The effect incorporation of Ni=0.05 at Mn site on microwave absorption properties of La$_{0.67}$Sr$_{0.33}$MnO$_3$ material

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Abstract. Nowadays we need material that can reduce electromagnetic interference (EMI). Doped LaMnO$_3$ has electromagnetic properties which makes it possible for this material to be used for microwave absorption material. In this study the Ni doped (Ni=0.05) La$_{0.67}$Sr$_{0.33}$MnO$_3$ was fabricated by sol-gel method and characterized by X-Ray Diffraction (XRD), Scanning Electron Microscopy-Electron Energy Dispersive Spectroscopy (SEM-EDS), and Vector Network Analyzer (VNA). The XRD result showed that the material was single phase and the crystal structure of the material was rhombohedral with space group R-3c. The lattice parameter of sample decreased after incorporation of Ni. The influence incorporation of Ni into LSMO on microwave absorption performance was investigated. The microwave absorption performance was improved after Ni doping. The maximum reflection loss was -6.29 dB at 11.47 GHz.

1. Introduction
Microwaves in the range 1-20 GHz increasingly used in the field of wireless communication, local area networks, radar system etc, so we need anti-electromagnetic interference material to reduce this problem [1]. The perovskite oxide especially Lanthanum manganite with the form La$_{1-x}$B$_x$MnO$_3$ (B is divalent element such Sr, Ca, and Pb) have been the subject of extensive investigation. Many variants of the doped perovskites had been synthesized and investigated [2]. The doped LaMnO$_3$ has unusual electromagnetic properties, which make it possible for this material to be used for absorbing material [3]. In this study authors purposed to enhance the microwave absorption ability of material by the incorporation of Ni at Mn site. As we know there have been several preparation methods to synthesize material[4]. In this study the sol-gel method was used to synthesize materials. The morphologies, crystal structure, composition, resistivity and microwave absorption ability have been investigated.

2. Methods
La$_{0.67}$Sr$_{0.33}$Mn$_{0.8}$Ni$_{0.2}$O$_3$ sample was synthesized using a sol gel method. La$_2$O$_3$, Sr(NO$_3$)$_2$, Mn(NO$_3$)$_2$.4H$_2$O, and Ni(NO$_3$)$_2$.6H$_2$O were used as starting materials and weighed according by stoichiometry. Each starting material then solved in aquabidest, while La$_2$O$_3$ precursor was solved in...
diluted HNO$_3$. The resulting solution of each starting material mixed and stirred at 80°C. Ammonia solution was added to the mixed solution to adjust pH until reached 7 this pH based on Gupta et al research’s [5]. Then, the solution was stirred and dried at 120°C for 2 h until sol gel formed. The gel then calcined at 500°C for 6 h, grinded, and sintered at 850°C for 10 h. The sintered sample was pressed into pellet and re-sintered at 1200°C for 2 h.

3. Result and discussion
Samples that have been synthesized by sol gel method then characterized by XRD, SEM-EDX and VNA.

3.1. Structure characterization
The structure of the La$_{0.67}$Sr$_{0.33}$Mn$_{0.8}$Ni$_{0.2}$O$_3$ material has been characterized using XRD. Figure 1 shows X-Ray diffraction Pattern of materials. It is clear that the pure perovskite structures have been successfully formed, and there were no phases for the residual materials. All the peaks were in good consistent with the chi-squared in the range 1-1.3.

![Figure 1. XRD pattern of material La$_{0.67}$Sr$_{0.33}$MnO$_3$ and La$_{0.67}$Sr$_{0.33}$Mn$_{0.95}$Ni$_{0.05}$O$_3$](image)

XRD characterization resultt was analyzed by rietvield refinement method. It is known that crystal structure of the sample is rombohedral with R-3c space group[6]. Incorporation of Ni at Mn site did not change the structure of the material. Lattice parameters of sample summarized in Table 1. Ionic size Mn larger than Ni so lattice parameter of sample decrease after incorporation of Ni[7]

| Sample | a =b (Å) | c (Å) | V (Å$^3$) | Crystallite Size (Å) | $\chi^2$ |
|--------|---------|-------|----------|---------------------|--------|
| Ni = 0 | 5.505   | 13.378| 351.191  | 451.3               | 1.100  |
| Ni = 0.05 | 5.492 | 13.344| 348.589  | 582.1               | 1.099  |

3.2. SEM and EDX characterization
The SEM image exhibit the morphologies of the samples in Figure 2. It is clear that the La$_{0.67}$Sr$_{0.33}$Mn$_{0.95}$Ni$_{0.05}$O$_3$ had smaller particle size. Although the samples were synthesized through the same process, the particle size was different which could be caused by different compositions.
3.3. Cryogenic Magnetometer (Resistivity)

The resistivity of La$_{0.67}$Sr$_{0.33}$Mn$_3$O$_3$ at room temperature (T= 25 °C) are shown in Figure 6. The resistivity indicate semiconductor properties, which increased after incorporation of Ni. Resistivity is one of the important parameters for a microwave absorbing material. When the resistivity of material is accesses to that metal, the microwave cannot enter easily to the material. However, since the resistivity of La$_{0.67}$Sr$_{0.33}$Mn$_3$O$_3$ has shown semiconductor range, it is suitable to act as microwave absorption material [1]. This transitions which can be explained by double exchange theory [6]. Zhou reported that the doping at B-site affects Mn$^{3+}$-O-Mn$^{4+}$ to a certain extent and cause a break point on the electronic channel to reduce the quantity of electron jumping position, which makes the resistivity increase to be in range of semiconductor [3] [9].

