Microwave Absorption Properties of La$_{0.8}$Ca$_{0.2-x}$Ag$_x$MnO$_3$ (x=0.05; x=0.15) Synthesized by Sol-Gel Method

B Kurniawan$^1$, W Laksmi$^1$, N A Sahara$^1$

$^1$Department of Physics, FMIPA Universitas Indonesia, Kampus UI Depok, Depok 16424, Indonesia

Email: bkuru@fisika.ui.ac.id

Abstract. Microwave absorption properties of La$_{0.8}$Ca$_{0.2-x}$Ag$_x$MnO$_3$ (x= 0.05; 0.15) is reported in this paper. Lanthanum manganite materials was reported as a potential absorber material [1][2][3]. In this paper, the material was synthesized by sol-gel method, calcined at 550˚C, and sintered at 900˚C. The material was characterized by X-Ray Diffractometer (XRD), and we found that the materials were single phased. Through SEM-EDS characterization it is found that the materials have compositional purity. The resistivity of the materials is obtained by four point probe method, and it is shown that Ag doped decreases the resistivity of the materials. Reflection loss of La$_{0.8}$Ca$_{0.15}$Ag$_{0.05}$MnO$_3$ reaches $-4.470$ dB and La$_{0.8}$Ca$_{0.05}$Ag$_{0.15}$MnO$_3$ reaches $-7.953$ dB.

1. Introduction
Research on microwave absorber material has been conducted by a number of researchers. Microwave Interference phenomenon is the reason why the material with a good microwave absorption is absolutely necessary. Perovskite manganite material with a formula ABO$_3$ is one of common material that examined in terms of microwave absorption. Group of lanthanum manganite material with A is Lanthanum, B is manganese, and O is oxygen, have been examined in terms of the microwave absorption, magnetoresistance properties and magnetocaloric.

Modification by dope site-A with another element done to see the impact on three properties that has been mentioned before. For example the addition of Silver on site-A [2]. The addition of silver on site-A makes this material has wide microwave absorption from 2 GHz to 18 GHz. The wide range of microwave absorption is the profit for this material to be used in wider frequency range. Other studies have found that Lanthanum Manganite doped by Calcium on Lanthanum site causes the reflection loss at microwave absorption increases to $-31$ dB [3]. But it has a very thin absorption region, about 11 GHz up to 13 GHz. This study will report the results of Lanthanum Manganite material doped with Silver and Calcium at once. The composition is La$_{0.8}$Ca$_{0.2-x}$Ag$_x$MnO$_3$ with x = 0.05 and 0.15. The method that used in this research is sol-gel method. This method is relatively easy and have a lower sintering temperature compared to solid state methods [4] and so on.

2. Experiment
All the raw materials that used during the synthesized are nitrate compound. This could simplify the process of sol-gel, because nitrate can be soluble in aquabidest. The entire raw materials blended on the
magnetic stirrer. The temperature kept at 80°C for 3 hours, with a pH of 7 until the entire solution turned into a gel and then hardened. Afterwards the samples entered the dehydration process for 3 hours. Then calcination process at 550 °C over 5 hours, this process eliminated organic compounds or nitrates which were still contained in the material. The last is the process of sintering at a temperature of 900 °C for 24 hours. A number of tests conducted after passing through this process.

3. Results and discussions

3.1. X-Ray Diffractometer

The samples were characterized by X-Ray Diffractometer. In the Figure 1, we can see that the additional of Ag composition, with x=0.15 changes the crystal structure of material. This marked by HKL value that changes, detected by the HKL of the highest peaks on the pattern. Based on data processing the crystal structure of La₀.₈Ca₀.₁₅Ag₀.₀₅MnO₃ material is orthorhombic. Meanwhile crystal structure of La₀.₈Ca₀.₀₅Ag₀.₁₅MnO₃ material is rhombohedral. Previous research reported that Lanthanum Manganites with Ca and Ag doped changed it crystal structure [5]. Based on scherrer’s formula, the crystallite size of material by x=0.15 must be smaller than x=0.05. This is confirmed by SEM results at the next chapter.

