Synthesis and characterization microwave absorber properties of La$_{0.7}$(Ca$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$ prepared by Sol-Gel method

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Abstract. In this research, structural engineering of lanthanum-manganate-based material was studied, starting with material synthesizing La$_{0.7}$(Ca$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$ with variation of $x=0; 0.1; 0.2$; and $0.3$ using the sol-gel method as a microwave material. The effects of Sr substitution on the stucture, size of grain, and microwave-absorbing properties were investigated in detail by various analytical methods. Using XRD (X-Ray Diffraction) showed that the sample had single phase and orthorombic structure (space group of Pnma), substitution of Sr$^{2+}$ ions did not cause changes in structure. Characterized using SEM (Scanning Electron Microscope) showed change in grain size which increase when given Sr substitution. Characterized using VNA (Vector Network Analyzer) in the 8-12 GHz range shows that the sample La$_{0.7}$(Ca$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$ with $x=0$ has been able to absorb up to 55.64% microwaves at 10.44GHz. The study concluded the material of La$_{0.7}$(Ca$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$ have a good potential to be a candidate of microwave absorbing materials.

1. Introduction
In recent years, many researchers investigated on perovskite manganite material. Perovskite-type lanthanum manganites (ABO$_3$) have a unique crystal structure, which makes them have excellent electromagnetic and phase change characteristics [1]. Changes in ion substitution greatly influence the changes in physical phenomena that occur in this material, for example to changes in crystal structure and electron transfer. With the form of RE$_{1-x}$AE$_x$MnO$_3$ (RE= trivalent rare earth elements; AE= divalent elements like Ca, Sr, Ba and Pb) have been the subject of extensive investigations [2].

In now days, the increasing expanding business of communication devices at telecommunication service providers such as mobile telephones and radar systems cause serious electromagnetic interference pollution, has attracted great interest in exploiting effective electromagnetic (EM) wave absorption materials with properties of wide frequency range, strong absorption, low density, and high resistivity [3, 4]. Electromagnetic wave absorbing material have good characteristic if it have a high value of permeability and permittivity. There have been a lot of researches on the electromagnetic and microwave absorption properties of doped La$_{1-x}$A$_x$MnO$_3$, with the vary on doped rare-earth oxide can...
exhibit rich electromagnetism characteristics such as magnetic transformation and conductivity change, which provides a foundation for the electromagnetic wave absorbing materials. J. Liu et al [1] confirmed optimal reflection loss calculated from the measured permittivity and permeability of LCMO is -42dB at 10.5 GHz with a thickness of 2.0 mm when the doping amount of Ca$^{2+}$ is 0.1. G. Li et al [2] studied the microwave absorbing property of La$_{1-x}$Sr$_x$MnO$_3$ prepared by solid state method, in the frequency range of 8-12 GHz the peak was -52dB when x=0.4. Zhang Shuyuan et al found that the La$_{0.7}$Sr$_{0.3}$MnO$_3$ had best reflection loss of microwave absorbing at 15.872 GHz is -17.65dB with a thickness 2.0 mm [5]. In Ref. [6] reported that lanthanum manganite with Ca doped cause reflection loss of microwave absorbing until -31dB.

In our present work, we investigate the stucture, size of grain, and microwave absorbing properties of La$_{0.7}$(Ca$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$ (LCSMO) with variation of x=0; 0.1; 0.2; and 0.3 with various analytical methods. La$_{0.7}$(Ca$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$ (LCSMO) prepared by sol-gel method, to control the stoichiometric ratio and the homogeneous composition of the materials. The perovskite-type structure been successfully formed, which studied the effects of Sr$^{2+}$ substitution on the structure and microwave-absorbing properties.

2. Method
The sol-gel process [7] was used to prepare La$_{0.7}$(Ca$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$. The precursor are La(NO$_3$)$_3$·6H$_2$O, Ca(NO$_3$)$_2$, Sr(NO$_3$)$_2$, and Mn(NO$_3$)$_2$ used for the prepared in accordance with the stoichiometry respectively. All of the raw materials were dissolved in distilled water and stirred until they were completely dissolved. The solution was evaporated on a hot plate with continuous stirring until thick gel was formed. The resulting gel was pra-calcined at 600°C for 6 hours then calcined at 1000°C for 12 hours to eliminate the organic material and sintered at 1200°C for 6 hours. The structure and phase purity were investigated by X-ray Diffraction (XRD) using a PanAlytical Xpert Pro diffractometer with Cu k$\alpha$ ($\lambda=1.54056$ Å) and the reflection loss (RL) of the samples was measured between 8-12GHz by using Vector Network Analyzer (VNA) Advantest type R3770.

