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Perovskite Manganit Analysis Based on $La_{0.7}Ca_{0.3}Mn_{1-x}Ti_xO_3$ (x=0, 0.1, 0.2, and 0.3) as Potential Microwave Absorber Material with Sol-Gel Method

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Abstract: Electromagnetic wave is an energy flow in the form of electric and magnetic field as the technology development causes electromagnetic wave exposure level changes significantly and resulting an electromagnetic wave radiation that leads bad impacts on human health. In this case, manganite perovskite became an interesting topic of study that aims to produce material engineering to obtain a material with the best property as absorber. This study is based on lanthanum manganite $La_{0.7}Ca_{0.3}Mn_{1-x}Ti_xO_3$ ($x = 0, 0.1, 0.2,$ and 0.3) using sol-gel method with the with a heating temperature in the oven of 200°C for 2 hours, calcination temperature of 600°C for 6 hours, and sintering temperature of 1000°C for 12 hours. The sample is characterized using X-Ray Diffraction (XRD) that shows the sample had succeeded to form single phase and had crystal cubic structure with space group p m -3 m, the substitution of Ti^{3+} ions did not cause the structural changes, but it was marked with the changes of lattice parameter, unit cell volume and average crystallite size. Meanwhile Vector Network Analyzer (VNA) on the frequency range 8-12 GHz shows that the sample has ability to absorb microwave until 90.16% on 10.4 GHz frequency. Therefore, the material based on lanthanum manganite $La_{0.7}Ca_{0.3}Mn_{1-x}Ti_xO_3$ has the potential as the microwave absorber material.

Keywords: $La_{0.7}Ca_{0.3}Mn_{1-x}Ti_xO_3$, microwave absorber, sol-gel.

1. Introduction

Nowadays, technology that continues to develop rapidly over the time can cause problems with electromagnetic wave radiation that endangers and affects human health, so it attracts interest material engineering to be applied as electromagnetic wavelength absorber material that effective with a wide range of frequency, strong absorption, low density, and high resistivity (Swamardika, 2009) (Y. L. Cheng, 2009). A good electromagnetic wave absorber material has characteristic of high permeability value (*magnetic loss properties*) and permittivity (*dialectric loss properties*) (W. A. Adi, 2018). There are a lot of studies about lanthanum manganite ($LaMnO_3$) that has the property of

high permittivity so it can be used as excellent material for electromagnetic wave absorber application by doing material engineering with doping on site A and site B (Intan Wandira, 2018).

Over the past few years, material engineering based on perovskite manganite had garnered a lot of attention (Jiyu Fan, 2010). The structure of perovskite $La_{1-x}A_xMnO_3$ is an interesting material with substituted $LaMnO_3$ that has the ability to absorb electromagnetic wave especially in ultra-high frequency (GHz) (S. A. Saptari, 2014). Other than that, when La is substituted with divalent ions then it will produce Mn^{3+} dan Mn^{4+} ions that resulted double exchange interaction that has effect on the changes of magnetic property on lanthanum manganite material (V. Santen, 1950). The ion substitution affects crystal structural change and electron transfer. With $RE_{1-x}AE_xMnO_3$ (RE = rare earth trivalent element, AE = divalent element such as Ca, Sr, Ba, Pb, etc) had become the study subject that can be applied extensive (X.-G. Li, 2002).

X. Zhu *et al* (Xuebin Zhu, 2010) synthesized $La_{0.7}Ca_{0.3}Mn_{1-x}Ti_xO_3$ ($x = 0$, 0.03, 0.05, 0.07, and 0.1) by using *solid state reaction method* where the experiment produces material with ferromagnetic property on all doping composition. J. W. Liu *et al* (Jia Wei Liu, 2018) conducted $La_{1-x}Ca_xMnO_3$ ($0 \leq x \leq 0{,}5$) experiment where microwave absorption is characterized on the range of frequency 2 – 18 GHz and resulted reflection loss value by -42 dB on 10.5 GHz when $x = 0.1$ as microwave absorption peak with the widest bandwidth value which is 3.5 GHz.

