Enhanced Knowledge in Sciences and Technology Vol. 3 No. 2 (2023) 263-269
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**EKST**

Homepage: http://publisher.uthm.edu.my/periodicals/index.php/ekst
e-ISSN : 2773-6385

# Influence of Sintering Temperature on Crystal Structure and Electrical Properties of Pr-based Manganites

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DOI: https://doi.org/10.30880/ekst.2023.03.02.031
Received on 16 January 2023; Accepted 06 February 2023; Available online 30 November 2023

**Abstract**: Manganite with monovalent doped of Pr-based have been attracted due to their astonishing properties such as structural, magnetic and electrical properties such as resistivity. Since $Ag^{+}$ ions had shown successful substitution and improvement to structural and electrical characteristics which has been seen in previous studies, influence of different sintering temperatures on growth of $Pr_{0.75}Na_{0.2}Ag_{0.05}MnO_3$ manganite compound during sintering process has not been previously studied. Preparation of manganite samples with high purity of $Pr_2O_3$, $Na_2CO_3$, $Ag_2O$ and $MnO_2$ powders were prepared using solid state reaction method. Sample characterization on crystalline structure was utilized using X-ray diffraction (XRD) while the electrical characterization performed using 4-point probe method. Bulk density of all samples was run using compact precision balance, then identified using Archimedes principle. XRD analysis depicted that crystalline structure of all the samples were figured out in an orthorhombic structure with *Pnma* space group. An increasing in unit cell volume has been observed with increasing of sintering temperature due to the strain relaxation in the sample's structure. Bulk density of all the samples was increased accompanying with decreasing in porosity as higher sintering temperature. Based on the data obtained from 4-point probe, the value of resistivity for all the samples was reduced with increasing of sintering temperature, which can be suggested due to the weakening of the carrier scattering as a result of reducing grain size and grain boundaries of the sample. Hence, this can be concluded that there is relationship between the crystalline structures and resistivity values of the manganite sample.

**Keywords**: X-ray Diffraction, 4-point Probe, Solid State Method

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## 1. Introduction

In past few years, since its unique properties of perovskite manganite materials such as physical properties, electrical and magnetic properties, it has attracted a lot of attention. Perovskite manganite oxides of rare-earth doped have a chemical structure formula of $Ln_xA_{1-x}MnO_3$, where Ln indicates lanthanum or rare-earth metal elements, and "A" is divalent metal elements of alkaline-earth might have a variety of electrical characteristics widely since doping of rare-earth elements was influenced on a change in valence states of manganese atom that will be important for properties transport [1].

Based on the perovskite manganites research, manganites with monovalent-doped tend to attract characterization in structure and electrical properties [2,3-4]. Furthermore, the study found that there had a reduction of the double-exchange (DE) mechanism, which resulted of the charged- order (CO) weakening state with the lowering of the Jahn-Teller effect, and more studies required to investigate the effect on electrical transport [4-5]. In addition, further studies were performed to study the effect on electrical transport due to Ag-doping process. The resistivity pattern of the $Pr_{0.75}Na_{0.25-x}Ag_xMnO_3$, where $0 \leq x \leq 0.10$ indicated that the activation and hopping energies increased with increasing of Ag concentration, probably due to the structure's octahedral distortion of $MnO_6$ [5]. However, influence of different temperatures towards growth of $Pr_{0.75}Na_{0.2}Ag_{0.05}MnO_3$ manganite compound during sintering process still not yet further investigated. Recent research was continued to study about manganite compound with a focus on the sintering temperature effect that was synthesized using solid-state reaction method.

This research study was focused on effect of sintering temperature towards structural and electrical properties. It can allows for a better understanding and also provide some information and comparison within the structural characteristic and electrical properties since this study was expected several unique phenomena which can be observed from its physical behavior such as double-exchange (DE) mechanism and charged-order (CO) exhibition, and also electrical behavior such as metal-insulator (MI) transition and magnetoresistance.

In this research study, Pr-based manganite, $Pr_{0.75}Na_{0.2}Ag_{0.05}MnO_3$ sample was chosen because it can be expected to provide information about charged-order states as well as deliver new information on the structural and electrical study. The reason for using Ag as dopant is due to $Ag^+$ ions has been seen in previous studies to show successful substitution within perovskite manganite and delivers enhancement to the grain boundaries, sizes as well as the compaction [4-5]. The sintering process will be performed at temperature dependence within 1100°C, 1150°C and 1200°C in this study to allow further discussion of the sintering effect in relation to the properties of the sample. 1100°C, 1150°C and 1200°C are commonly chosen temperatures for sintering manganite samples because they are within a range that allows for optimal densification of the material while also avoiding damage to the crystal structure. Doing this study also was allowing discussion towards sintering temperature that relate to the structural properties such as grain size, density, and porosity, and as well as electrical properties.

