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Analysis of crystal structure and reflection loss of material based on $La_{0.7}Sr_{0.3}Mn_{1-x}(Ni, Ti)_{x/2}O_3$ (x=0.1, 0.3, and 0.5) applications for microwave absorbers

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Abstract: In this research, structural engineering of lanthanum manganite material based on $La_{0.7}Sr_{0.3}Mn_{1-x}(Ni,Ti)_{x/2}O_3$ (x = 0.1; 0.3 and 0.5) was synthesized using the sol-gel method. The prepared samples were then characterized using X-ray Diffraction (XRD) and Vector Network Analyzer (VNA). X-Ray Diffraction (XRD) characterization results obtained a single. Substitution of Ni and Ti ions with a concentration of x = 0.1; 0.3; and 0.5 indicate that the formed sample has a rhombohedral structure with a space group R -3c, the presence of Ni and Ti ion substitution does not cause a change in the structure but there is a change in the lattice parameters and crystal size. Vector Network Analyzer (VNA) characterization in the range of 8 – 12 GHz produces the most optimal reflection loss intensity value of -11.8 dB at an optimal frequency of 10.58 GHz at a concentration of x = 0.5 with the ability to absorb microwaves of 93.39%. Thus the material $La_{0.7}Sr_{0.3}Mn_{1-x}(Ni,Ti)_{x/2}O_3$ (x = 0.1; 0.3 and 0.5) can be used as a microwave absorbent material.

Keywords: LSMO, reflection loss, sol-gel.

1. Introduction

The rapid development of technology in tshe telecommunications sector causes electromagnetic wave interference pollution, specifically microwaves, which can reduce the performance of vital electronic-based equipment systems. It is also believed that radiation from microwaves originating from cell-phone signals can trigger cancer cells (Admi et al. 2021). This has made many researchers interested in developing a material that is able to absorb electromagnetic waves. This material can withstand interference from unwanted electromagnetic waves. Electromagnetic wave absorbing material can convert electromagnetic wave energy into heat energy or reflection loss (Ahmiatri and Priyambodo 2013)(Liang et al. 2017).

In recent decades, lanthanum manganite material $La_{1-x}A_xMnO_3$ (A: Ca, Sr, Ba) has attracted the attention of many researchers because of its structural modification through doping. This is because it has a magnetoresistance phenomenon, namely a change in electrical resistance when there is an external magnetic field, as well as the presence of unusual electrical and magnetic properties (Ari Adi et al. 2018) in addition it was also found that lanthanum manganite as a microwave absorbent material at high frequencies (Zhang and Cao 2012). If the lanthanum manganite material is doped at the Mn site with transition metals (Ni, Ti, Fe, etc.) it can increase the ability of microwave absorbers by increasing the resistivity properties and decreasing the ferromagnetic properties (Li et al. 2002)(Ardani, Saptari, and Tjahjono 2021).

In a research conducted by Anita D Souza et al (Souza et al. 2019), experiments were carried out on $La_{0.7}Sr_{0.3}MnO_3$ material with the solid state method. The results of the characterization using XRD obtained a single phase forming a rhombohedral crystal structure with a space group R -3 c. The material $La_{0.7}Sr_{0.3}MnO_3$ has a stable ferromagnetic phase (Urushibara et al. 1995)(Lau et al. 2021). Furthermore, the research conducted by Saptari et al on $La_{0.67}Ba_{0.33}Mn_{1-x}Ni_xO_3$ and $La_{0.67}Ba_{0.33}Mn_{1-x}Ti_xO_3$ materials showed that the greater the Ni doping in $LaBaMnO_3$, the reflection loss value will increase with absorption reaching 64%, while in $LaBaMnO_3$ doped by Ti the absorption properties reach 75% (S. A. Saptari, Manaf, and Kurniawan 2014)(S. Saptari, Manaf, and Kurniawan 2014). Particle size also affects the magnetic properties of materials as in the results of research conducted by Yadav et al which showed that the smaller the particle size, the lower the magnetization (Gupta et al. 2012).

Therefore, this material is very interesting because the characteristics of this absorber material are related to magnetic and electrical properties. So, in this experiment we are interested in engineering lanthanum manganite material by doping Sr at the La site and doping Ni and Ti at the Mn site. So we get the following formula $La_{0.7}Sr_{0.3}Mn_{1-x}(Ni,Ti)_{x/2}O_3$ (x=0.1, 0.3, and 0.5). Doping at these two sites is expected to make this material potential as a good absorber material.