3. Result and Discussion
3.1. Characteristic and Phase
The XRD study of polycrystalline La$_{0.7}$(Ca$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$ (x=0; 0.1; 0.2; and 0.3) was carried out at room temperature and data were analysed with Rietveld refinement technique. XRD analyses of all the samples show the typical characteristic spectra of perovskite - like structures without the characteristic peaks from impurity and can be indexed to a single orthorombic crystal structure with the Pnma symmetry [shown in Figure 1]:

![Figure 1. XRD patterns of La$_{0.7}$(Ca$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$ (x=0; 0.1; 0.2; and 0.3).](image-url)
It can be seen from the figure, compared with no doping samples, doping did not cause the diffraction peaks disappeared. With the increase of doping concentration, the diffraction peak moves towards a low angle (2θ) [shown in Figure 2]. This is because the ionic radius of Sr$^{2+}$ (1.34 Å) is larger than Ca$^{2+}$ (0.99 Å) [7]. According to the Bragg equation: $2\sin\theta = n\lambda$ [9], because the X ray has a certain wavelength, d becomes bigger and $\theta$ decreases, which causes the diffraction peak to move to the low angle [10].

Table 1. Refinement results of La$_{0.7}$(Ca$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$ samples.

| Parameter                  | X=0     | X=0.1  | X=0.2  | X=0.3  |
|----------------------------|---------|--------|--------|--------|
| Space Group                | P n m a | P n m a| P n m a| P n m a|
| a (Å)                      | 5.4665  | 5.4662 | 5.4632 | 5.466  |
| b (Å)                      | 7.7250  | 7.7267 | 7.7211 | 7.7255 |
| c (Å)                      | 5.4811  | 5.4869 | 5.4878 | 5.4962 |
| V (Å$^3$)                  | 231.460 | 231.744| 231.48 | 232.089|
| Average Crystallite Size  | 61      | 73     | 56     | 59     |
|   (nm)                     |         |        |        |        |
| Discrepancy Factors        |         |        |        |        |
| RwP (%)                    | 8.71    | 7.30   | 8.57   | 8.12   |
| Rp (%)                     | 6.54    | 5.62   | 6.39   | 6.12   |
| GoF                        | 1.15    | 1.15   | 1.28   | 1.15   |
| Bondlengths (Å)            |         |        |        |        |
| Mn-O(1)                    | 1.93555/1.980 | 1.93725/1.982 | 1.9584 | 1.96024/1.965 |
| Mn-O(2)                    | 1.9576  | 1.96139| 1.9646 | 1.9657 |
| <Mn-O>                     | 1.958   | 1.9603 | 1.9615 | 1.9638 |
| Bondangles (°)             |         |        |        |        |
| Mn-O(1)-Mn                 | 162.57  | 162.24 | 161.72 | 161.72 |
| Mn-O(2)-Mn                 | 161.16  | 160.03 | 158.55 | 158.53 |
| <Mn-O-Mn>                  | 161.865 | 161.135| 160.13 | 160.125|
| Bandwidth (u.a)            |         |        |        |        |
| W ($10^{-2}$)              | 9.40    | 9.35   | 9.31   | 9.28   |
| Tolerance Factor           |         |        |        |        |
| Goldscmidth                | 0.885   | 0.890  | 0.895  | 0.899  |

Double exchange interaction is depended on Mn–O–Mn and Mn–O. The existence of bandwidth values is a attachment between bondlength and bondangle. Sr substitution decrease Mn–O–Mn angle and increase Mn–O bond length, therefore electrons transfer will be more difficult. The results are suitable with Y.B. Zhang et al who discussed the magnetic transition in La$_{2/3}$A$_{1/3}$MnO$_3$ oxide. Double exchange interaction is depended on Mn–O–Mn and Mn–O. The existence of bandwidth values is a attachment between bondlength and bondangle. Sr substitution decrease Mn–O–Mn angle and increase Mn–O bond length, therefore electrons transfer will be more difficult. The results are suitable with Y.B. Zhang et al who discussed the magnetic transition in La$_{2/3}$A$_{1/3}$MnO$_3$ oxide [11].
From the Table 1 we know the chi-square value obtained by the sample with variations in the value of $x = 0; 0.1; 0.3$ doesn’t exceed than 1.15, and for the sample $x = 0.2$ is 1.28, these results indicate that there is a suitability for a good material [9]. The lattice parameters for the a and b values of each sample are not much different, the c lattice values from 5.4811Å to 5.4962Å indicate an increasing linear data value [9]. XRD analysis shows with the Sr$^{2+}$ substitution sample doesn’t changes in structure and phase, but there is a difference in electromagnetic properties of the sample.

