of 0.05 Ag into the Ca site did not change the crystal structure but changed the lattice parameters of perovskite manganite material. The monovalent Ag ion substitution into Ca ion can also shorten the bond distance between Mn-O and increase the angle of Mn-O-Mn bond. According to bandwidth theory when the length of Mn-O-Mn bond gets smaller and the angle of the Mn-O-Mn bond increases, the double exchange interaction will be stronger, which will affect electron transport of the material. From the SEM results it can be seen that the grain size increases when La$_{0.8}$Ca$_{0.2}$MnO$_3$ is doped with Ag. EDX results indicate that Ag has been substituted in the La$_{0.8}$Ca$_{0.2}$MnO$_3$. 
material. The composition of EDX analysis is close to the results of using manual calculations, and both samples can be said to have high purity in the absence of other elements besides material elements.

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