Effect of copper substitution on the structure of La$_{0.7}$Sr$_{0.25}$Nd$_{0.05}$Mn$_{1-x}$Cu$_x$O$_3$ ($x=0, 0.03, 0.05,$ and $0.07$) manganites

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Abstract. The effect of copper substitution on the structure of La$_{0.7}$Sr$_{0.25}$Nd$_{0.05}$Mn$_{1-x}$Cu$_x$O$_3$ ($x=0, 0.03, 0.05,$ and $0.07$) has been studied by using X-ray diffraction (XRD). The samples were successfully synthesized by using citrate-nitrate sol-gel method. Rietveld refinement analysis showed that all samples crystallized in rhombohedral system with $R3c$ space group without any detectable trace of impurities. Further analysis on the crystal structural of the samples revealed that copper substitution decreases the average Mn-O-Mn bond angle ($\langle$Mn-O-Mn$\rangle$) and increases the Mn-O bond length ($d_{\langle\text{Mn-O}\rangle}$). Scherrer equation showed the samples are in nanocrystalline. X-ray fluorescence (XRF) results indicate that copper has successfully substituted the manganese ion.

Keywords: LSNMCuO, sol-gel method, crystal structure, bond angle

1. Introduction
Perovskite manganite with general formula La$_{1-x}$AMn$_x$BO$_3$ ($A=$ Ba, Ca, Sr or Nd; $B=$ Ni, Cu or Ti) has attracted the interest of many researchers for quite a long time. This is due to the fact that such material can exist in many types of structure and possesses diverse physical properties such as magnetoresistance (MR), magnetocaloric effect (MCE), and charge ordering. Several earlier studies have proven that perovskite manganite with different structure will present different electrical and magnetic properties [1–3]. One of most studied of perovskite manganite is La$_{1-x}$Sr$_x$MnO$_3$ (LSMO). LSMO is an interesting and promising material to be studied because it has high Curie temperature and relatively low resistivity compared to other kind of lanthanum manganite [4,5]. Therefore, LSMO is attracted to be modified in order to achieve a Curie temperature close to room temperature while maintaining its low resistivity. A close ambient temperature of Curie temperature will be needed in order to be applied in daily life.

A more advanced modification of LSMO can be done by introducing another rare-earth metal into the $A$-site of LSMO. Cherif et al. [3] has shown that when neodymium was substituted into LSMO, it can change the crystal structure of (La, Nd)$_x$Sr$_{1-x}$MnO which affected the magnetization and resistivity. They also have shown that even when there is no significant change in crystal structure, in particular only lattice parameter occurred, the resistivity and maximum magnetization of the material still
change according to the substituent concentration [3]. (La, Nd), Sr, MnO is an interesting material that need a further study because it still has relatively low temperature while relatively low Curie temperature compared to LSMO.

The (La, Nd), Sr, MnO can be a candidate for magnetic refrigerant material based on MCE because the lanthanum rare-earth metal doped manganite have Curie temperature close to room temperature and relatively low resistivity [3]. On the other hand, it has been proven that B-site substitution by copper can reduce Curie temperature of the substituted lanthanum manganite [6, 7]. Therefore, we suggest that there is a possibility to reduce Curie temperature of (La, Nd), Sr, MnO by substituting some manganese ion with copper ion. It will be our next work to report the result. However, the aim of this research is to study the effect of copper substitution on the structure of La, Sr, Nd, Mn, CuO. (LSNMCuO) with 0 ≤ x ≤ 0.07. This study is important because it has been proven that even a slight change in the crystal structure can affect the resistivity and magnetization of a substituted lanthanum manganite system [3].