3.2. Morphology

In SEM characterization, the magnification is 10000 for $x = 0$ and 5000 times for $x = 0.1; 0.2; and 0.3$. We can see on the Figure 3 it can be seen that the sample with $x = 0$ has a very small grain size compared to after the Sr$^{2+}$ substitution. With the increase of Sr$^{2+}$ substitution, the grain size will increase even though the addition is not linear with increasing substitution. Characterization using SEM produces morphological data from the sample La$_{0.7}$(Ca$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$ using the secondary electron mode as shown in the following figure 3.

From Figure 3 it can be seen that there are morphological differences between each sample. Sample $x = 0$ shows the small grain size and cavity between each grain, but in sample $x = 0.1; 0.2; and 0.3$ shows larger grains clinging to each other. Seen by the existence of Sr$^{2+}$ substitution the grain size produced by the SEM has an increased, this result has the same pattern of values as the average crystallite size value in the XRD. The grain size greatly affects the electron transfer process in the material, an enlargement of the grain size causes the electrons to move more easily, so the resistivity value in the material will be smaller [10].
Figure 3. SEM characterization of La$_{0.7}$(Ca$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$ sample with (a) x=0 (b) x=0.1 (c) x=0.2 and (d) x=0.3.

3.3. Absorbance
The increase in grain size when the Sr$^{2+}$ substitution has been shown by SEM testing is in line with the results obtained in the VNA test related to the absorption value, where the increase in grain size causes the ability of a material to absorb electromagnetic waves to decrease. This research uses the X band frequency range (X band) which has a range of 8 GHz - 12 GHz. The results of characterization using VNA are in the form of $S_{11}$ (reflection coefficient) and $S_{21}$ (transmission coefficient) data from electromagnetic wave sources, but this study only takes the value from $S_{11}$. From this characterization an RL (Reflection Loss) curve is obtained which describes the ability of a material to absorb electromagnetic waves, as shown in Figure 4:

The Figure 4. shows the frequency dependencies of microwave absorbing properties of La$_{0.7}$(Ca$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$ with the same thickness, d = 1.5mm, for four different samples with (x=0; 0.1; 0.2; and 0.3). Microwave absorption performance of the La$_{0.7}$(Ca$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$ samples were investigated with absorber’s thickness of 1.5mm. The reflection loss spectra of the La$_{0.7}$(Ca$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$ (x=0; 0.1; 0.2; and 0.3) single phase samples in the frequency range of 8 – 12 GHz.

Table 2 reveals the microwave absorption properties of the La$_{0.7}$(Ca$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$ (x=0; 0.1; 0.2; and 0.3) samples. The sample had the highest microwave absorption performance. The maximum reflection loss was -3.53dB at matching frequency 10.44GHz with 55.64% through power or microwave. The decrease in absorption ability is caused by several factors, it can be caused by the ionic radii from the substitution ion, double exchange interaction among the samples, permeability and permittivity properties of La$_{0.7}$(Ca$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$ (x=0; 0.1; 0.2; and 0.3) samples [1].
Figure 4. Microwave absorption performance of $\text{La}_{0.7}(\text{Ca}_{1-x}\text{Sr}_x)_{0.3}\text{MnO}_3$.

Table 2. Microwave absorption properties of $\text{La}_{0.7}(\text{Ca}_{1-x}\text{Sr}_x)_{0.3}\text{MnO}_3$ samples.

| $x$  | Frequency (GHz) | Reflection Loss (dB) | Through Power (%) |
|------|-----------------|----------------------|-------------------|
| 0    | 10.44           | -3.53                | 55.64             |
| 0.1  | 10.42           | -3.11                | 51.13             |
| 0.2  | 10.44           | -2.88                | 48.48             |
| 0.3  | 10.52           | -2.77                | 41.15             |

4. Conclusion
Investigation of $\text{La}_{0.7}(\text{Ca}_{1-x}\text{Sr}_x)_{0.3}\text{MnO}_3$ ($x=0; 0.1; 0.2; \text{and } 0.3$) compound synthesized using sol-gel method have been carried out. Refinement result of XRD showed a single phase without impurities product and possess orthorhombic structure with Pnma space group. Sr$^{2+}$ substitution did not change the crystal structure but causes increasing unit cell volume and Mn–O–Mn bond angles, along with the decreasing of Mn–O bond length. SEM characterization results showed an increase of the average grain size value when substiti Sr. The microwave-absorbing properties of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ manganese oxides in the frequency range of 8–12GHz are studied. Experimental results show that the optimal absorption peak is about -3.53dB for $x=0$ sample with the thickness of 1.5mm.

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