In this study, we analyzed the formed phase, crystal structure, and microwave absorbing properties of $La_{0.7}Ca_{0.3}Mn_{1-x}Ti_xO_3$ material with variations of x = 0, 0.1, 0.2, and 0.3 using the *sol-gel* method to control the stoichiometric ratio and produce a homogeneous material composition by studying the effect of Ti^{3+} substitution on the crystal structure and the ability to absorb microwaves.

2. Experimental

$La_{0.7}Ca_{0.3}Mn_{1-x}Ti_xO_3$ material is synthesized using sol-gel method with precursor material La_2O_3, $Ca(NO_3)_2.4H_2O$, $Mn(NO_3)_2.4H_2O$, TiO_2, and $C_6H_8O_7.H_2O$ which were weighed according to stoichiometry and dissolved with aquabidest. In the precursor material La_2O_3 and TiO_2 using HNO_3 solvent to convert the oxide into a nitrate base. All solutions were mixed and stirred to form a homogeneous solution and then added ammonia solution until the pH value reached 7 at 80^{o}C (353 K). After the solution was in the form of a gel, then the sample was heated at a temperature of 200^{o}C for 2 hours to remove the water content. After that, the samples were calcined at a temperature of 600^{o}C for 6 hours and sintered at a temperature of 1000^{o}C for 12 hours. All samples were then characterized using X-Ray Diffraction (XRD) to determine the phase, lattice parameters, and crystal structure formed as well as Vector Network Analyzer (VNA) testing with a frequency range of 8 – 12 GHz to see the value of reflection loss in order to determine the ability of the material as microwave absorber.

3. Results and Discussion

3.1. Characteristic and Phase

$La_{0.7}Ca_{0.3}Mn_{1-x}Ti_xO_3$ material ($x = 0, 0.1, 0.2,$ and 0.3) were analyzed by X-Ray Diffraction (XRD) using the Rietveld refining method. The results of the characterization using XRD are in the form of a diffractogram graph with a relationship between intensity and 2θ. XRD analysis shows that all samples have formed a single phase which is characterized by the absence of the addition of new peaks as a result of the addition of the value of x which is the addition of Ti composition at the Mn site and free from impurities.

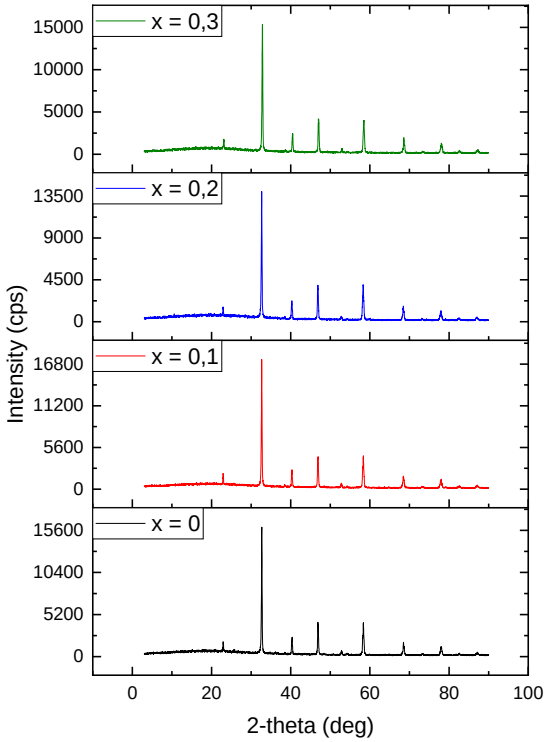

Figure 1. XRD patterns of $La_{0.7}Ca_{0.3}Mn_{1-x}Ti_xO_3$ ($x = 0, 0.1, 0.2,$ and 0.3).

It can be seen in Figure 2, in general there is a shift in the peak towards a smaller direction as the composition of the x value increases. This shift occurs because as the composition of the x value increases, it produces a larger lattice parameter value because the radius of the Ti^{3+} ion (0.67 Å) is greater than the radius of the Mn^{3+} ion (0.58 Å). This is in accordance with Bragg's law which shows that a small value of will be produced if the distance between the crystal planes has a large value. The Bragg law is written in equation (1) as follows.

$$2\,d\sin\theta = n\,\lambda \tag{1}$$

Where d is distance between planes, θ is diffraction anglesudut difraksi, n is integer (order of diffraction), and λ is x-ray wavelength used (Hikam, 2007).