## 2. Methods

Preparation of Pr-based manganite, $Pr_{0.75}Na_{0.2}Ag_{0.05}MnO_3$ samples were done using solid state reaction method. On characterization, crystalline structure of the sample was determined using X-ray diffraction while electrical properties of the samples will be carried out using 4-point probe measurement technique.

### 2.1 Sample Preparation

For the starting step, a stoichiometric high purity mixture of $Pr_2O_3$, $Na_2CO_3$, $Ag_2O$ and $MnO_2$ powders was weighed using digital weighing balance, and then were grinded and mixed carefully using agate mortar with pestle. After that, calcination process began at a temperature of 1000°C for24 hours, with several subsequent grindings. Then, the powder was undergone pellet-pressing by estimation

thickness of 2-3mm and 13mm diameter under 5 tones pressure. After formation of pellet was done, sintering process was began at 1100°C, 1150°C and 1200°C for 24 hours in air.

2.2 Sample Characterization

Next, characterization towards crystalline structure was determined using Bruker D2 Phaser model powder X-ray diffraction (XRD) with CuKα radiation at room temperature. Then the electrical resistivity was measured using Lelos TMXpert 4-point probe model in a room temperature. In 4-point probe method measurement, voltage and current were applied in the model software to get the value of the resistivity.

The bulk density was determined using the Archimedes principle and propanol as the buoyant substance. A compact precision balance was applied to weigh the sample in air and in propanol. Then bulk density was determined using Equation 1. [3-4]

$$\rho_{bulk} = \frac{w_{air}}{w_{air} - w_{propanol}} \rho_{propanol} \qquad Eq.1$$

where $w_{air}$ denotes the sample's weight in air, $w_{propanol}$ is the sample's weight while submerged in propanol, and $\rho_{propanol}$ denotes the propanol density. Upon bulk density, porosity was identified from Equation 2[3-4]

$$\text{Porosity (\%)} = (1 - \frac{\rho_{bulk}}{\rho_{theoretical}}) * 100 \qquad Eq.2$$

where $\rho_{bulk}$ is the sample's bulk density derived from Equation 1, and $\rho_{theoretical}$ value is the sample's theoretical density obtained from measurement of XRD using Equation 3 [3-4]

$$\rho_{theoretical} = \frac{n'(\sum A_C + \sum A_A)}{V_c N_A} \qquad Eq.3$$

where *n'* referred as the formula's unit cell number, $\Sigma Ac$ referred as sum of atomic weights of cations within the formula units, $\Sigma A_A$ is sum of atomic weight of anions within the formula units, $Vc$ is the unit cell volume and $N_A$ preferred as Avogadro's numbers.

The lattice parameter information such as *a, b* and *c* were determined using formula from Equation 4 and normal simultaneous equation where three *hkl* value from each peak of XRD graph pattern was chosen to verify the crystalline phase of the samples, while unit cell volume was calculated by multiplication of lattice parameter (*a*b*c*). The lattice parameters were evaluated using formulareferred in Equation 4,

$$\frac{1}{d_{hkl}^{\ 2}} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \qquad Eq.4$$

where $d_{hkl}$ is interplanar spacing, *h, k,* and *l* is Miller indices, and *a, b* and *c* referred as the length of each of the unit cell in 3-dimensions [4].

## 3. Results and Discussion

Figure 1 shown the XRD pattern for $Pr_{0.75}Na_{0.2}Ag_{0.05}MnO_3$ samples sintered at 1100°C, 1150°C and 1200°C. All the samples seem to have a single-crystalline phase with an orthorhombic structure and *Pnma* space group, based on the XRD analysis. This can be stated that the sintering temperature does not influence the sample's crystalline structure [6-7]. The XRD result revealed that there are no visible impurity peaks as well as secondary peaks.

