Structural Studies of La$_{0.7}$Sr$_{0.2}$Ba$_{0.1}$Mn$_{1-x}$Ni$_x$O$_3$ ($x = 0$ and $x = 0.1$) perovskite manganite synthesized by sol-gel method

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Abstract. La$_{0.7}$Sr$_{0.2}$Ba$_{0.1}$Mn$_{1-x}$Ni$_x$O$_3$ ($x = 0$ and $x = 0.1$) material has been successfully synthesized using sol-gel method. The XRD pattern shows the sample has a single phase without impurities. The result of refinement showed that both samples formed a rhombohedral structure with R-3c (167) space group. The addition of nickel ions with a concentration of 10% does not change the crystal structure, but causes a decrease in lattice parameters, unit cell volume, Mn-O-Mn Bond angle, and increase Mn-O Bond length. The unit cell volume of La$_{0.7}$Sr$_{0.2}$Ba$_{0.1}$MnO$_3$ and La$_{0.7}$Sr$_{0.2}$Ba$_{0.1}$Mn$_{0.9}$Ni$_{0.1}$O$_3$ are 353.382 Å$^3$ and 352.036 Å$^3$. The Mn-O-Mn angle for both is 168.021° and 163.829°, while the Mn-O bond lengths are 1.9559 Å and 1.9624 Å respectively. Goldschmidt’s tolerance factor was calculated to know the stability of the crystal structure. Tolerance factor calculation results confirm that the stable crystal structure is rhombohedral perovskite structure (0.97372 and 0.97154).

1. Introduction
Doped perovskite manganites with general formula $A_{1-x}AE_x$MnO$_3$ with site $A$ is rare earth element and $AE$ is Alkaline Earth element has attracted the attention of many researchers in the last ten years. It has been known that doped perovskite manganites possess many unique physical properties such as charge ordering, colossal magnetoresistance (CMR), and magnetocaloric effect (MCE) [1-8]. All the physical properties of manganites are useful to be applied in everyday life and yet there still a limited number of its application that could be seen. The reason being is that many researchers still sought the optimum physical properties that could emerge at room temperature and low applied magnetic field. The physical properties of perovskite manganites can be easily altered in several ways such as partial substitution, different synthesize methods and varying the sintering temperature [3].

It has been commonly known that the physical properties of perovskite manganite have a strong correlation with some parameter such as its structure and microstructure [1,10]. Therefore, the study regarding the structural properties of manganites holds an important value in order to understand the physical properties that can emerge from perovskite manganite. Doped lanthanum manganites by divalent alkaline earth element such as Ca$^{2+}$, Ba$^{2+}$, and Sr$^{2+}$ with general formula La$_{1-x}$AE$_x$MnO$_3$ exhibit many significant properties like metal-insulator transition, ferromagnetic-paramagnetic phase change, charge and orbital ordering depending on several parameters as charge density, temperature, atomic structure, average ionic radius $<r_A>$ of the A-site cations and Mn$^{3+}$/Mn$^{4+}$ ratio [1,4,12]. Study structural of Lanthanum Manganite is important to predict its properties [6]. Influence the interaction ferromagnetic double exchange (DE) couplings by changing the Mn$^{3+}$-O-Mn$^{4+}$ bond angle and Mn–O bond length. The phenomena double exchange have attracted much attention because of their peculiar electrical transport and magnetic properties [6-10].
One of the famous examples of doped perovskite manganites, La\(_{1-x}\)Sr\(_x\)MnO\(_3\) (LSMO), has been studied by several researchers for quite a long time. Due to its high Curie temperature (Tc) and low resistivity [2,3]. Another famous example of research reported on La\(_{1-x}\)Ba\(_x\)MnO\(_3\) (LBMO) materials has a close Tc at room temperature and low resistivity [4,12]. In other studies reported, the substitution of nickel at the Mn site can be used as a good tuning temperature and increase the value of Magnetoresistance [5-10].

With the aim to find a suitable material to be applied in everyday life, in this research LSMO will be substituted using barium ions to replace some of the lanthanum site and nickel ions to replace some of manganese site thus, changing the chemical formula into La\(_{0.7}\)Sr\(_{0.2}\)Ba\(_{0.1}\)Mn\(_{1-x}\)Ni\(_x\)O\(_3\) (\(x = 0\) and 0.10) we expect to get new behavior on physical properties. Before the physical properties of both samples will be investigated, we study the structure of the crystal material to get information for our future work. This study becomes a significant matter since partial substitution can induce a difference in the physical properties of manganites, we have prepared samples of La\(_{0.7}\)Sr\(_{0.2}\)Ba\(_{0.1}\)Mn\(_{1-x}\)Ni\(_x\)O\(_3\) (\(x = 0\) and 0.10) which have been synthesized using a sol-gel method and the crystal structure of the samples was examined using X-Ray Diffractometer (XRD).