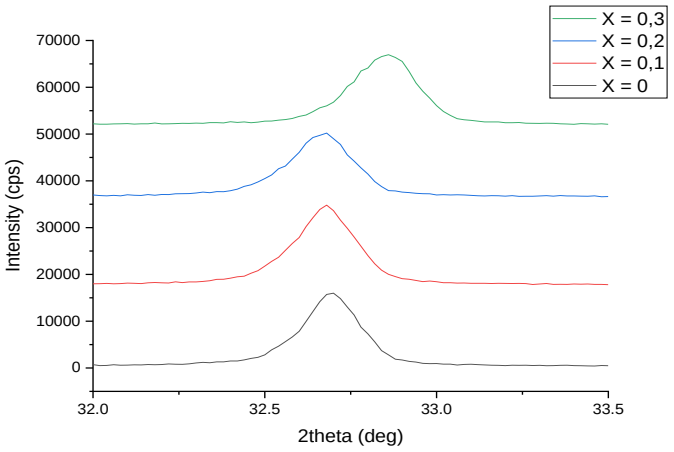

Figure 2. Diffraction peak of samples at highest intensity.

Double exchange mechanism that happens on the initial state of Mn^{3+} - O^{2-} - Mn^{4+} and the final state of Mn^{4+} - O^{2-} - Mn^{3+} where electron transfer occurs simultaneously from Mn^{3+} to O^{2-} and from O^{2-} to Mn^{4+}. Ti^{3+} substitution increases bond length of Mn – O so the electron transfer will be more difficult (Siwach, 2008).

Table 1. Refirement results of $La_{0.7}Ca_{0.3}Mn_{1-x}Ti_xO_3$ samples.

Parameter	$x = 0$	$x = 0.1$	$x = 0.2$	$x = 0.3$
Crystal Structure	Cubic	Cubic	Cubic	Cubic
Space Group	P m -3 m	P m -3 m	P m -3 m	P m -3 m
$a = b = c$ (Å)	3.872702	3.873231	3.875350	3.876231
$\alpha = \beta = \gamma$ (°)	90	90	90	90
V (Å^3)	58.082	58.106	58.201	58.241
Density (gr/cm^3)	6.067	6.044	6.014	5.990
Average Crystallite Size (nm)	34.36091097	32.20445754	31.59342614	29.75936081

Parameter	$x = 0$	$x = 0.1$	$x = 0.2$	$x = 0.3$
Discrepancy Factors				
wRp	0.1418	0.1353	0.1402	0.1496
Rp	0.1104	0.1038	0.1080	0.1141
Chi	1.085	1.021	1.053	1.198
Bond Length (Å)				
$< Mn - O >$	1.93635	1.93662	1.93767	1.93812
Bond Angles (°)				
$< Mn - O - Mn >$	180	180	180	180
Tolerance Factor				
Goldschmidt	0.9984422	0.993772	0.989145	0.984561

Based on Table 1, it can be seen that $La_{0.7}Ca_{0.3}Mn_{1-x}Ti_xO_3$ material with $x = 0, 0.1, 0.2,$ and 0.3 has a cubic crystal system by showing a proportional and minimum chi-square value according to the convergent matching requirement which is in the value between 1 to 1.3 (Hikam, 2007). In addition, in the presence of Ti^{3+} substituted in $La_{0.7}Ca_{0.3}Mn_{1-x}Ti_xO_3$ material, in general, the lattice parameter value increases as the composition of the x value increases which directly contributes to the increase in unit cell

volume. XRD analysis showed that the sample with Ti^{3+} ion substitution did not change the structure and phase.

The crystal size can be calculated using the Debye Scherrer (M. A. Gdaiema, 2016) method in equation (2).

$$D = \frac{K \,.\, \lambda}{\beta \,.\, \cos\theta}. \tag{2}$$

Where D is crystal size (Å), K is constants associated with crystal shape (0.9), is the wavelength of x-rays (1.540598), λ is the value of Full Width at Half Maximum (FWHM) (rad) and θ is the angle of diffraction (degrees).