Table 1 referred as the result of lattice parameter and unit cell volume of the sample based on different sintering temperature. Based on the data shown in the table, for lattice parameter *a*, *b* and *c* of the sample that sintered at 1100 ℃, the value for each parameter are 5.459Å, 7.728Å and 5.456Å respectively. While for the sample sintered at 1150℃, the value for each parameter is 5.447Å, 7.732Å and 5.483Å respectively. And for the sample sintered at 1200℃, the value for each parameter is 5.461Å, 7.726Å and 5,483Å respectively. From these values, it can be depicted that *b*-lattice undergone an increase then decrease trend while *a*-lattice experienced a decrease then increase trend, and whereas *c*-lattice depicted an increase trend, as the sintering temperature increases. This lattice parameter analysis can be supported with the previous research which had been done on $Pr_{0.67}Ba_{0.33}MnO_3$ manganite sample, by Kuen, W. J. *et al*, in 2010, where the lattice parameter calculation was done using X'Pert HighScore Plus software [8]. Based on the data in table 1, it can be concluded that higher sintering temperature will increase the unit cell volume due to the strain relaxation [9]. This conclusion can be supported with the previous research that was done on $La_{0.7}Ba_{0.1}Sr_{0.2}Mn_{0.85}Cu_{0.15}O_3$ manganite sample sintered at 1100 °C and 1200 °C by D. S. Razaq *et. al*, in 2019.

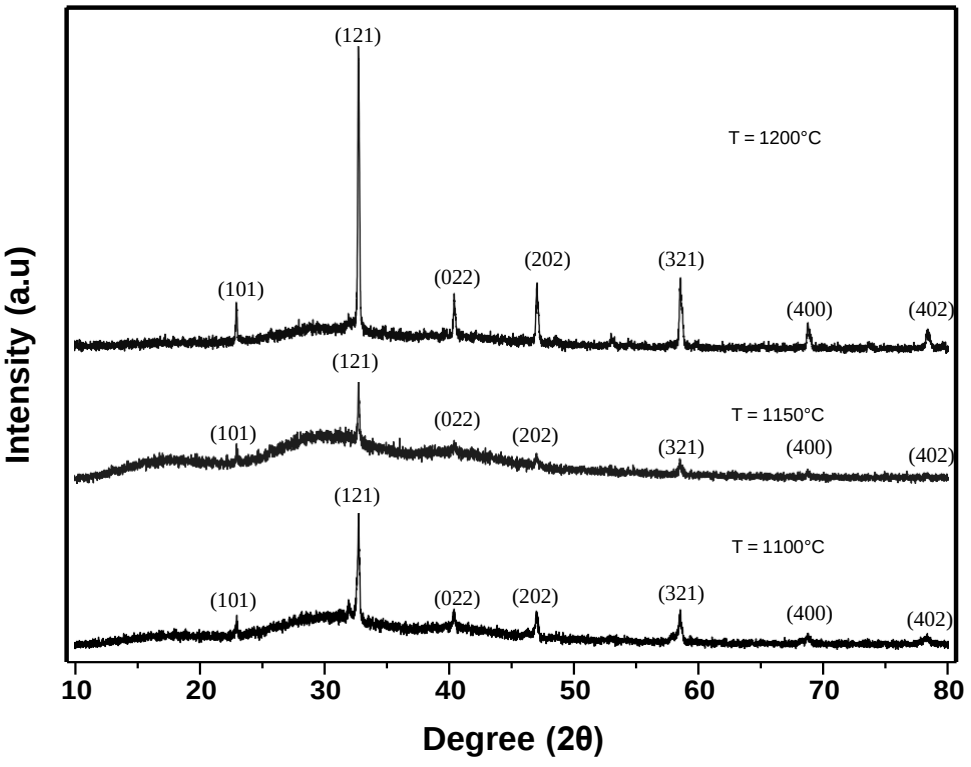


**Figure 1: X-ray Diffraction (XRD) graph pattern for $Pr_{0.75}Na_{0.2}Ag_{0.05}MnO_3$ sample sintered at 1100°C, 1150°C and 1200°C**

**Table 1: Lattice parameters and unit cell volume (*V*) of $Pr_{0.75}Na_{0.2}Ag_{0.05}MnO_3$ sample sintered at 1100°C, 1150°C and 1200°C**

| Sintering temperature (°C) | Lattice parameter, Å (± 0.001) | | | *V*, Å$^3$ (± 0.1) |
|---|---|---|---|---|
| | *a* (Å) | *b* (Å) | *c* (Å) | |
| 1100 | 5.459 | 7.728 | 5.456 | 230.2 |
| 1150 | 5.447 | 7.732 | 5.483 | 230.9 |
| 1200 | 5.461 | 7.726 | 5.483 | 231.3 |

