Structure, Morphology, Electrical Transport, and Magnetoresistance Properties of La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{0.9}$Cu$_{0.1}$O$_3$

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Abstract. The structure, morphology, electrical transport and magnetoresistance properties of La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{0.9}$Cu$_{0.1}$O$_3$ has been investigated. The sample has been successfully prepared using sol-gel method. Structural investigation using X-ray diffraction (XRD) shows that the sample crystallizes in rhombohedral structure with $R3c$ space group. The surface morphology of the sample shows that the sample consists of irregular polygonal grain. Furthermore, resistivity measurement shows that the sample undergoes a transition from metal to semiconductor behaviour upon heating. The electrical properties of the sample follow the electron-phonon-magnon scattering theory. Under the influence of the external magnetic field, the sample shows that up to 8% of the resistivity decreased at 200 K.

1. Introduction
Colossal magnetoresistance has attracted the attention of many researchers due to its important application in technology. Moreover, recent development have increased the needs to find a material with high MR% value, high chemical stability, low manufacturing cost, and a Curie temperature (Tc) near room temperature. In order to attain this objective, a great amount of effort have been deployed to find a new material which possess the required properties. One of the most promising material in this context are substituted lanthanum manganite system.

Earlier research has shown that La$_{2/3}$Ca$_{1/3}$MnO$_3$ compound which have been substituted by copper ions have a better MR% value compared to the parent compound. It has been reported that 4% copper ions which have been substituted to the parent compound can improve its MR% value up to 300% [1]. Despite the great improvement in the MR% value, the maximum value of MR% in La$_{2/3}$Ca$_{1/3}$Mn$_{0.96}$Cu$_{0.04}$O$_3$ compound can only obtained at low temperature around 160K. In order to apply this compound into an advanced device, the compound needs to have high MR% value and it should be obtained at near ambient temperature. Thus, further research need to be employed to find a new material for this purpose. A recent research has shown that lanthanum manganite which have been substituted by strontium and barium ions simultaneously can achieve up to 11% in the MR% value at 300K [2].

In the present work, the magnetoresistance properties of La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{0.9}$Cu$_{0.1}$O$_3$ will be studied along with the possible correlation with its structural, morphological, and electrical transport. Such
material is interesting to be studied as La$_{0.7}$(BaSr)$_{0.3}$MnO$_3$ material possess quiet high MR% value at near room temperature. Additionally, copper substitution also proven to improve MR% value in a substituted lanthanum manganite compound.

2. Experimental
Polycrystalline sample of La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{0.9}$Cu$_{0.1}$O$_3$ (LBSMCO-10) were prepared using sol-gel method. The detailed procedure regarding this method have been reported elsewhere [3]. The obtained dried gel was calcined at 500°C for 5 hours. The resulting powder from calcination process were sintered at 1100 °C for 3 hours. The structural analysis of the compound was carried out at room temperature using Panalytical X-ray powder diffractometer from 20 angle of 10-90° with scan step of 0.02°. The morphology of the sample was examined using Scanning Electron Microscope (SEM). The electrical transport and magnetoresistance properties of the sample was examined using cryogenic magnetometer from 10 to 285 K with magnetic field up to 1T.

3. Result and Discussion
The structural analysis using Rietveld refinement process shows that LBSMCO-10 sample was single phase without any detectable impurities. The refined diffraction pattern of the sample is shown in Figure 1. According to Miller indices of the sample, it can be concluded that LBSMCO-10 crystallize in rhombohedral R$3c$ space group. The obtained result is in a good agreement with similar sample which have been discussed in another work [4]. The comparison between the two samples are listed in Table 1.

Despite the same composition of the sample, it can be seen that the obtained structural parameter for LBSMCO-10 is slightly different compared to the previous work. This result can be caused by the different in the sintering temperature. It has been discussed in several papers that sintering temperature can slightly affect the structural parameters of a substituted LMO compound [5]. The slight difference between both samples also suggests that the sol-gel method which have been used to prepare the sample is a good method with high reproducibility level.