As shown in Table 1, the substitution of Ti^{3+} did not change the basic crystal structure. This result is supported by the Goldschmidt tolerance factor (t_G) which is calculated when Ti^{3+} substituted at the Mn site causes a decrease in the amount of Mn^{3+} shown in equation (3).

$$t_G = \frac{0.7r_{La^{3+}} + \ 0.3r_{Ca^{2+}} + r_{O^{2-}}}{\sqrt{2}\,[\,(0.7-x)r_{Mn^{3+}} + 0.3r_{Mn^{4+}} + xr_{Ti^{3+}} + r_{O^{2-}}\,]} \tag{3}$$

The ideal cubic perovskite has a tolerance factor of 1, but most cubic perovskites have a t_G value between 0.9 and 1 (Schinzer, 2012).

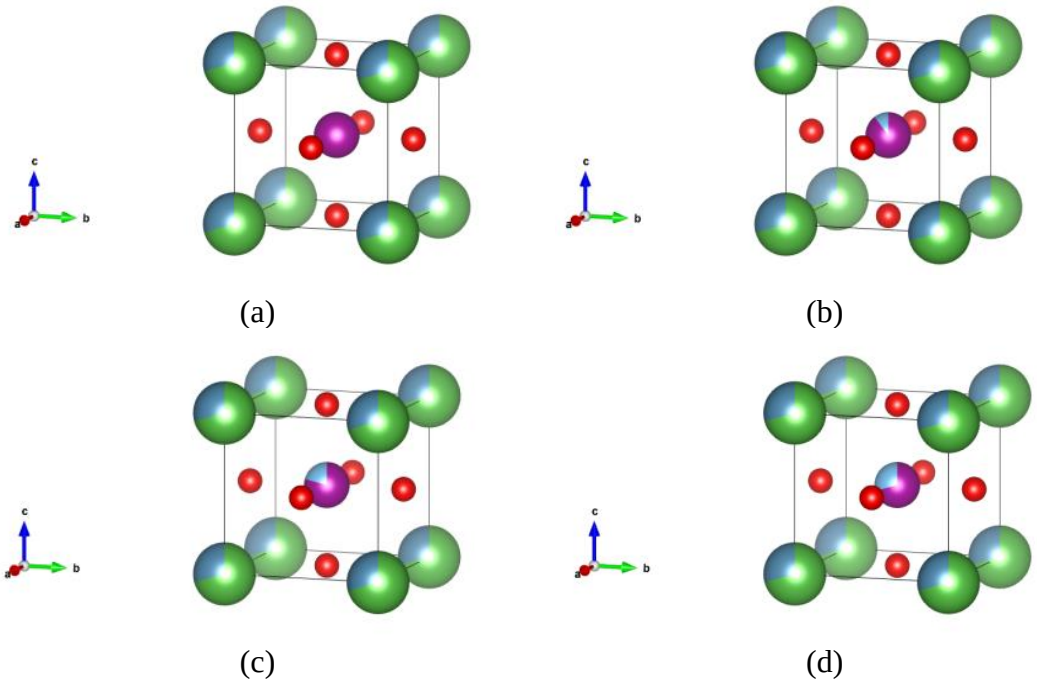

Figure 3. Visualization crystal structure of material $La_{0.7}Ca_{0.3}Mn_{1-x}Ti_xO_3$ with (a) $\boldsymbol{x = 0}$; (b) $\boldsymbol{x = 0.1}$; (c) $\boldsymbol{x = 0.2}$; dan (d) $\boldsymbol{x = 0.3}$.

As for in this study, the calculation of the Goldschmidt tolerance factor uses the value of the radius as shown in Table 2.

Table 2. Ionic radius of the material $La_{0.7}Ca_{0.3}Mn_{1-x}Ti_xO_3$.

$La_{0.7}Ca_{0.3}Mn_{1-x}Ti_xO_3$		
Ion	**Charge**	**Ionic Radius (Å)**
La	+3	1.36
Ca	+2	1.34
	+3	0.58
Mn	+4	0.53
Ti	+3	0.67
O	-2	1.35

The crystal structure produced in this study can be visualized which is input into the VESTA software as shown in Figure 3.