2. Experimental

The material $La_{0.7}Sr_{0.3}Mn_{1-x}(Ni,Ti)_{x/2}O_3$ is made using the wet chemical method, namely sol gel. mass of ingredients Lanthanum (III) Oxide (La_2O_3), Strontium Nitrate ($Sr(NO_3)_2$), Manganese (II) Nitrate Tetrahydrate ($Mn(NO_3)_2.4H_2O$), Nickel (II) Nitrate Hexahydrate ($Ni(NO_3)_2.6H_2O$), Titanium (IV) Oxide (TiO_2), Citric Acid Monohydrate ($C_6H_8O_7.H_2O$) were weighed according to stoichiometric calculations, Citric Acid Monohydrate was used as a catalyst in the manufacturing process. La_2O_3 and TiO_2 materials were dissolved with Nitric Acid to obtain a nitrate-based solution.

The nitrate solution of each ingredient was mixed and stirred together with a magnetic stirrer while heated. If the temperature of the solution has reached a temperature of 70°C, then the pH is adjusted by dripping the ammonia solution little by little until the pH of the solution reaches a value of 7. This is so that the reaction in the sample solution can thicken and form a gel.

The sample that has thickened or formed a gel can then be put into the oven to dehydrate the sample at a temperature of 150°C for 2 hours to remove the remaining water content. After that, the sample was transferred to a crucible container and carried out by heating or calcining at a temperature of 600°C for 6 hours to remove organic compounds in the sample. Furthermore, the samples were ground using a mortar and put in the sintering heating stage at a temperature of 1000°C for 12 hours to grow the perovskite phase. The finished sample can be characterized using X-Ray Diffraction (XRD) And Vector Network Analyzer (VNA). X-Ray Diffraction (XRD) to determine the phase, lattice parameters, and crystal structure. This characterisized uses a Benchtop Powder X-Ray Diffraction (XRD) Instrument with Cu kα (λ= 1.54056) with measurements ranging from 3° to 90° with a scanning speed of 10°/min. Vector Network Analyzer (VNA) testing with a frequency range of 8 – 12 GHz to see the value of reflection loss to determine the ability of the material as microwave absorber.

3. Results and Discussion

3.1. X-Ray Diffraction

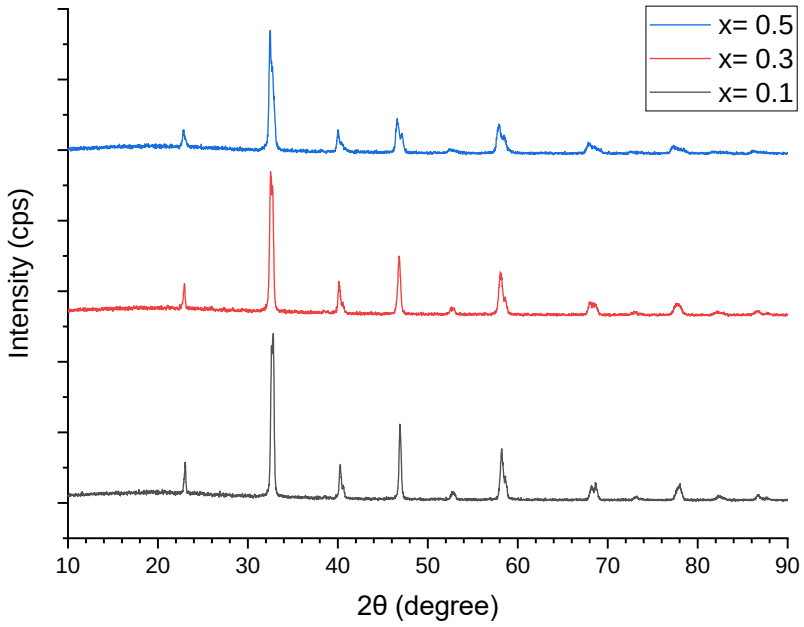

Figure 1. X-Ray Diffraction pattern of sample $La_{0.7}Sr_{0.3}Mn_{1-x}(Ni,Ti)_{x/2}O_3$ (x=0.1, 0.3 and 0.5).