2. Experimental

Nanocrystalline samples of LSNMCuO with x = 0, 0.03, 0.05, and 0.07 (referred as LSNMCuO-0, LSNMCuO-0.03, LSNMCuO-0.05, and LSNMCuO-0.07) were synthesized by citrate-nitrate sol-gel method. Stoichiometric amount of Sr(NO$_3$)$_3$, Mn(NO$_3$)$_2$, Cu(NO$_3$)$_2$, and citric acid (C$_3$H$_5$O$_3$) were diluted in double distilled water until a clear transparent solution was obtained. The citric acid amount can be calculated using molar ratio of metal nitrate to citric acid amount equal to 1:1.2. Stoichiometric amount of La$_2$O and Nd$_2$O were converted into metal nitrate (M(NO$_3$)$_3$) form by reacting it with dilute nitric acid until a clear and transparent solution were obtained. All precursors in solution form were then mixed inside a beaker glass followed by constant stirring on a magnetic hotplate. Afterwards, dried gel was ground into a fine powder and calcined at 550 °C for 5 h. The sample was re-ground and sintered at 700 °C for 24 h. continued by cooling to room temperature inside the furnace. Powder X-ray diffraction (XRD) measurement at room temperature was conducted using Cu Kα radiation. Diffraction data were collected from 10° ≤ 2θ ≤ 90° with step size of 0.02° and scan time over one second for each step. Chemical composition of the samples was examined using X-ray fluorescence (XRF).

3. Results and discussion

Figure 1 shows the result of Rietveld refinement from XRD pattern of LSNMCuO. Based on figure 1, all samples have achieved a single-phase. All main diffraction peaks are matched between experiments compared to the calculated value. Further refinement process reveals that all samples are rhombohedral structure with R$_3$c space group.

According to Rietveld refinement, it can be concluded that copper-doped does not change crystal structure up to 7% of all the manganese ion significantly. The structural parameters obtained from Rietveld refinement are displayed in table 1. Based on the values of discrepancy factors yielded from Rietveld refinement, it shows that the refinement process was good. Moreover, GOF factor values are close to unity with small Rwp and Rp values.

From table 1, it can be seen that the lattice a-parameter increases; meanwhile c-parameter decreases monotonously with increasing copper substitution content. Slight crystal disorder suggests that copper ion has successfully substituted manganese ion at B-site of perovskite structure. Furthermore, the change in lattice parameter leads to reduction of unit cell volume. Liu et al. [8] reported that the reduction of unit cell volume in copper substitution on manganite occurred in order to maintain the ionic stability. Copper substitution on manganite will induce the existence of Mn$^{3+}$ with smaller ionic radius (0.53 Å) compared to Mn$^{4+}$ ion (0.645 Å). Thus, it is expected that the unit cell volume will decrease as the copper content increases [8].

The Goldschmidt tolerance factor (t$_G$) has been calculated in this research and the result is presented at table 1. Goldschmidt tolerance factor can be calculated using a mathematical expression:

$$t_G = \frac{0.7r_{La} + 0.25r_{Sr} + 0.05r_{Nd} + r_O}{\sqrt{2} \left[(1-x)r_{Mn}^{3+} + x r_{Cu}^{2+} + r_O \right]} \quad (1)$$
Table 1. Rietveld refinement on structural parameter obtained for LSNMCuO.

|                  | LSNMCuO-0  | LSNMCuO-03 | LSNMCuO-05 | LSNMCuO-07 |
|------------------|------------|------------|------------|------------|
| crystal structure| rhombohedral| rhombohedral| rhombohedral| rhombohedral|
| space group      | R̃3c       | R̃3c       | R̃3c       | R̃3c       |
| lattice parameter|            |            |            |            |
| a (Å)            | 5.4928(7)  | 5.4936(6)  | 5.4999(6)  | 5.5006(7)  |
| c (Å)            | 13.354(3)  | 13.345(2)  | 13.351(2)  | 13.347(2)  |
| unit cell volume (Å³) | 348.9248     | 348.8023    | 349.7532   | 349.7255   |
| discrepancy factor| GOF       |            |            |            |
|                   | 1.165      | 1.177      | 1.167      | 1.151      |
| Rwp (%)           | 6.138      | 6.151      | 6.237      | 6.204      |
| Rp (%)            | 4.881      | 4.908      | 4.923      | 4.909      |
| Goldschmidt factor (tₚ) | 0.966      | 0.965      | 0.964      | 0.963      |
| average crystallite size (nm) | 20.114    | 21.220    | 21.832    | 20.609    |
| d (<Mn–O>) (Å)    | 1.951      | 1.953      | 1.955      | 1.958      |
| <Mn, Cu–O–Mn, Cu (o) | 166.417    | 165.453    | 165.13     | 163.819    |

Figure 1. Rietveld refinement of XRD pattern for LSNMCuO samples at room temperature (a) LSNMCuO-0, (b) LSNMCuO-03, (c) LSNMCuO-05, and (d) LSNMCuO-07