![Figure 1. XRD Patterns of La₀.₈Ca₀.₁₅Ag₀.₀₅MnO₃ and La₀.₈Ca₀.₀₅Ag₀.₁₅MnO₃](image)

Goldschmidt tolerance factor calculation verified the changing of crystal structure material. The Goldschmidt equation (τ) shows below:

$$\tau = \frac{r_A + r_0}{\sqrt{2}(r_B + r_0)}$$  \hspace{1cm} (1)

With rₐ is the ionic radii of La³⁺, Ca²⁺, and Ag⁺. Meanwhile r₀ and rₜ are the ionic radii of O²⁻ and Mn³⁺/⁴⁺. Perovskite manganite structure distorted into rhombohedral when 0.96 ≥ τ ≥ 1. But when τ < 0.96 the crystal structure turn into orthorhombic. The calculation using ionic radii reference shows that La₀.₈Ca₀.₀₅Ag₀.₁₅MnO₃ has τ=0.95 and La₀.₈Ca₀.₀₅Ag₀.₁₅MnO₃ τ=0.96 [6]. This calculation verified that the crystal structure of material was changing.
Table 1. Lattice parameter of La$_{0.8}$Ca$_{0.15}$Ag$_{0.05}$MnO$_3$ and La$_{0.8}$Ca$_{0.05}$Ag$_{0.15}$MnO$_3$

| Material                  | a (Å) | b (Å) | c (Å) | V (Å$^3$) |
|---------------------------|-------|-------|-------|-----------|
| La$_{0.8}$Ca$_{0.15}$Ag$_{0.05}$MnO$_3$ | 5.500 | 7.740 | 5.467 | 232.476   |
| La$_{0.8}$Ca$_{0.05}$Ag$_{0.15}$MnO$_3$ | 5.514 | 5.514 | 13.366| 352.011   |

3.2. SEM-EDS results

SEM and EDS results of La$_{0.8}$Ca$_{0.05}$Ag$_{0.15}$MnO$_3$ and La$_{0.8}$Ca$_{0.15}$Ag$_{0.05}$MnO$_3$ are reported. Figure 2 and figure 3 show the morphology of materials. By these pictures we can approximate the size of particles. For La$_{0.8}$Ca$_{0.15}$Ag$_{0.05}$MnO$_3$ and La$_{0.8}$Ca$_{0.05}$Ag$_{0.15}$MnO$_3$ the size of materials are 203 nm and 136 nm respectively. These results verified the previous approximation with Scherrer’s formula that obtained the crystallite size with more silver composition is smaller than the other one.

![Figure 2. The morphology of La$_{0.8}$Ca$_{0.15}$Ag$_{0.05}$MnO$_3$](image1)

![Figure 3. The morphology of La$_{0.8}$Ca$_{0.05}$Ag$_{0.15}$MnO$_3$](image2)

To verified that the materials are compositionally pure, the EDS characterization are reported. The composition of materials shown in table 2.

Table 2. The results of EDS characterization

| X  | La At% (Calculation) | Ca | Ag | Mn | O  | La At% (Observation) | Ca | Ag | Mn | O  |
|----|----------------------|----|----|----|----|----------------------|----|----|----|----|
| 0.05| 16                   | 3  | 1  | 20 | 60 | 15.77                | 2.96 | 0.95 | 17.54 | 62.7 |
| 0.15| 16                   | 1  | 3  | 20 | 60 | 15.64                | 2.05 | 1.98 | 17.71 | 62.62 |

The additional of silver shows by the increasing from silver percentage at the materials. However this method is semi-quantitative calculation. The composition of the elements not 100% accurate, according to the formula La$_{0.8}$Ca$_{0.2-x}$Ag$_x$MnO$_3$. But as shown in table 2, the additional of x relates with the increasing of Ag in atomic percent. Also there is no element that is shown in the table. It is caused by the purity of the samples that is not contained any elements besides La, Ca, Ag, Mn, and O.