Table 2 below shows bulk density, porosity, and resistivity value of the sample sintered at different temperature. Based on the data in the table, for the bulk density value of the sample that sintered at 1100℃ is 5.105 g/cm$^3$, while for the sample that sintered at 1150℃ which is 5.287 g/cm$^3$, and for the sample that sintered at 1200℃, the value is 5.537 g/cm$^3$. From these values, it can be stated that the bulk density value shown an increasing trend with increasing of sintering temperature. Meanwhile for the porosity value of the sample that sintered at 1100℃ is 19.21%, compared to the sample sintered at 1150℃ which is 16.43%, and 12.62% for the porosity value of the sample sintered at 1200℃. These values also can be stated that the sample's porosity also depicted a decrease trend when the sintering temperature increase, due to the sample grains keen to become more packed densely [10]. Other than that, this porosity effect can be suggested due to the sample's boundary have become compact and connected, where higher sintering temperature can promote growth of grain size and agglomeration, in relation with reducing of grains' microstructures, leaving packed grains closely [11].

For resistivity analysis measurement method, compliance voltage and current level were applied by 2V and 0.003A, respectively. As referred to Table 2 too, the value of resistivity for the sample sintered at 1100℃ is 354.978 Ωmm, while for the sample sintered at 1150℃ which is 323.543 Ωmm, and 299.627 Ωmm for the resistivity value of the sample sintered at 1200℃. It can be seen that the values of resistivity for all the samples were reduced with increasing of sintering temperature. This can be suggested with increasing in the crystallite size and the size of the sample's grain, which indicates a correlation within the surface structure and the resistivity of the sample, most probably due to the weakening of carrier scattering as a result of reducing grain size and grain boundaries of the sample. In fact, our suggestion is in line with the previous study reported by M. Oumezzine, *et. al* in 2004 which had been done on doped $La_{0.67}Ba_{0.3}Mn_{0.9}Cr_{0.1}O_3$ manganite sample [11]. Moreover, Das *et. al*, demonstrated that grain boundaries had more magnetic disorder than the grain core. As a result, decreasing the number of grain boundaries reduces the sample's resistivity. [12].

**Table 2: Bulk density ($\rho_{bulk}$), porosity and resistivity of $Pr_{0.75}Na_{0.2}Ag_{0.05}MnO_3$ sample sintered at 1100℃, 1150℃ and 1200℃**

| Sintering temperature, (℃) | $\rho_{bulk}$, g/cm$^3$ (± 0.001) | Porosity, % (± 0.01) | Resistivity, ρ *(*Ohm mm / Ω mm) (±0.001) |
|---|---|---|---|
| 1100 | 5.105 | 19.21 | 354.978 |
| 1150 | 5.287 | 16.43 | 323.543 |
| 1200 | 5.537 | 12.62 | 299.627 |

## 4. Conclusion

In conclusion, study about effect of sintering temperature had given some information as well as obtained a lot of improvement towards the crystalline structure and electrical properties of Pr-based manganite compound. Overall, the three objectives of this study were done, achieved and satisfied. Since the crystalline structure did not influenced by difference of sintering temperature, it had been observed to affect towards the density, porosity, and electrical transport of the samples. Based on the lattice parameter, *b*-lattice undergone an increase then decrease trend while *a*-lattice experienced a decrease then increase trend, and whereas *c*-lattice depicted an increase trend with increasing of sintering temperature, which caused the unit cell volume to be increased due to relaxation of strain within the structure of the sample. Bulk density shown an increasing trend when sintering temperature increase, while porosity depicted a decreasing trend due to the sample grains keen to become more packed densely. Meanwhile, increasing of sintering temperature had impacted the sample resistivity to be decreased, due to the weakening of carrier scattering which can be affected by the grains to grow larger and reducing the grain size and grain boundaries of the sample. Further research on characterization such as on magnetic properties and ultrasonic anomaly are recommended so that it can gain more knowledge to the researchers on the influence of sintering temperature towards the manganite compound since the study related to it are still limited.

## Acknowledgement

This research was supported by TIER 1 Vot H967 Research Grant from Universiti Tun Hussein Onn Malaysia. Thanks to Ceramic and Amorphous Group, Faculty of Applied Sciences and Technology, Pagoh Higher Education Hub, Universiti Tun Hussein Onn Malaysia, 84600 Panchor, Johor for the facilities provided.

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