The morphology of the sample is presented in Figure 2(a). It was observed that the microstructure of the sample is constructed by a cuboid shaped grain. The chemical composition of the sample has been examined using Energy Dispersive X-ray spectroscopy (EDS). The resulting spectra is presented in Figure 2(b) and each of the spectrum matched with the targeted compound.
Table 1. A crystallographic data comparison of LBSMCO-10 and reported LBSMCO [4]

| Parameters                        | LBSMCO-10 | La0.7Ba0.1Sr0.2Mn0.9Cu0.1O3 [4] |
|-----------------------------------|-----------|---------------------------------|
| Space group                       | R3c       | R3c                             |
| Sintering temperature (°C)        | 1100      | 1200                            |
| \(a = b\) (Å)                    | 5.5122(5) | 5.5135(1)                       |
| \(c\) (Å)                        | 13.4037(6)| 13.3991(4)                      |
| Volume (Å³)                      | 352.7467  | 352.7404                        |
| \(d_{Mn-O}\) (Å)                 | 1.9573(1) | 1.9607                          |
| Mn-O-Mn angle (°)                | 166.74(2) | 165.1356                        |
| Goodness of Fit                  | 1.0659    | 1.2237                          |
| Rp (%)                           | 6.2083(9) | 4.1754                          |
| Rwp (%)                          | 7.8243(9) | 5.2748                          |

Figure 2. (a) SEM micrograph and (b) EDX Spectrum LBSMCO-10

The electrical transport property of the sample is presented in Figure 3. It is clear that the sample experience a transition from ferromagnetic metal behaviour to paramagnetic insulator behaviour upon heating. It can be seen from the inset of Figure 3 that the sample possess a local minimum followed by a maximum value in the temperature dependence resistivity data. The local minimum suggests that the sample electrical transport is influenced by Kondo effect at low behaviour [6].

In order to explain the electrical transport behaviour of the sample, a theoretical model was used in this work. According to the research by Li et al, a substituted LMO compound are composed by two distinct phases which are ferromagnetic metal and paramagnetic insulator [7]. These two phases coexist one another inside the sample and the volume fraction of the phase change as a function of temperature. The mathematical expression to explain electrical transport which was used in the present work is written in Equation 1. The first six terms are the terms that represents electrical transport behaviour at low temperature. In detail, \(\rho_0\) represents resistivity due to grain boundary, \(\rho_e T^{1/2}\) represents correlation between electron-electron interactions, \(\rho_s \ln T\) represents the resistivity due to kondo-like spin dependent scattering, \(\rho_p T^5\) represents the contribution of electron-phonon interactions, and \(\rho_0/2 T^{9/2}\) represents the combination of scattering process between electron-electron, electron-magnon, and electron phonon. The resistivity behaviour at high temperature (greater than transition temperature (Tmi)) can be represented by small polaron hopping model which is
represented in the model by $\rho_\alpha T \exp\left(\frac{E_a}{k_B T}\right)$ term where $\rho_\alpha$ is residual resistivity and $E_a$ is polaron’s activation energy. Moreover, $U_0$ in this model represents energy difference between ferromagnetic metal and paramagnetic insulator phase at low temperature and $T_{c,mod}$ is the theoretical Curie temperature value. The result of fitting using Equation 1 is presented in Figure 3 and the best fit parameters obtained from fitting process are presented in Table 2.

$$
\rho(T) = \left[\rho_0 + \rho_e T^2 - \rho_s \ln T + \rho_p T^5 + \rho_z T^2 + \rho_9 T^9\right]
\left(\frac{1}{1 + \exp\left(-\frac{U_0 \left(1 - \frac{T}{T_{c,mod}}\right)}{k_B T}\right)}\right)
+ \left[\rho_\alpha T \exp\left(\frac{E_a}{k_B T}\right)\right]
\left(\frac{\exp\left(-U_0 \left(1 - \frac{T}{T_{c,mod}}\right)\right)}{1 + \exp\left(-\frac{U_0 \left(1 - \frac{T}{T_{c,mod}}\right)}{k_B T}\right)}\right)
$$