The X-Ray Diffraction (XRD) pattern in the sample $La_{0.7}Sr_{0.3}Mn_{1-x}(Ni,Ti)_{x/2}O_3$ (x=0.1, 0.3 and 0.5) shown in Figure 1 shows that the sample already has a single phase without impurities. The result of the match between the observation data and the calculated data from the analysis using the Rietveld smoothing method has a convergent match. It is also known that the sample has a rhombohedral crystal structure with space group R-3c.

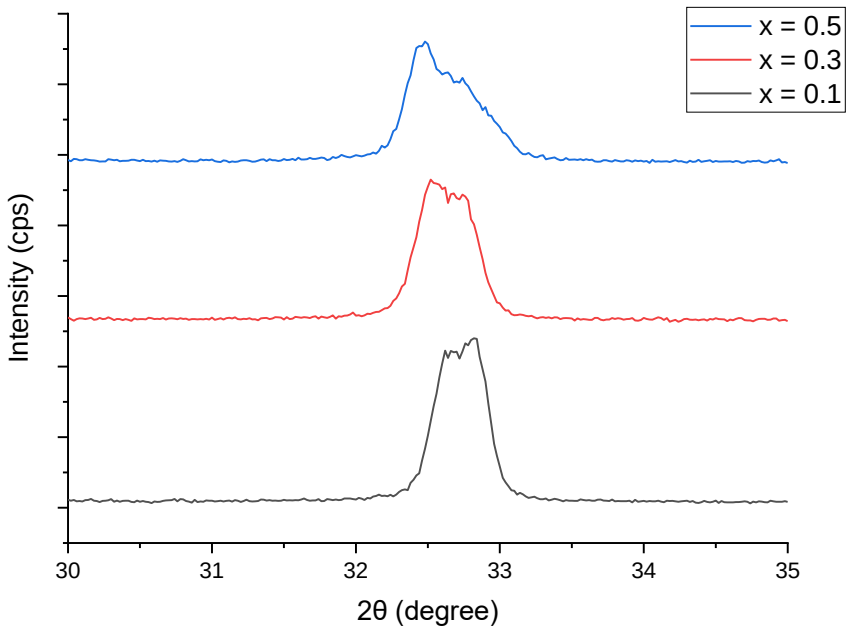

Figure 2. X-Ray Diffraction (XRD) pattern shift of the sample $La_{0.7}Sr_{0.3}Mn_{1-x}(Ni,Ti)_{x/2}O_3$ (x=0.1, 0.3 and 0.5) at the highest intensity.

The increase in the substitution of Ni and Ti along with the increase in doping did not change the X-Ray Diffraction (XRD) pattern of the material, but had an impact on the shift in the position of the diffraction peak with respect to the 2Θ angle. The diffraction peak is known to shift to the left as shown in Figure 2.

The diffraction peak is known to shift to the left as shown in Figure 2. It can be seen that in the presence of substituted Ti in the $La_{0.7}Sr_{0.3}Mn_{1-x}(Ni,Ti)_{x/2}O_3$ material, in general, there is an increase in the value of the lattice parameter which contributes directly to the diffraction peak. Increase in unit cell volume. Shift of 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. 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, resulting in a larger lattice parameter value (Liu, Wang, and Gao 2018).

The results of the quantitative analysis of the X-Ray Diffraction (XRD) pattern are summarized in Table 1. Based on these results, it can be seen that there is an increase in the value of the volume lattice parameter, and a decrease in crystal size.

Table 1. The results of the analysis of the crystal structure parameters of $La_{0.7}Sr_{0.3}Mn_{1-x}(Ni,Ti)_{x/2}O_3$ obtained from the X-Ray Diffraction (XRD) characterization.

Structure Parameters	x = 0.1	x = 0.3	x = 0.5
Space Group	R -3 c	R -3 c	R -3 c
Crystal Structure	Rhombohedral	Rhombohedral	Rhombohedral
a (Å) = b (Å)	5.505071	5.510983	5.523336
c (Å)	13.355908	13.352847	13.357766
α (°) = b (°)	90	90	90
g = (°)	120	120	120
Volume ($Å^3$)	350.534	351.207	352.913
Bond Length (Å)	1.96511	1.95705	1.96025
Bond Angle (°)	161.7209	165.5051	165.4963
wRp	0.1408	0.1305	0.1501
Rp	0.1070	0.1003	0.1174
Chi	1.225	1.084	1.433
Tolerance Factor			
Goldschmidt	0.970525711	0.966997443	0.963494735