3.3. Resistivity by four point probe methods

The resistivity of materials decreases as the composition of Ag increases. La$_{0.8}$Ca$_{0.15}$Ag$_{0.05}$MnO$_3$ material resistivity is 0.036 Ω.m, and La$_{0.8}$Ca$_{0.05}$Ag$_{0.15}$MnO$_3$ material resistivity is 0.013 Ω.m. The resistivity decreases may caused by the electrical properties of Ag as a good electrical conductor that has very small resistivity. Another conjecture this is caused by crystal structure of material that changed.
The microwave absorption material itself, represented by reflection loss. This value shows how much material absorb the microwave that given. The reflection loss calculated by the equation below [7].

\[ RL = 20 \log \left( \frac{z_{in} - z_0}{z_{in} + z_0} \right) \]  \tag{2}

Reflection loss relates with impedance in \((z_{in})\) and impedance 0 \((z_0)\). The impedance itself relates with permittivity (electrical property, \(\varepsilon\)), permeability (magnetic property, \(\mu\)), and also material thickness. These three factors may influence the ability of materials to absorb the microwave. The research before claimed that higher resistivity at semiconductor resistivity range, could posses more reflection loss. Although our result shows that the material resistivity decreases after doped by more Ag, these value still in the semiconductor resistivity range. Further discussion is reported in the next part.

3.4. Vector Network Analyzer Characterization

Reflection loss of materials are investigated by vector network analyzer. This characterization investigated the reflection loss of materials at X-Band frequency range, 8-12 GHz. The maximum reflection loss of La\(_{0.8}\)Ca\(_{0.15}\)Ag\(_{0.05}\)MnO\(_3\) reaches -4.470 dB at frequency 19.24 GHz, and La\(_{0.8}\)Ca\(_{0.05}\)Ag\(_{0.15}\)MnO\(_3\) reaches -7.953 dB at frequency 14.68 GHz. In the X-Band frequency range (8-12 GHz) the maximum reflection loss of La\(_{0.8}\)Ca\(_{0.15}\)Ag\(_{0.05}\)MnO\(_3\) and La\(_{0.8}\)Ca\(_{0.05}\)Ag\(_{0.15}\)MnO\(_3\) only reach -4.310 dB and -4.674 dB respectively. Although the resistivity of La\(_{0.8}\)Ca\(_{0.05}\)Ag\(_{0.15}\)MnO\(_3\) is lower than La\(_{0.8}\)Ca\(_{0.15}\)Ag\(_{0.05}\)MnO\(_3\) the reflection loss shows the opposite. With \(x = 0.15\), the material has deeper reflection loss.

\[ z_{in} = \left( \frac{\mu \varepsilon}{\varepsilon_0} \right)^{\frac{1}{2}} \tanh \left( j2\pi f d (\mu \varepsilon)^{\frac{1}{2}} \right) \]  \tag{3}

\[ z_0 = \left( \frac{\mu_0 \varepsilon_0}{\varepsilon} \right)^{\frac{1}{2}} \]  \tag{4}

Where \(f\) is electromagnetic frequency, \(d\) is material thickness, \(\mu\) permeability, \(\varepsilon\) is permittivity. Equation 3 and 4 show that is not only dielectric property that can determine the value of impedance in, but also
magnetic properties, the dimension of samples, and also the frequency that apply on the materials. The VNA characterization shows that imaginary permeability of La\textsubscript{0.8}Ca\textsubscript{0.05}Ag\textsubscript{0.15}MnO\textsubscript{3} higher than La\textsubscript{0.8}Ca\textsubscript{0.15}Ag\textsubscript{0.05}MnO\textsubscript{3}. The magnetic loss of material represented by imaginary permeability [8]. It shows that La\textsubscript{0.8}Ca\textsubscript{0.15}Ag\textsubscript{0.05}MnO\textsubscript{3} has higher reflection loss caused by its magnetic loss.

4. Conclusion
XRD pattern shows that all the samples were single phase. Lattice parameters show that the crystal structure is orthorhombic for x=0.05 and rhombohedral for x=0.15. The resistivity for x=0.05 and x=0.15 respectively 0.036 Ω.m and 0.013 Ω.m. VNA characterization shows that the Reflection loss of La\textsubscript{0.8}Ca\textsubscript{0.15}Ag\textsubscript{0.05}MnO\textsubscript{3} reaches -4.470 dB and La\textsubscript{0.8}Ca\textsubscript{0.05}Ag\textsubscript{0.15}MnO\textsubscript{3} reaches -7.953 dB.

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