Space group and morphology evolution of nanosized Nd\(_{(x)}\)Sr\(_{(1-x)}\)MnO\(_3\) (\(x = 0.3; 0.7\) and 0.9) manganite

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Abstract. Polycrystalline series sample of Nd\(_{(x)}\)Sr\(_{(1-x)}\)MnO\(_3\) (\(x = 0.3; 0.7\) and 0.9) has been prepared with sol-gel method. Refinement result from X-ray diffractometer shows that the sample are crystallize in the same orthorhombic structure with different space group of \(Imma\) and \(Pnma\). Scanning Electron Microscope result also indicated that the different amount of substitution modified the grain size and both particle and crystallite size. After all, Nd\(_{0.3}\)Sr\(_{0.7}\)MnO\(_3\) has the largest cell volume followed by the largest grain and crystallite size compared to other two samples. Therefore, each different amount of substitution into the sample will give different impact and further investigation were needed to explore its relation to the physical properties.

1. Introduction

The research in substituted perovskite structure of rare earth manganite with general formula \(RE_xAE_yMnO_3\) (\(RE = \) rare-earth and \(AE = \) alkaline earth) have been investigate extensively due to their unique properties such as charge order, colossal magnetoresistance (CMR) and magnetocaloric effect (MCE) [1 – 3]. Perovskite-type manganites has a wide range of physical, morphology and structural properties [4 – 5]. Recently, the studies has been focused on Nd\(_{(x)}\)Sr\(_{(1-x)}\)MnO\(_3\) perovskite-type manganites with various amount of substitution [6 – 7].

The value of \(T_C\) was variously obtain from \(\sim 203\) K – \(272\) K for different amount of substitution for NdSrMnO\(_3\) [8 – 10]. The range of \(\Delta S\) is between \(0.93\) J kg\(^{-1}\) K\(^{-1}\) – \(3.82\) J kg\(^{-1}\) K\(^{-1}\) with relative cooling power about \(70.87\) J kg\(^{-1}\) – \(246\) J kg\(^{-1}\) [11 – 13]. Even though Nd\(_{(x)}\)Sr\(_{(1-x)}\)MnO\(_3\) has been studied by several researcher, it was found that different results were obtain from the research [14 – 15]. There are also few works that shows different methods of synthesis also lead to different structure and space group which also affected the different results in grain and crystallite size [16 – 18]. The work about Nd\(_{(x)}\)Sr\(_{(1-x)}\)MnO\(_3\) compound which study about the physical properties and it relations to crystal structure and morphology are hard to find compared to other rare-earth based compound, such as La\(_{(x)}\)A\(_E\)\(_{(1-x)}\)MnO\(_3\). Considering this issues, in this work, we present the investigation of Nd\(_{(x)}\)Sr\(_{(1-x)}\)MnO\(_3\) (\(x = 0.3; 0.7\) and 0.9) that were prepared using sol – gel method.
2. Methods
A set sample of Nd$_x$Sr$_{1-x}$MnO$_3$ (x = 0.3; 0.7 and 0.9) were prepared using sol-gel methods. The precursors that were used to make the sample are Sr(NO$_3$)$_2$ (≥ 99.0 %), Nd$_2$O$_3$ (≥ 99.0 %), Mn(NO$_3$)$_2$.4H$_2$O (≥ 98.5 %), and C$_6$H$_8$O$_7$.H$_2$O. The Nd$_2$O$_3$ were converted into Nd(NO$_3$)$_3$ by reacting it with nitric acid solutions, it was obtained when the clear light blue colour solution was formed. Specific amount of precursors that was already been calculated were dissolved into solutions with double distilled water until it were mixed into a single solutions. The solution was kept under the constant stirring and heat treatment until it reach 80 °C and ammonium solution were added to adjust the pH until it reaches 7. All the sample were stirred under constant temperature until such form of viscous gel were obtained. After that, it was dried at 110 °C and calcined at 600 °C. Afterward, the sample pressed into a pellet form with axial pressure of 10 tons for 2 minutes. The sample finalized with sintered at 1200 °C for 6 hours before examining using X-Ray Diffractometer (XRD) and Scanning Electron Microscope (SEM) to obtain the structural and morphological of the sample.

The stability value of the perovskite structure was determined using Goldschmidt tolerance factor ($t_G$) using following equation:

$$ t_G = \frac{r_A + r_x}{\sqrt{2} [r_B + r_x]} $$

The one-electronic bandwidth ($W$) used to studies the relation between physical and structural properties in double exchange framework were calculated with the following equation:

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

In this work, the average crystallite size of the sample was obtained using Scherrer equation with following equation:

$$ D = \frac{0.9 \lambda}{B_{hkl} \cos \theta} $$

3. Results and Discussion
Powder diffraction pattern that are obtained using XRD measurement are refined using Rietvield refinement method. From the result shown in Figure 1, the samples can be seen all as single phase. All the samples were crystallized in the same crystal structure as written on the Table 1. The detail explanation of each structural and parameters of the sample were needed to investigate more.

![Figure 1. XRD results for Nd$_x$Sr$_{1-x}$MnO$_3$ (x = 0.3; 0.7 and 0.9).](image-url)
The sample were all crystallized in orthorhombic structure. Adding different amount of strontium into the sample also changed space group from \textit{Imma} to \textit{Pnma}, and few other parameters. It is in a good term with previous study about \textit{Nd}_{1-x}\text{Sr}_x\text{MnO}_3 that obtain orthorhombic structure with \textit{Imma} or \textit{Pbnm} space group [19 – 22]. Even the fact that they all have the same structure as shown in the Table 1. Compare to two other samples, \textit{Nd}_{0.7}\text{Sr}_0.3\text{MnO}_3 has different space group with a largest volume cell. It is due to the existence of ion Mn$^{4+}$ and Mn$^{3+}$. The previous research also stated that larger ionic used to substitute in perovskite could lead to change of cell volume [23 – 24].

