Influence of silver (Ag) doping on a crystal structure of La$_{0.7}$Ag$_{0.1}$Ca$_{0.2}$MnO$_3$ and La$_{0.65}$Ag$_{0.15}$Ca$_{0.2}$MnO$_3$ manganites synthesized by sol-gel method

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Abstract. Perovskite manganite material has been extensively investigated because it has many attractive properties. In this paper, crystal structure of La$_{0.7}$Ag$_{0.1}$Ca$_{0.2}$MnO$_3$ (LACMO1) and La$_{0.65}$Ag$_{0.15}$Ca$_{0.2}$MnO$_3$ (LACMO15) materials will be reported. LACMO1 and LACMO15 materials were synthesized by sol-gel method with sintering temperature 900°C for 24h. Structural properties of LACMO1 and LACMO15 materials were characterized using X-Ray Diffractometer (XRD). The characterized results show a crystal structure transition from orthorhombic (Pnma spacegroup) to rhombohedral (R$\bar{3}$c space group) along with increasing the concentration of Ag doping. The crystal structure transition show there is a distortion of the material structure caused by Ag-doping. Increasing the concentration of Ag doping may affect the tolerance factor (t) that used to measure the degree of distortion of a perovskite.

1. Introduction
Perovskite manganite material has attracted much attention of world researchers because it has various interesting properties, such regarding structural, electrical, magnetic, and thermal properties [1-3]. The perovskite manganite material which has the initial chemical formula REMnO$_3$ (RE = Rare Earth cation) is mostly engineered by alkaline earth (AE), so the chemical formula can be written into RE$_{1-x}$AE$_x$MnO$_3$ [4-6]. By doping another element could provide an interesting interaction called the Double Exchange (DE). The DE interaction is a phenomenon where there is double hopping of $e_g$ electron from Mn$^{3+}$ ion to Mn$^{4+}$ ion through oxygen. The strength of the DE interaction becomes one of electrical and magnetic properties factor of material [7]. The strength of the DE interaction must be affected by the structural properties of a material, such as the crystal structure, the distance of the nearest Mn-O bond length, and the angle of the Mn-O-Mn bond [8]. Structural properties such as crystal structure, lattice parameters, volume unit cell, Mn-O bond nearest distance, Mn-O-Mn bond angle, must be influenced if the material being substituted by another element. Moreover, the crystallite size of material also becomes one of the factors that can affect the electrical property of a material. Hence, knowing the effect of doping another element of material on structural properties of material becomes important.

In this paper, we will know the influence of structural properties of a La$_{0.8}$Ca$_{0.2}$MnO$_3$ material with increasing the concentration of Ag$^+$ ion on La$_{0.8}$Ca$_{0.2}$MnO$_3$ material by substituting it on La$^{3+}$ ion. The Ag doping is chosen because it is a conductor and could provide conduction paths between the boundaries to improve the electrical properties of the perovskite material [4]. By increasing
concentrations of Ag⁺ doping in substituting La³⁺, it is hoped it could shorten the distance of the Mn-O bond and increase the angle of Mn-O-Mn. Along with increasing concentration of doping Ag⁺ to substitute La³⁺ could decrease the crystallite size of the material.

The LACMO1 and LACMO15 materials were synthesized via sol-gel method because this method only needs low temperature and rapidly synthesize process [9]. Previous researches mostly used conventional method, such as solid-state method, to synthesize the material which needs high temperature and long synthesize process [2, 7, 10-11].

2. Experimental
The LACMO1 and LACMO15 materials were synthesized using the sol-gel method. The precursor materials used in the synthesizing process were La₂O₃, AgNO₃, Ca(NO₃)₂.4H₂O, Mn(NO₃)₂.4H₂O, C₆H₈O₇.H₂O (citric acid) was mixed into the solution as a catalyst to accelerate the sol-gel process. HNO₃ (ammonia solution) was also used to adjust pH of the solution to be neutral. The solution with high viscosity (gel) furthermore was heated three times; there is dehydration (120 °C; 3h), calcination (550 °C; 5h), and sintering (900 °C; 24h).

Synthesized LACMO1 and LACMO15 materials were characterized by XRD. The XRD tool was used to confirm the phase of LACMO1 and LACMO15 materials, also to know the effect on crystal structure and crystal lattice parameters LACMO1 and LACMO15 materials by increasing concentration of Ag doping. The XRD pattern results then processed using High Score Plus software program using Rietveld analysis method which is one of processing method by comparing the results obtained with database peak from previous research.

3. Results and Discussions
The structural properties of LACMO1 and LACMO15 materials were characterized by XRD. Figure 1 and 2 show the XRD patterns of LACMO1 and LACMO15 materials. The XRD pattern results of both materials indicate that there is a presence of another peak emerging beside lanthanum manganite peak. The peak is from Ag that appears as the second phase. With increasing the concentration of Ag⁺ to substitute La³⁺ on a La₀.₈Ca₀.₂MnO₃ material, the higher second phase peak of Ag will appear.