After tₚ values are known, the structure of perovskite can be deduced theoretically. It has been proven that tₚ value above 0.96 will form a rhombohedral structure [9]. We confirm that all the samples are rhombohedral structure obtained from Rietveld refinement analysis. Table 1 shows that Goldschmidt tolerance value decreases as copper content increases. Reduction in tₚ value suggests that there is a tendency of a distorted crystal structure compared to cubic perovskite. One may observe an increasing trend in average Mn-O bond length (d(<Mn–O>) followed by a decreasing trend in average Mn, Cu–O–Mn, Cu bond angle (<Mn, Cu–O–Mn, Cu>). Radaelli et al. [10] reported that crystal structural disorder in substituted of lanthanum manganite system was indicated from the changes in average...
Table 2. Comparison of metal concentration obtained from XRF measurement compared to theoretical measurement

| Element | Concentration measured (%) | Concentration calculated (%) |
|---------|----------------------------|------------------------------|
|         | \( x = 0 \) | \( x = 0.03 \) | \( x = 0.05 \) | \( x = 0.07 \) | \( x = 0 \) | \( x = 0.03 \) | \( x = 0.05 \) | \( x = 0.07 \) |
| Mn      | 27.54 | 26.62 | 25.77 | 25.21 | 30.30 | 29.35 | 28.72 | 28.09 |
| Cu      | 0     | 1.12  | 1.89  | 2.60  | 0.00  | 1.05  | 1.75  | 2.45  |
| Sr      | 11.47 | 11.64 | 11.83 | 11.79 | 12.08 | 12.07 | 12.05 | 12.04 |
| La      | 55.92 | 55.65 | 55.55 | 55.42 | 53.63 | 53.56 | 53.51 | 53.46 |
| Nd      | 5.06  | 4.97  | 4.97  | 4.98  | 3.98  | 3.97  | 3.97  | 3.97  |
| Total   | 100.00| 100.00| 100.00| 100.00| 100.00| 100.00| 100.00| 100.00|

Figure 2. X-ray fluorescence spectra of all metal detected for (a) LSNMCuO-0, (b) LSNMCuO-0.03, (c) LSNMCuO-0.05, and (d) LSNMCuO-0.07. Dashed-circle shows copper spectra.

bond length and average bond angle because of the electrical transport and magnetic properties of the material. Table 2 also shows the average crystallite size of samples, which have been calculated using Scherrer equation as follow:

\[
D_{sc} = \frac{0.9 \lambda}{\beta_{HKL} \cos \theta}
\]

where \( D_{sc} \) is average crystallite size, \( \lambda \) is Cu-K\( \alpha \) radiation (1.5406 Å), \( \beta_{HKL} \) is full-width at half maximum (FWHM) of each diffraction peaks in radian unit, and \( \theta \) is diffraction peak position for each diffraction peaks. It is interesting to note that the average crystallite size increased as copper concentration increased, and it reaches maximum value at 5% of copper content. The average crystallite size was found to decrease when copper content in the sample were bigger than 5%.

The chemical compositions of all the synthesized samples were examined by using X-ray fluorescence (XRF) measurement. The XRF spectra results of LSNMCuO are presented in figure 2. It can be seen that copper spectrum started to emerge from LBSNMCuO-0.03. These results support the previous argument of structural analysis that copper ions have successfully substituted manganese ion. Additionally, table 2 also provides information that no other traces of impurities are detected in the sample. This fact supports previous claim that sample has reached single-phase.
4. Conclusions
The effect of copper-doped on structural properties of $\text{La}_{0.7}\text{Sr}_{0.25}\text{Nd}_{0.05}\text{Mn}_{1-x}\text{Cu}_x\text{O}_3$ ($x = 0, 0.03, 0.05$, and 0.07) synthesized by sol-gel method has been studied in this research article. X-ray diffractometer analysis indicates that copper-doped does not affect the crystal structure, remain rhombohedral with $R\overline{3}c$ space group. Furthermore, as copper-doped increase implies to a decrease unit cell volume of the samples. Copper-doped concentration influences the average bond length and average bond angle. This result indicates that there will be a change in the transport and magnetic properties of the sample.

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