The presence of Ni and Ti substitution at the Mn site in the LSMO material did not cause a change in the basic crystal structure. This result is reinforced by the calculation of the Goldschmidt tolerance factor whose value is obtained by performing calculations using Equation (1). The results of the calculations for each sample have a Goldschmidt tolerance value between 0.96 - 1. Where at that value the crystal structure formed is a rhombohedral structure (Manjunatha et al. 2015).

$$t_G = \frac{0{,}7r_{La^{3+}} + 0{,}3r_{Sr^{+2}} + r_{O^{-2}}}{\sqrt{2}\,[(1-x)r_{Mn^{3+}} + 0{,}3r_{Mn^{4+}} + xr_{Ni^{3+}} + xr_{Ti^{3+}} + r_{O^{2-}}]} \quad (1)$$

In this research, the average crystal size was obtained by taking 8 peaks that have the highest intensity in the diffraction pattern for each composition x, which can be seen in Table 2. These results were obtained based on calculations using the Scherrer equation (2).

$$D = \frac{K\,x\,\lambda}{\beta\,cos\theta} \quad (2)$$

Where D is the average crystal size, K is a constant, is the X-ray wavelength (Cu = 1.54056), is the Full Width Half Maximum (FWHM) value, and is the position of the diffraction peak.

Table 2. The average value of crystal size, the average value of Full Width Half Maximum (FWHM) of the material $La_{0.7}Sr_{0.3}Mn_{1-x}(Ni,Ti)_{x/2}O_3$ with various values (x = 0.1; 0.3; 0.5).

x	D (nm)	Full Width Half Maximum (rad)
0.1	24.14454126	0.006996
0.3	18.53596333	0.010002
0.5	15.75151107	0.010509

The average crystal size of the sample $La_{0.7}Sr_{0.3}Mn_{1-x}(Ni,Ti)_{x/2}O_3$ as the composition of the x value has been plotted in the form of a graph shown in Figure 3, it can be seen that in general there is a decrease in crystal size along with increased Ni and Ti doping. Based on calculations using the Scherrer equation (2), it can be seen that the larger Full Width Half Maximum (FWHM) value results in a smaller crystal size because D and have inversely proportional values (Masruroh et al. 2013). The resulting crystal size in nanometre (nm) scale is one of the advantages of the previously known sample preparation synthesized using the sol-gel method (Elma 2018).

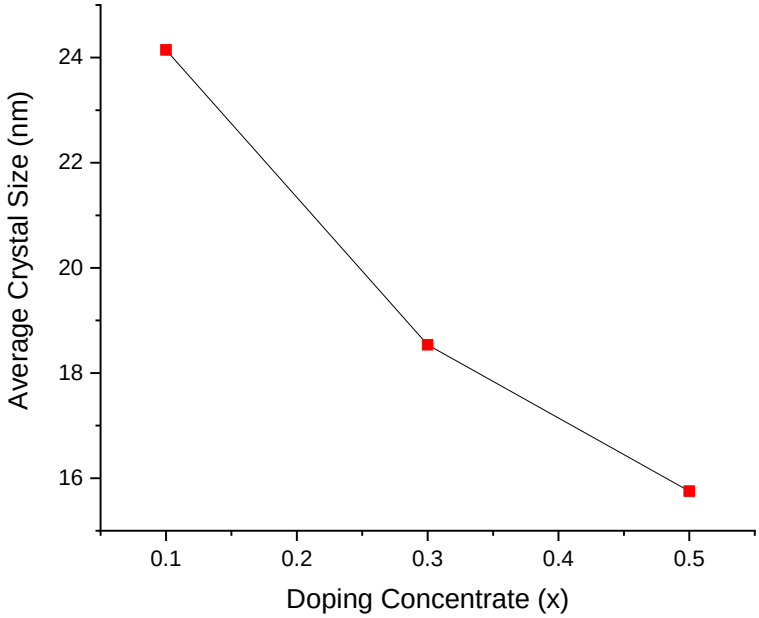

Figure 3. The average crystal size (nm) to the doping composition (x) in the sample $La_{0.7}Sr_{0.3}Mn_{1-x}(Ni,Ti)_{x/2}O_3$.

The crystal structure produced in this research can be visualized which is input into the VESTA software as shown in Figure 4 as follows.