3.2. Absorbance

This research uses the frequency range (x-band) 8 – 12 GHz. The results of the characterization using VNA in the form of S_{11} (reflection coefficient) and S_{21} (transmission coefficient) data from electromagnetic wave sources, but in this study only took the value of the S_{11} reflection coefficient. This characterization is obtained by the Reflection Loss (R_L) curve which describes the ability of a material to absorb electromagnetic waves.

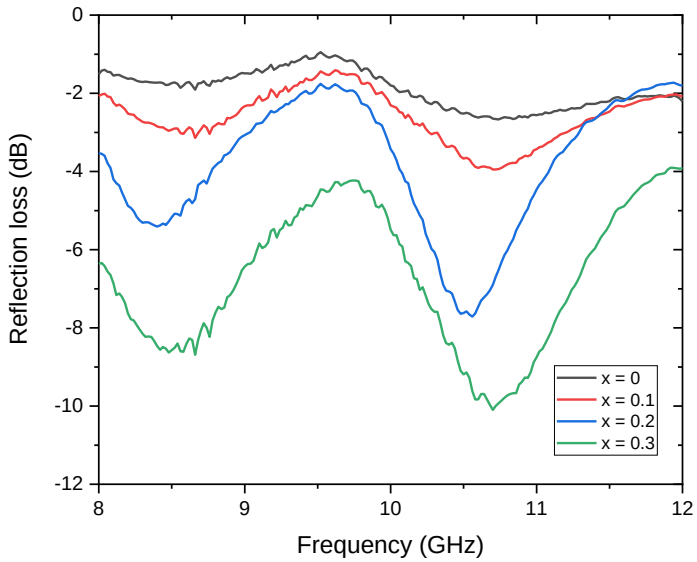

Figure 4. Microwave absorption performance of $La_{0.7}Ca_{0.3}Mn_{1-x}Ti_xO_3$.

Figure 4 shows the combined reflection loss curve for each sample, it can be seen that the sample with x=0.3 has a deeper curve than the other samples. This indicates that the sample has the best ability to absorb microwaves. In addition, it can also be seen at $x = 0.3$ that the microwave absorption peak is in the far right position, this represents the highest frequency range.

Table 3. Microwave absorption properties of $La_{0.7}Ca_{0.3}Mn_{1-x}Ti_xO_3$ samples.

x	Frequency (GHz)	*Reflection Loss* (dB)	*Through Power* (%)
0	10.74	−2.666267	45.88
	8.66	−1.90857	35.56
0.1	10.72	−3.950329	59.73
	8.76	−3.043006	50.38
0.2	10.54	−7.658528	82.85
	8.4	−5.413738	71.25
0.3	10.4	−10.07202	90.16
	8.66	−8.690956	86.48

It can be seen that the sample $x = 0.3$ has an absorption capability of -10.07202 dB at an optimal frequency of 10.4 GHz. Judging from the percent absorption (through power) this material is able to absorb microwaves up to 90.16%. The absorption ability is caused by several factors, namely the interaction of double exchange, permeability, and permittivity in the sample (Jia Wei Liu, 2018).

4. Conclusion

$La_{.0.7}Ca_{0.3}Mn_{1-x}Ti_xO_3$ material with $x = 0, 0.1, 0.2,$ and 0.3 that synthetized using sol-gel method had successfully conducted with XRD result that shows single phase without any impurities also has cubic crystal structure with space group p m -3 m. Ti^{3+} substitution does not change crystal structure but an increase in the unit cell volume and a decrease in the bond length of the Mn-O. The VNA results showed that the sample with $x = 0.3$ had the highest absorption ability up to 90.16% and reached a value of -10.07202 dB at the optimal frequency is 10.4 GHz.

5. Suggestion

Based on this research that has been done, some suggestions for further research are to do Scanning Electron Microscope (SEM) characterization to determine the effect of ion substitution on the morphology of the material, Vibrating Sample Magnetometer (VSM) characterization to determine the magnetic properties of the material, and Cryogenic Magnetometer using the principle Four Point Probe (FPP) work to determine the electrical properties of the material.

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