2. Material and Methods

The La\(_{0.7}\)Sr\(_{0.2}\)Ba\(_{0.1}\)Mn\(_{1-x}\)Ni\(_x\)O\(_3\) (\(x = 0\) and 0.1) has been synthesized using the sol-gel method. The stoichiometric calculation of the precursor used is La(NO\(_3\))\(_3\)·6H\(_2\)O, Ba(NO\(_3\))\(_2\), Sr(NO\(_3\))\(_2\), Mn(NO\(_3\))\(_2\)·4H\(_2\)O, and Ni(NO\(_3\))\(_2\)·6H\(_2\)O with high purity of the Merck Product. All precursors were diluted with a minimum amount of aquabidest water to get a clear solution. The precursor was mixed together to synthesize La\(_{0.7}\)Sr\(_{0.2}\)Ba\(_{0.1}\)Mn\(_{1-x}\)Ni\(_x\)O\(_3\) sample according to the reaction:

\[
0.7\text{La(NO}_3\text{)}_3 + 0.2\text{Sr(NO}_3\text{)}_2 + 0.1\text{ Ba(NO}_3\text{)}_2 + (1 - x)\text{Mn(NO}_3\text{)}_2·4\text{H}_2\text{O} + x\text{Ni(NO}_3\text{)}_2·6\text{H}_2\text{O} + \beta\text{C}_6\text{H}_5\text{O}_7·\text{H}_2\text{O} \\
\rightarrow \text{La}_{0.7}\text{Sr}_{0.2}\text{Ba}_{0.1}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3 + \delta\text{N}_2 + \gamma\text{H}_2\text{O} + \alpha\text{CO}_2
\]

and then mixed with constant stirring. Citric acids were used as metal ion complexant [13]. The mass of citric acid can be calculated using ratio citric acid to metal ion as much as 1.2 [14]. The solution is stirred and heated to 80°C on the magnetic hot plate. Ammonia Solution was used to adjust pH until it reaches 7. After the viscous gel is formed, the process was continued by dehydrating at 120°C in oven overnight to eliminate the water content. After that, calcination was done at 550°C for 6 hours. Last step, sintering with a temperature of 1200°C for 6 hours. The structure of the samples was characterized by X-ray diffractometer (XRD) using X'pert PANalytical diffractometer with CuK\(_\alpha\) (\(\lambda = 1.5406\) Å).

3. Result and Discussion

The sample which synthesized by sol-gel method then characterized using X-ray Diffractometer (XRD) to analyze the crystal structure and lattice parameter of the sample. Figure 1 shows the XRD pattern after the calcination process. The result shows that the sample phase has not yet formed, the sample is still amorphous after calcined. The perovskite structure for doped lanthanum manganites phase begins to form above 700°C [15,16].
Figure 1. XRD pattern after the calcined at 550°C for 6 hours.

Figure 2 shows the XRD pattern after sintering in both samples and figure 2b comparison at the highest intensity shows a shift of 2θ after doping of nickel which indicates the change in lattice parameters. The result of refinement showed that both samples have a single phase and formed a rhombohedral structure with R-3c (167) space group, which is confirmed from the same miller index at each diffraction peak and observation and calculation data. The XRD measurement data is quite good based on discrepancy factor as Goodness of Fit (GoF) and Reliability factors (R_p and R_w) shown in Table 1. Figure 3a and 4a show a good agreement between observed and calculated profil. The atomic positions are occupied at 6a (0,0,1/4) for (La/Sr/Ba), 6b (0, 0, 0) for (Mn/Ni), and 18e (x, 0, 1/4) for O. The crystal structures of both samples are illustrated in Figures 3b and 4b with Virtualization of Electronic Structural Analysis (VESTA) Program.

Nickel substitution causes changes in the concentration of Mn^{3+}-O-Mn^{4+} bond. Many researchers regarding partial substitution by nickel ions have been reported and proven by X-ray photoelectron spectra (XPS) measurements [6-8], which substitute Mn-site in lanthanum manganites is nickel with The oxidation number is +2 (Ni^{2+}) [6-11]. The effect of substitution of nickel on structural in this material does not change the crystal structure but changes the lattice parameters and volume of cell units. Ni^{2+} ion (radius 0.56 Å) replaces Mn^{3+} ion (radius 0.65 Å) by having the bigger ionic radius, which causes increasing the ratio of Mn^{4+} (radius 0.53 Å) to cause a decrease in lattice parameters [4,6-11].

Figure 2. (a) A comparison of diffraction pattern both samples (b) A comparison of both sample at the highest intensity shows a shift in 2θ after nickel doping.
Figure 3. (a) Results of Rietveld analysis of the XRD pattern and (b) Crystal structure of La$_{0.7}$Sr$_{0.2}$Ba$_{0.1}$MnO$_3$.