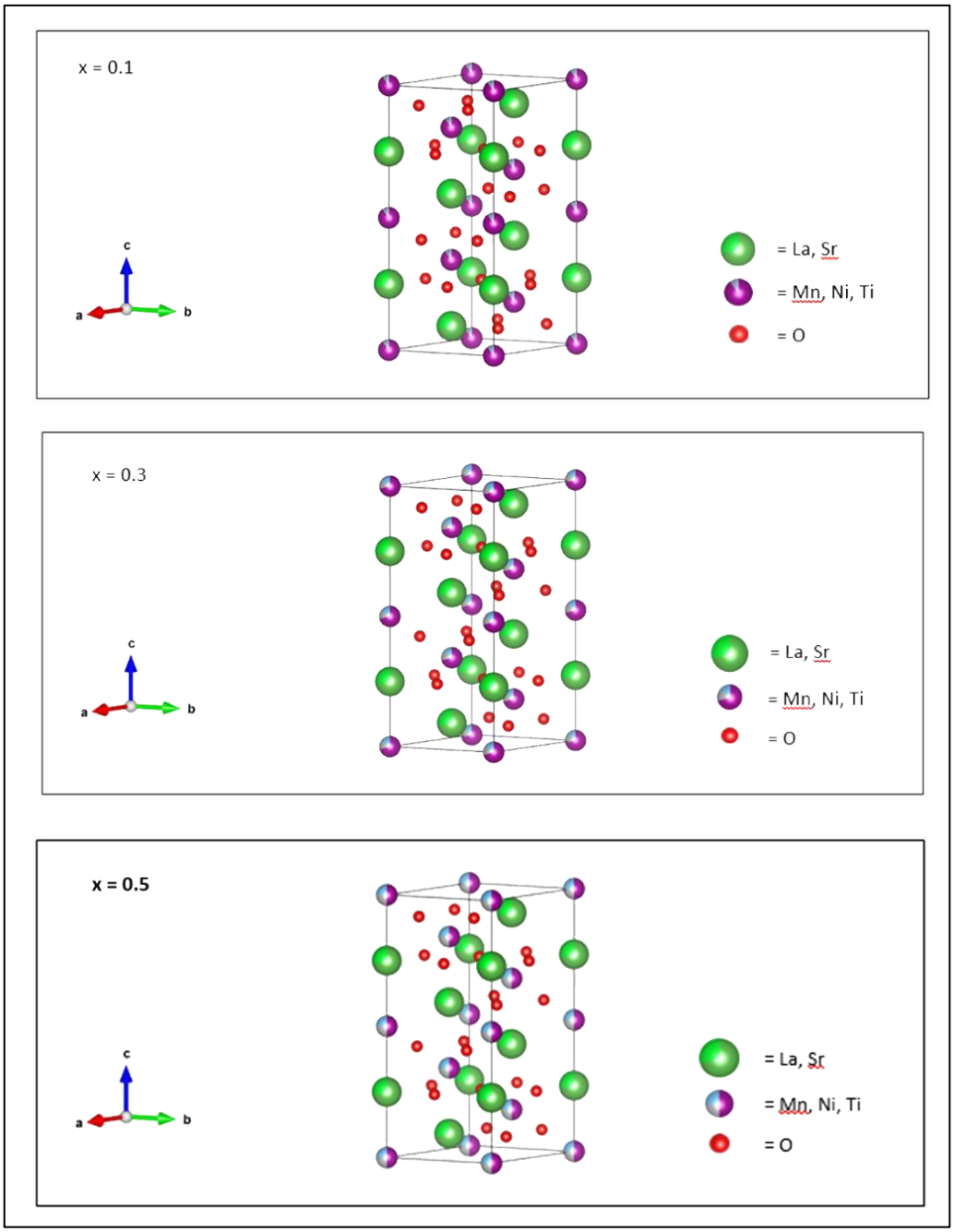

Figure 4. Visualization of $La_{0,7}Sr_{0,3}Mn_{1-x}(Ni,Ti)_{x/2}O_3$ with VESTA software.

3.2. Vector Network Analyzer

Characterization using Vector Network Analyzer (VNA) obtained an R (Reflection Loss) curve with a frequency range of X Band (X band) 8 GHz -12 GHz. The results of the characterization using Vector Network Analyzer (VNA) data are taken in the form of the value of S_{11} (reflection coefficient) from the source of electromagnetic waves. Where in this characterization is obtained a Reflection Loss (R_L) curve that describes the ability of a material to absorb microwaves.

