Influence of sintering temperature on the structure and electrical transport properties of La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{0.85}$Cu$_{0.15}$O$_3$ manganites

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Abstract. A systematic study of the La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{0.85}$Cu$_{0.15}$O$_3$ manganites have been conducted, mainly to understand the influence of sintering temperature on structure, microstructure, and electrical transport properties in the materials. Polycrystalline sample of La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{0.85}$Cu$_{0.15}$O$_3$ were prepared using sol-gel method and sintered at 1100 °C and 1200 °C. X-ray diffraction result shows that sintering temperature does not affect the crystal structure of the materials which remain rhombohedral with R-3c space group. A more detailed examination shows that sintering temperature change the unit cell volume, $<$Mn-O-Mn$>$ bond length, and $<$Mn-O$>$ bond angle of the samples. The electrical resistivity decreases followed by the decrease in the grain size with the increase in sintering temperature. Analysis using theoretical model shows that both samples can be well explained using percolation model. Fitting result suggests that the transport properties of the materials at low temperature were governed by the scattering and interaction between electron, phonon, and magnon. At high temperature, the electrical transport of the samples was governed by the hopping of polarons.

1. Introduction

LaMnO$_3$ (LMO) based manganites, which have been modified by partial substitution, have attracted considerable attention due to its interesting physical properties. Among the many examples of its physical properties, the electrical property of a substituted LMO based manganites deserve a special attention. This is due to several unique phenomena which can be observed from its electrical behavior such as metal-insulator transition and magnetoresistance effect [1,2].

It has been widely known that the electrical property of a substituted LMO based manganites are governed by the sample preparation method, which consists of synthesis method, sintering temperature, and compaction pressure [3-5]. Among these factors, sintering temperature plays a significant role in the electrical property of a substituted LMO based manganites [6].

Although several studies have been conducted in order to examine the influence of sintering temperature on the electrical property of a substituted LMO based manganites, to date, there still no specific study which have been conducted on La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{0.85}$Cu$_{0.15}$O$_3$ system. In the present work, the influence of sintering temperature on the structure, morphology, and its correlation with the electrical property of
La_{0.7}Ba_{0.1}Sr_{0.2}Mn_{0.85}Cu_{0.15}O_3 will be studied. Additionally, theoretical approach using percolation model will be used to analyze the electrical property of the sample. This model was chosen due to the limitation of double exchange framework which fails to explain the electrical behavior of a substituted LMO based manganites [7].

2. Method
Samples with chemical formula La_{0.7}Ba_{0.1}Sr_{0.2}Mn_{0.85}Cu_{0.15}O_3 have been prepared using sol-gel method. Details regarding the sample preparation method have been reported elsewhere [8]. In the final step of sample preparation method, the samples were sintered at 1100 °C and 1200 °C for 6 hours. The structural characterization of the samples was done through x-ray diffraction (XRD) using Cu-Kα radiation (λ = 1.5406 Å) with 15 seconds scan rate and 0.02θ scan step. The XRD data were collected in the range of 20 from 10 to 90°. The morphology characterization of the samples was done through scanning electron microscope (SEM). The temperature dependence of resistivity was measured using the standard four-point probe with cryogenic magnetometer working without external magnetic field and in the temperature between 10K and 295K.

3. Result and discussion
The XRD spectra of both samples in figure 1, shows that both samples can be indexed with rhombohedral structure with R3c space group. It can be seen also be seen that sintering temperature does not affect structure of the samples.

![Figure 1](image)

*Figure 1. (a) XRD patterns for La_{0.7}Ba_{0.1}Sr_{0.2}Mn_{0.85}Cu_{0.15}O_3 sintered at different temperatures and (b) Refined XRD patterns for La_{0.7}Ba_{0.1}Sr_{0.2}Mn_{0.85}Cu_{0.15}O_3 sample sintered at 1100 °C.*

The structural characterization results which have been refined using the standard rietveld refinement method is shown in figure 2 and the obtained structural parameters are listed in table 1. According to low values of discrepancy factors listed in table 1, it can be concluded that the fitting is quite good. It can be seen that higher sintering temperature increase the unit cell volume as well as the average crystallite size of the sample which have been calculated using Scherrer equation. The increase in grain size and unit volume of the sample at higher sintering temperature can be caused by the relaxation of strain [9]. Furthermore, sintering temperature increase the average Mn-O bond length while decreasing the average Mn-O-Mn bond angle. This will reduce the one-electron bandwidth (W) which will weaken the overlap between O 2p and Mn 3d orbital, thus favors the charge localization [10].