### Table 1. Crystal structure parameter of \textit{Nd}_{x}\text{Sr}_{(1-x)}\text{MnO}_3 (x = 0.3; 0.7 and 0.9) material.

| Structure                  | \(x = 0.3\) | \(x = 0.7\) | \(x = 0.9\) |
|----------------------------|-------------|-------------|-------------|
| Space group                | \textit{Imma} | \textit{Pnma} | \textit{Imma} |
| \(a\) (Å)                 | 5.387       | 5.459       | 5.452       |
| \(b\) (Å)                 | 7.721       | 7.712       | 7.627       |
| \(c\) (Å)                 | 5.405       | 5.467       | 5.434       |
| \(V\) (Å$^3$)             | 224.861     | 230.160     | 225.959     |
| \(t_G\)                   | 0.963       | 0.819       | 0.748       |
| Average crystallite size (nm) | 37.671     | 91.013      | 64.065      |
| \(\chi^2\) (%)            | 0.664       | 0.330       | 1.804       |
| \(R_p\) (%)               | 5.37        | 5.83        | 9.61        |
| \(R_wp\) (%)              | 6.79        | 7.37        | 13.25       |

Perovskite structure has their own value of stability which could be determined using Goldschmidt tolerance factor \((t_G)\) as in equation (1). According to this equation, the Goldschmidt tolerance factor \((t_G)\) value of perovskite is where \(0.825 < t_G < 1.059\) [25]. Goldschmidt tolerance factor \((t_G)\) value from the sample were calculated and referred that all the sample belong to perovskite structure. It is interesting to notice that it all has the value <1 which indicated that the sample are related to material with low symmetry [26].

![Figure 2. Crystal structure model of unit cell volume.](image)

Hence, despite some reports about \textit{NdMnO}_3 compound, the relation between physical and structural properties are still hard to be investigated. In a term of double exchange, this relation was studied using the one-electronic bandwidth \((W)\). Its value was calculated using equation (2). Different amount of strontium that was substituted in the material changed the parameter of bond length of between...
manganese and oxygen ions (Mn – O) and bond angles of two closest manganese ions which connected by oxygen ions (Mn – O – Mn). The value of this parameter can be seen on the table 2.

**Table 2.** The average bond length and bond angle of Nd\(_{4x}\)Sr\(_{(4-x)}\)MnO\(_3\) (x = 0.3; 0.7 and 0.9) material

|                  | Nd\(_{0.3}\)Sr\(_{0.7}\)MnO\(_3\) | Nd\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\) | Nd\(_{0.9}\)Sr\(_{0.1}\)MnO\(_3\) |
|------------------|----------------------------------|----------------------------------|----------------------------------|
| Mn-O\(_1\) (Å)   | 1.951                            | 1.962                            | 1.928                            |
| Mn-O\(_2\) (Å)   | 1.919                            | 1.950                            | 1.935                            |
| <Mn-O> (Å)       | 1.935                            | 1.956                            | 1.931                            |
| Mn-O\(_1\)-Mn (deg) | 163.116                          | 158.607                          | 162.820                          |
| Mn-O\(_2\)-Mn (deg) | 167.527                          | 159.938                          | 167.785                          |
| <Mn-O-Mn> (deg)  | 165.322                          | 159.273                          | 165.302                          |
| W (10\(^{-2}\))  | 9.833                            | 9.392                            | 9.895                            |

The average crystallite size of the sample was obtained using Scherrer equation in equation (3). Crystallite size was stated as \(D\), where \(\lambda\) is Cu – K\(\alpha\) wavelength radiation that was used in the experiment. While \(B_{hkl}\) represent the full width at half maximum (FWHM) and \(\theta\) as the diffraction angle, which both were acquired from the most prominent peak [27]. The largest crystallite size belongs to Nd\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\) as shown in the Table 1.

In this work, according to the table 2, it could be predicted that the sample of Nd\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\) will have the highest Tc. It is due to increasing magnetic exchange energy which could happen in the sample with the larger particle size [28].

![Figure 3. SEM Results were taken at 10\(^4\) times magnification.](image)

SEM results for Nd\(_{4x}\)Sr\(_{(4-x)}\)MnO\(_3\) (x = 0.3; 0.7 and 0.9) were presented in Figure 3, it can be seen that Nd\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\) has the largest grain particle compare to the other two samples. Noted for the fact that each sample has different size of grain determined using SEM has a good correlation with the crystallite that was calculated using Scherrer equation. Besides the size, it was also indicated that different amount of strontium substituted to the sample also affect the shape of the sample.

4. **Conclusions**

The investigation of structural and morphological sample of Nd\(_{4x}\)Sr\(_{(4-x)}\)MnO\(_3\) (x = 0.3; 0.7 and 0.9) has denote that each sample are crystallize in a same structure, which is proved by the Rietveld refinement of XRD. However, Nd\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\) has the only different space group compare to the other two samples. It has the largest cell volume with the largest grain shape and crystallite size. The physical properties of
the sample will be affected by change of Mn – O and Mn – O – Mn. Since the SEM results also shows a different result for each sample, it can be concluded that substituting different amount of chemical compound to $RE_1AE_2MnO_3$ will modified the shape and size of the grain sample.

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