![Figure 1. XRD pattern of LACMO1 material.](image1)

![Figure 2. XRD pattern of LACMO15 material.](image2)

The XRD pattern of LACMO15 material is following the research that has been done by M.Koubaa et al. [12]. In his research, Koubaa et al synthesized La₀.₆₅Ca₀.₃₅₋ₓAgₓMnO₃ (x = 0; 0.05; 0.1; 0.15; 0.2) using solid-state method [12]. Koubaa states that for x > 0.1, the material has a system with mixed phases, which consist of manganite phase and residual Ag metal [13]. According to Tang et al., interesting physical properties will be reached of a material which has two phases, such as large magnetoresistance (MR) value at room temperature [12-13].
In LACMO1 material, a material with the same composition was ever synthesized by Tran Dang Thanh using solid-state method [7]. Thanh stated that the XRD pattern of the synthesized material is single phase, where there is no other peak appears except manganite peak [7]. The difference XRD pattern result between this study and previous research could be occurred due to the different use of synthesis method so there are some factors that could cause different characterization results.

Table 1. Refinement results of crystal structure parameters on LACMO1 and LACMO15 materials

| Structural Parameters | x = 0.1       | x = 0.15      |
|-----------------------|---------------|---------------|
| Crystal structure     | Orthorhombic  | Rhombohedral  |
| Space group           | Pnma          | R3c           |
| a (Å)                 | 5.4667        | 5.4734        |
| b (Å)                 | 7.7281        | 5.4734        |
| c (Å)                 | 5.4960        | 13.3389       |
| Volume (Å³)           | 232.1939      | 346.0728      |
| <d_{Mn-O}> (Å)        | 1.9616        | 1.952         |
| <Mn-O-Mn> (°)         | 161.252       | 163.715       |
| x²                    | 1.0597        | 1.117         |
| Tolerance factor (t)  | 0.9564        | 0.9605        |

The refinement results of crystal structure parameters on LACMO1 and LACMO15 materials that have been refined with standard Rietveld techniques are listed in Table 1. From the refinement, results indicate a transition of crystal structure from orthorhombic-LACMO1 to rhombohedral-LACMO15. The crystal structure could be determined by the Goldschmidt tolerance factor (t). The Goldschmidt tolerance factor (t) is used to measure the degree of distortion of a perovskite [14]. The equation of the Goldschmidt tolerance factor is:

$$t = \frac{R_A + R_B}{2} \frac{1}{(R_A + R_B)}$$

Where $R_A$ is the ionic radius of site A, $R_B$ is the ionic radius of site B, and $R_O$ is the ionic radius of Oxygen. For $t$ value in the range 0.96 < $t$ < 1, the material has a rhombohedral structure and for $t$ < 0.96, the material has an orthorhombic structure [14]. The LACMO1 material has a value of $t = 0.9564$, so it has an orthorhombic structure, whereas the LACMO15 material has a value of $t = 0.9605$ so its structure is rhombohedral. Hence, increasing the concentration of Ag doping may affect the tolerance factor (t) that used to determine crystal structure. By increasing the concentration of Ag doping on La$_{0.8}$Ca$_{0.2}$MnO$_3$ material can affect the stability of the material structure to enable a distortion that causing a transition of the crystal structure.

Furthermore, the average crystallite size is calculated using Debye Scherrer’s equation obtained 48.97 nm for LACMO1 material and 26.63 nm for LACMO15 material. The decrease of crystallite size in along with increasing the concentration of Ag doping could be caused of the ionic radius of Ag$^+$ (1.28 Å) which is smaller than the ionic radius of La$^{3+}$ (1.36 Å) [15].

The refinement result also obtains the distance of Mn-O bond and Mn-O-Mn angle from LACMO1 and LACMO15 materials. As increasing the concentration of Ag doping, the Mn-O bond distance on the material is shortened. With the shortening of the Mn-O bond distance, the hopping of e$_g$ electrons,
from Mn$^{3+}$ to Mn$^{4+}$ with Oxygen as intermediate, should be easier so that the strength of the DE phenomenon could increase \[8\]. An increase in the strength of the DE phenomenon may affect the electrical and magnetic properties of the material \[7\]. The increasing concentration of Ag doping on La$_{0.8}$Ca$_{0.2}$MnO$_3$ material tends to increase its Mn-O-Mn angle.

4. Conclusion

LACMO 1 and LACMO15 materials were synthesized via sol-gel method. The XRD pattern results show the second phase peak of Ag-doping in both materials. The second phase peak Ag increases with increasing Ag doping concentration. The transition of crystal structure occurs from orthorhombic becomes rhombohedral when there is an increase in doping concentration. One of the factors that affect the stability of the crystal structure is the Goldschmidt tolerance factor.

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