The result of morphology characterization using SEM is shown in figure 2. SEM images show that the average grain size of the sample sintered at 1200 °C are bigger compared to sample sintered at 1100 °C. This result is consistent with similar topics which have been reported previously [6]. SEM images also in
line with the increase in the average crystallite size which have been determined from structural characterization. It can be seen that the average grain size observed from morphology characterization is larger compared to the average crystallite size calculated from structural characterization. This result suggests that each grain observed from SEM image might be consisted of several smaller crystallized grains [11].

Table 1. Structural parameters obtained from rietveld refinement process for La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{0.85}$Cu$_{0.15}$O$_3$ sample sintered at 1100 °C and 1200 °C.

| Structural parameter               | Sintering temperature (°C) |
|-----------------------------------|-----------------------------|
|                                   | 1100 | 1200 |
| Lattice parameter                 |      |      |
| a (Å)                             | 5.5096 | 5.5103 |
| c (Å)                             | 13.3930 | 13.3902 |
| Unit cell volume (Å$^3$)           | 352.0820 | 352.1009 |
| Rp (%)                            | 6.0772 | 4.7648 |
| Rwp (%)                           | 7.8559 | 6.0757 |
| Average crystallite size (nm)     | 37.0171 | 50.7805 |
| $<\text{Mn-O}>$ (Å)               | 1.9530 | 1.9570 |
| $<\text{Mn-O-Mn}>$ (degree)       | 168.3430 | 166.3510 |
| W ($\times 10^{-2}$)              | 9.556 | 9.470 |

Figure 2. SEM image of La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{0.85}$Cu$_{0.15}$O$_3$ sample sintered at (a) 1100 °C and (b) 1200 °C.

The temperature dependence of resistivity measured without external magnetic field for La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{0.85}$Cu$_{0.15}$O$_3$ sample sintered at 1100 °C and 1200 °C is shown in figure 4.
It can be seen that higher sintering temperature decrease the resistivity of the sample. The decrease in resistivity is consistent with the increase in the average crystallite size as well as the grain size of the sample. This suggests that there is a strong dependence between the morphology and the temperature dependence resistivity of the sample. Furthermore, higher sintering temperature will cause the grain to grow bigger, thus decreasing the number of grain as well as the number of grain boundaries in the sample. This will result in the weakening in carrier scattering thus decreasing the resistivity of the sample [6]. It has been shown by das et al. that grain boundaries carry more magnetic disorder compared to the core of the grain. Therefore, reducing the number of grain boundaries will reduce the resistivity of the sample [12]. In order to understand the electrical transport mechanism of the sample sintered at different temperatures, a theoretical approach is used to analyze the temperature dependence resistivity data. In the present work, percolation model was used to fit the temperature dependence resistivity through whole range temperature. The equation used to fit the data are written in equation 1 [13].

\[
\rho(T) = \rho_0 + \rho_e T^2 - \rho_s \ln T + \rho_p T^5 + \rho_2 T^2 + \rho_{9/2} T^{9/2} \left[ \frac{1}{1 + \exp \left( -\frac{U_o}{k_B T} \left( 1 - \frac{T}{T_{c_{mod}}} \right) \right)} \right] \\
+ \left[ \rho_a T \exp \left( \frac{E_a}{k_B T} \right) \right] \left[ \frac{\exp \left( -\frac{U_o}{k_B T} \left( 1 - \frac{T}{T_{c_{mod}}} \right) \right)}{1 + \exp \left( -\frac{U_o}{k_B T} \left( 1 - \frac{T}{T_{c_{mod}}} \right) \right)} \right]
\]