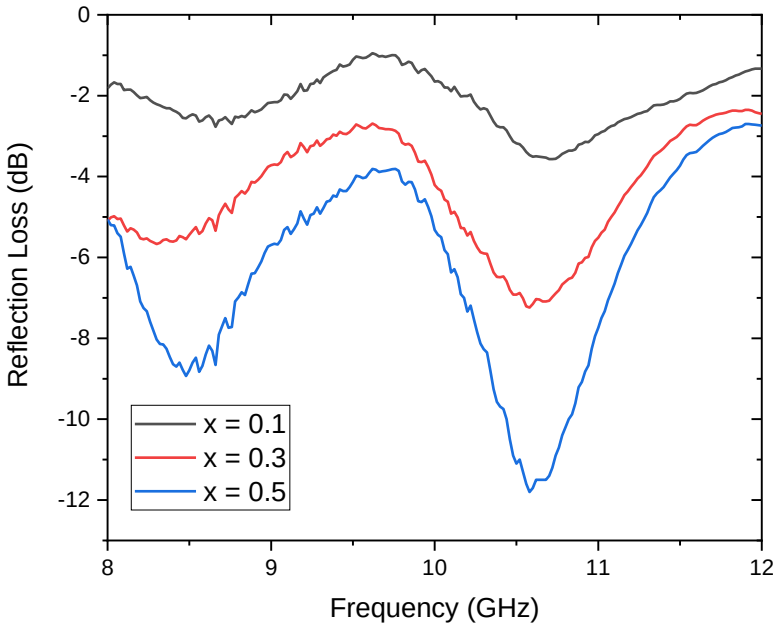

Figure 5. The absorption curve of electromagnetic waves on the material $La_{0.7}Sr_{0.3}Mn_{1-x}(Ni,Ti)_{x/2}O_3$ (x = 0.1; 0.3; and 0.5).

Based on the graph in Figure 5, two significant absorption frequency regions are obtained, because the higher the absorption peak in a material indicates a good microwave absorption potential.

If the reflection loss value is known, the percent absorption strength of a material can be determined using Equation (3) and Equation (4) as follows:

$$\Gamma = 10^{\left(-return\frac{loss}{20}\right)} \quad (3)$$

$$Through\ Power\ (\%) = 100\ (1 - \Gamma^2) \quad (4)$$

Table 3. The results of the absorption of electromagnetic waves on the material La0.7Sr0.3Mn1-x(Ni,Ti)x/2O3 (x = 0.1; 0.3 and 0.5).

x	Frequency (GHz)	Reflection Loss (dB)	Through Power (%)
0.1	8.66	-2.773	47.18
	10.7	-3.572	56.06
0.3	8.3	-5.666	72.87
	10.58	-7.239	81.11
0.5	8.48	-8.925	87.19
	10.58	-11.8	93.39

The results of the ability of the material $La_{0.7}Sr_{0.3}Mn_{1-x}(Ni,Ti)_{x/2}O_3$ (x= 0.1, 0.3 and 0.5) to absorb microwaves based on calculations are summarized in Table 3 Where in this material the highest reflection loss value is x = 0.5 with an absorption ability of 93.39%.

4. Conclusion

Investigation of the material $La_{0.7}Sr_{0.3}Mn_{1-x}(Ni,Ti)_{x/2}O_3$ (x= 0.1, 0.3 and 0.5) synthesized using sol-gel method have been carried out. Refinement result of X-Ray Diffraction (XRD) showed a single phase without impurities product and possess rhombohedral structure with R -3c space group. The presence of Ni and Ti substitution at the Mn site in the LSMO material did not cause a change in the basic crystal structure but there is an increase in the value of the volume lattice parameter, and a decrease in crystal size. The Vector Network Analyzer (VNA) results from the material $La_{0.7}Sr_{0.3}Mn_{1-x}(Ni,Ti)_{x/2}O_3$ with a concentration of x = 0.5 showed the highest reflection loss value of -11.8 dB with the ability to absorb microwaves of 93.39% at a frequency optimized 10.58 GHz.

5. Suggestion

In the next research, it's expected to test using Scanning Electron Microscope (SEM) to determine morphology, using Vibrating Sample Magnetometer (VSM) to determine the magnetic properties of the material, and using Four Point Probe (FPP) to determine the electrical properties.

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