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**Figure 2.** SEM image of La$_{0.67}$Sr$_{0.33}$MnO$_3$ sample in BSE mode

**Figure 3.** SEM image of La$_{0.67}$Sr$_{0.33}$Mn$_{0.95}$Ni$_{0.05}$O$_3$ in SE mode

For confirm the XRD results the element composition of the samples were characterized by EDX. From the EDX results (Figure 4 and Figure 5) we know that there is no impurites on the sample because no other element have been detected. Figure 5 indicated that Ni have been successfully added to La$_{0.67}$Sr$_{0.33}$MnO$_3$.

**Figure 4.** SEM image of La$_{0.67}$Sr$_{0.33}$MnO$_3$ sample in BSE mode

**Figure 5.** SEM image of La$_{0.67}$Sr$_{0.33}$Mn$_{0.95}$Ni$_{0.05}$O$_3$ in SE mode

Based on XRD and EDX results we can conclude that the La$_{0.67}$Sr$_{0.33}$Mn$_{0.95}$Ni$_{0.05}$O$_3$ (x= 0, 0.05) material have been successfully synthesized using sol-gel method.
3.4. VNA (Vector Network Analyzer) characterization

At last the material was characterized by VNA to determine it microwaves absorption ability. Figure 7 shows the frequency dependencies of microwave absorption properties of $\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ with the same thickness $d = 2.00$ mm, for two different samples with $x = 0.0$, and 0.05. From the Figure 6 we can see with incorporation of Ni the absorbing peak moved lower and wider at some frequency such as $8.2 \text{ GHz}$, $10.05 \text{ GHz}$, and $11.48 \text{ GHz}$ with the highest peak is $-16.02 \text{ dB}$ at frequency $8.2 \text{ GHz}$.

![Figure 6](image.png)

**Figure 6.** The resistivity of $\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ at room temperature ($T= 25^\circ \text{C}$)

| Sample | Frequency (Hz) | Reflection Loss (dB) | Reflectance (%) | Absorbance (%) |
|--------|----------------|----------------------|-----------------|----------------|
| Ni =0  | 12.4           | -2.59                | 74.2            | 25.8           |
| Ni= 0.05 | 8.2           | -16.02               | 15.8            | 84.2           |

**Table 2.** The microwave absorption ability of the sample $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ and $\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{0.95}\text{Ni}_{0.05}\text{O}_3$
Reflectivity is usually used as a parameter to characterize the microwave absorption performance. The reflectivity could be expressed by the following equation [10][11]

\[
RL = 20 \log |R|
\]  

(1)

According the equation (1), the relation between the reflectance (R) and reflection loss (RL) indicate the % ability of sample to reflect the microwave. The above results indicate that the incorporation of Ni can exhibit an excellent microwave absorption property. This result is agree with the previously research by zhang [10]

4. Conclusion
In summary, the La$_{0.67}$Sr$_{0.33}$Mn$_{1-x}$Ni$_x$O$_3$ (x = 0, 0.05) have been prepared using sol-gel method. The incorporation of Ni on microwave absorption properties in the frequency range 8-12 GHz are studied. Experimental results show that the highest absorption peak is 16.02 dB at frequency 8.2 GHz

Acknowledgements
This work was supported by University of Indonesia grant “Hibah PITTA (Hibah Publikasi Internasional Terindeks untuk Tugas Akhir) with contract number 634/UN2.R3.1/HKP.05.00/2017. The authors would like to thank Department of physics University of Indonesia for providing the facility for the research.

References
[1] Zhou K S, Xia H, Huang K L, Deng L W, Wang D, Zhou Y P, Gao S H 2009 Phys. B Condens. Matter 404 175
[2] Huang S, Deng L, Zhou K, Hu Z, Sun S, Ma Y, Xiao P 2012 J. Magn. Magn. Mater. 324 3149
[3] Zhou K S, Da W A, Huang K L, Yin L S, Zhou Y P and Gao S H 2007 Trans. Nonferrous Met. Soc. China 17 1294
[4] Wang B, Cao Q and Zhang S. 2014 Mater. Sci. Semicond. Process. 19 101
[5] Gupta M, Khan W, Yadav P, Kotnala R K, Azam A and Naqvi A H 2012 J. Appl. Phys. 111 937
[6] Ginting D, Nanto D, Zhang Y D, Yu S C and Phan T L 2013 Phys. B Condens. Matter 412 17
[7] Zhang Y D, Phan T L, Yang D S and Yu S C 2012 Curr. Appl. Phys. 12 803
[8] Zhou K S, Deng J J, Yin L S and Gao S H 2007 Trans. Nonferrous Met. Soc. China 17 947
[9] Skini R, Khilifi M, Wali M, Dhahri E, Hlil E K and Lachkar P 2014 J. Magn. Magn. Mater. 363 217
[10] Zhang S and Cao Q 2012 Mater. Sci. Eng. B. 177 678
[11] Cheng Y L, Dai J M, Zhu X B, Wu D J, Yang Z R and Sun Y P 2009 Nanoscale Res. Lett. 4 1153