(1)

where \( \rho_0 \) term represents resistivity due to grain boundary, \( \rho_e T^{1/2} \) term represents resistivity due to electron-electron interaction, \( -\rho_s \ln T \) term represents resistivity due to kondo-like spin dependent scattering, \( \rho_p T^5 \) term represents resistivity due to electron-phonon interaction, \( \rho_2 T^2 \) term represents resistivity due to electron-electron scattering, and \( \rho_{9/2} T^{9/2} \) term represents resistivity due to a series of combination between electron-electron, electron-magnon, and electron-phonon scattering. \( \rho_a \) term represents residual resistivity, \( E_a \) is activation energy for hopping conduction, \( k_B \) is Boltzmann constant, \( U_o \) represents the energy difference between ferromagnetic metal (FM) phase and paramagnetic insulator (PM) phase at a temperature below its Curie temperature and \( T_{c_{mod}} \) is the theoretical Curie temperature [13]. The fitting result of both samples can be seen in figure 4 and the obtained best parameters are listed in table 2.
Table 2. The best fit parameters obtained from fitting with percolation model.

| Best fit parameters | Sintering temperature |
|---------------------|-----------------------|
|                     | 1100                  | 1200                  |
| $\rho_0$ (Ohm cm)   | 620.549               | 223.818               |
| $\rho_e$ (Ohm cm/$K^{0.5}$) | -41.310               | -11.044               |
| $\rho_s$ (Ohm cm)   | -24.516               | -6.753                |
| $\rho_p$ (Ohm cm/$K^5$) | $-3.22 \times 10^{-9}$ | $-5.07 \times 10^{-10}$ |
| $\rho_2$ (Ohm cm/$K^2$) | 0.0235                | 0.00705               |
| $\rho_{9/2}$ (Ohm cm/$K^{9/2}$) | $7.61 \times 10^{-8}$ | $1.29 \times 10^{-8}$ |
| $\rho_a$ (Ohm cm)   | -0.1035               | -0.1014               |
| $U_0/k_B$ (K)        | 1068.843              | 1074.696              |
| $E_a/k_B$ (K)        | 571.067               | 481.694               |
| $T_{c_{\text{mod}}}$ | 159.319               | 189.264               |

It can be seen that metal-insulator transition temperature (Tmi) shifted to higher temperature due to higher sintering temperature. The shifting of Tmi into can be caused by the enhancement in the long-range ferromagnetic order of the sample [14]. Thus, it can be concluded that higher sintering temperature also improve the long-range ferromagnetic order of LMO based manganites.

Table 2 shows that $\rho_0$ value of sample sintered at 1100 °C is bigger than sample sintered at 1200 °C. this suggests that the scattering process which happen at grain boundaries are reduced, hence reducing the resistivity of the sample [15]. the significant reduction of resistivity as well as $\rho_0$ indicates that grain boundaries is a dominant factor in the electrical transport of LMO based manganites. Additionally, $\rho_2$ and $\rho_{9/2}$ value also decreasing at higher sintering temperature. the reduction of these three parameters indicates the weakening of double exchange mechanism [15]. This result also in parallel with the reduction of one-electronic bandwidth value. It can also be observed that $\rho_e$, $\rho_s$, and $\rho_p$ values are bigger at higher sintering temperature. Based on the research of Lee and Ramakrishnan, and Lalitha et al., the increase in $\rho_e$, $\rho_s$, and $\rho_p$ values indicates that sintering temperature will affect the electron-electron interaction, phonon scattering at low temperature, and the intensity of spin scattering process [16, 17]. The activation energy is decreasing with increasing the sintering temperature. This might be caused by the enhancement of the connection between grains which will ease the conduction electron to hop into the neighboring sites [15]. Additionally, $T_{c_{\text{mod}}}$ value is increasing as sintering temperature increases. This result indicates that sintering temperature change the paramagnetic insulator phase of the sample into ferromagnetic metal phase [18].

4. Conclusion

The influence of sintering temperature on the Structure and Electrical Transport Properties of La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{0.85}$Cu$_{0.15}$O$_3$ sample sintered at 1100 °C and 1200 °C has been studied. It was found that although sintering temperature does not change the crystal structure of the sample, it changes the average Mn-O bond length and average Mn-O-Mn bond angle of the sample which reduce the double exchange mechanism in the sample. furthermore, sintering temperature greatly affect the morphology of the sample. the electrical properties of both samples have been analyzed using percolation model. Based on the best fit parameters obtained, it can be concluded that the electrical properties of the sample are dominated by gran
boundary factor. It was found that sintering temperature also affect the scattering and interaction between electron, phonon, and magnon. Additionally, sintering temperature also reduce the activation energy of the sample which will ease the conduction electron to hop into the neighboring sites.

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