Figure 4. (a) Results of Rietveld analysis of the XRD pattern and (b) Crystal structure of La$_{0.7}$Sr$_{0.2}$Ba$_{0.1}$Mn$_{0.9}$Ni$_{0.1}$O$_3$.

The stability of the perovskite structure depends heavily on the size of the ions that fill the A-site and the B-site. If there is a difference between the ionic radius of the dopant and the A-site or B-site ions, the perovskite structure will be distorted [12]. Goldschmidt defines the tolerance factor as:

$$
\tau = \frac{1}{\sqrt{2}} \left( \frac{r_A - r_O}{r_B - r_O} \right)
$$

where $<r_A>$ and $<r_B>$ are the average radius of ions that fill the A-site and B-site, and $r_O$ is the oxygen ionic radius. The stable manganite perovskite structure has a $\tau$ factor which is in the range $0.89 < \tau < 1.02$ [12]. Result of Goldschmidt calculation can be seen in Table 1, the results in both samples are between $0.96 < \tau < 1$ range, which belongs to rhombohedral structures [12]. The average crystallite size ($D$) was determined using the Scherrer’s equation given below

$$
D = \frac{K\lambda}{\beta_{hkl} \cos \theta}
$$

where $K$ is a numerical shape factor which $K = 0.9$ is a good approximation for the absence of detailed
shape information and many kinds of researches using this value [9], $\lambda$ is the incident x-ray wavelength ($\lambda$ Cu =1.5406 Å), $\beta$ is full width at half maximum (FWHM) of the peak corresponding to maximum intensity, and $\theta$ represents the diffraction angle in degrees [6-10]. The crystallite sizes ($D$) of both samples are given below in Table 1. Nickel Substitution decreases average crystallite size.

The most important things in the investigation of the structure of the perovskite manganite are to know the parameters of the Mn-O bond length and the angle of the Mn-O-Mn bond, which is where the double exchange occurs. One of them is research conducted by Radaelli, et.al. and confirmed by many researchers on perovskite manganites material is the width of the electronic bandwidth ($W$) one of which is influenced by the average of Mn-O bond distance ($d_{\text{Mn-O}}$) and the average of the Mn-O-Mn bond angle ($<\text{Mn-O-Mn}>$) expressed by the equation [1,10,11]:

$$W \sim \frac{\cos \frac{1}{2} (\pi <\text{Mn-O-Mn}>)}{d_{\text{Mn-O}}^{3.5}}$$ (3)

In several studies, it has been reported that the $W$ value decreases with decreasing magnetization saturation and Curie temperature [1,10,11]. In this work, partial substitution of nickel causes changes the average of the Mn-O-Mn bond angle decreases and the average Mn-O bond length increases causes difficult transfer of electrons in the bond of Mn$^{3+}$-O-Mn$^{4+}$ ions, thus affecting this electrical and magnetic properties.

| Table 1. Structural parameter from Rietveld analysis for both samples. |
|-----------------|-----------------|
| Parameter       | Nickel concentration ($x$) |
| Space Grp       | R-3c (167)       | R-3c (167)       |
| Structure       | Rhombohedral     | Rhombohedral     |
| $a = b$ (Å)     | 5.5164           | 5.5095           |
| $c$ (Å)         | 13.4093          | 13.3917          |
| $V$(Å$^3$)      | 353.3815         | 352.0363         |
| $d_{\text{Mn-O}}$ (Å) | 1.9559(2)      | 1.9624(3)        |
| $<\text{Mn-O-Mn}>$ (degrees) | 168.02(1)     | 163.83(1)        |
| average crystallite size (nm) | 119.055       | 67.9361          |
| $\tau$          | 0.9737           | 9.7155           |
| Discrepancy factor | GoF             | Rwp (%)          |
|                 | 1.7552           | 5.9898           |
|                 | 1.8545           | 6.18172          |
|                 | 4.5701           | 4.7448           |

4. Conclusion
La$_{0.90}$Sr$_{0.10}$Mn$_{1-x}$Ni$_x$O$_3$ ($x=0$ and 0.1) material has been successfully synthesized using sol-gel method. The XRD pattern shows the sample has a single phase without impurities. The result of refinement showed that both samples formed a rhombohedral structure with R-3c space group. The substitution of nickel ions with a concentration of 10% does not change the crystal structure but causes a change in lattice parameters, unit cell volume, Mn-O-Mn bond angle, Crystallite size and increase the Mn-O bond length.
Acknowledgment
The present work was financially supported by Universitas Indonesia under research grant “Hibah PITTA 2018 with grant contract number 2241/UN2.R3.1/HKP.05.00/2018.

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