Based on Figure 3, it can be seen that the fitting function almost fits perfectly with the temperature dependence resistivity data. This result also supported by the $\chi^2$ value which close to unity. Based on this result, it can be concluded that the resistivity behaviour in LBSMCO-10 sample at low temperature mainly governed by the scattering and interaction between electron, phonon, and magnon [8]. Furthermore, at high temperature, it can be concluded that the electrical transport behaviour of the sample at high temperature are caused by hopping of polarons since this model fits quite well with the obtained data. It can also be seen that $p_0$ has the biggest value compared to other parameters. Thus, it can be concluded that electron transport at grain boundary plays a major role in the electrical transport behaviour of the sample. This result is in a good agreement with several previous research for similar compound [9,10].

![Figure 3](image-url)

**Figure 3.** Temperature dependence of the resistivity for $\text{La}_{0.7}\text{Sr}_{0.2}\text{Ba}_{0.1}\text{Mn}_{0.9}\text{Cu}_{0.1}\text{O}_3$. The red solid line is the best fit of experimental data by Eq. 1. Inset is $d\rho/dT$ dependence temperature.
Table 2. Fitting parameters of the percolation model for La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{0.9}$Cu$_{0.1}$O$_3$

| Fitting Parameter | Value |
|-------------------|-------|
| $\rho_0$ (Ohm cm) | 6.696 |
| $\rho_e$ (Ohm cm/$K^{0.5}$) | -0.599 |
| $\rho_s$ (Ohm cm) | -0.5765 |
| $\rho_p$ (Ohm cm/$K^5$) | $1.032 \times 10^{-10}$ |
| $\rho_2$ (Ohm cm/$K^2$) | $3.915 \times 10^{-4}$ |
| $\rho_a$ (Ohm cm) | 0.014 |
| $E_A/k_B$ (K) | 432.91 |
| $U_0/k_B$ (K) | 1012.49 |
| $T_c^{\text{mod}}$ (K) | 248.608 |
| $T_{\text{MA}}$ (K) | 148.530 |
| $R^2$ (%) | 99.98 |

In this paper, the magnetoresistance properties of LBSMCO-10 is also reported. The magnetic field dependence of magnetoresistance from sample LBSMCO-10 is presented in Figure 4. It is interesting to note that LBSMCO-10 sample experience a low field magnetoresistance (LFMR) at low temperature (15 and 100K) and only high field magnetoresistance (HFMR) at higher temperature (200K). LFMR phenomenon in LBSMCO-10 is suggested by the significant drop in MR% value at external field lower than 0.3 T [2]. Based on this result, it can be concluded that the magnetoresistance property of the sample at low temperature is mainly caused by spin-polarized tunnelling between grain or the spin dependent scattering of charge through grain boundaries, surfaces, and poorly conducting region. Additionally, it can be concluded that the magnetoresistance property at high temperature is caused by slow domain rotation of the core of the grains and the decrement in the domain-wall scattering process [11].

4. Conclusion
A detailed study regarding the structure, morphology, electrical transport, and magnetoresistance properties of La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{0.9}$Cu$_{0.1}$O$_3$ manganite have been conducted. It was observed that La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{0.9}$Cu$_{0.1}$O$_3$ crystallize in rhombohedral $R3c$ space group. SEM examination shows that the microstructures of the sample are constructed by cuboid shaped grains. The temperature
dependence resistivity data suggests that La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{0.9}$Cu$_{0.1}$O$_3$ experience a transition from ferromagnetic metal to paramagnetic insulator upon heating. Furthermore, the electrical transport behaviour of La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{0.9}$Cu$_{0.1}$O$_3$ at low temperature is mainly governed by scattering and interaction between electron, phonon, and magnon while at high temperature it was governed by polaron hopping mechanism. Moreover, it was found that La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{0.9}$Cu$_{0.1}$O$_3$ exhibit both LFMR and HFMR phenomena at low temperature while HFMR was only found to happen at higher temperature.

Acknowledgement
This work was supported by Universitas Indonesia under research grant PIT 9 with contract number of NKB-0021/UN2.R3.1/HKP.0500/2019.

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