Effect of Sintering Temperature and Cu Substitution on the Structure of \( \text{La}_{0.7}\text{Ba}_{0.291}\text{Ca}_{0.009}\text{Mn}_{1-x}\text{Cu}_x\text{O}_3 \) (\( x = 0 \) and 0.10) Manganite

I N Rahman\(^1\), Budhy Kurniawan*\(^1\) and Setia Budi\(^2\)

\(^1\)Departement of Physics, Universitas Indonesia, Depok 16424, Indonesia  
\(^2\)Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Jakarta, Rawamangun, Jakarta 13220, Indonesia

*Corresponding author: budhy.kurniawan@sci.ui.ac.id

**Abstract.** Series of Cu substituted manganese \( \text{La}_{0.7}\text{Ba}_{0.291}\text{Ca}_{0.009}\text{Mn}_{1-x}\text{Cu}_x\text{O}_3 \) (\( x = 0 \) and 0.10) has been studied and it has affect in the structure. The powder sample was elaborated using sol-gel method. Samples were sintered at two different temperatures, 1173 K and 1473 K. Structures of all samples were investigated by X-ray diffraction (XRD). The Rietveld analysis of the powder x-ray diffraction shows that the samples crystallize in rhombohedral structure with \( R_3c \) space group symmetry without any impurity phase. The values of tolerance factor (\( t_G \)) shows that the sample without Cu substitution (\( t_G = 0.98486 \)) and with Cu substitution (\( t_G = 0.980703 \)) are still in perovskite structure. Substitution by Cu does not change the structure but it decreases unit cell volume, lattice parameters and Mn-O-Mn bond angle and increases Mn-O bond length. The result of experiments confirms that the Cu substitution at Mn-site interrupt the Mn\(^{3+}\)-O\(^{2-}\)-Mn\(^{4+}\) bridges and weaken the double exchange (DE) interaction between Mn\(^{3+}\) and Mn\(^{4+}\) ions. This phenomenon is indicated by a decrease in the bandwidth value.

1. **Introduction**

Perovskite manganite with general formula \( \text{RE}_{1-x}\text{A}_x\text{MnO}_3 \), where \( \text{RE} = \text{trivalent rare earth} \) and \( \text{A} = \text{Ba, Ca, Sr, etc} \) has been extensively investigated to study the physical phenomena such as colossal magnetoresistance (CMR), magnetocaloric effect (MCE), electronic phase separation, transition of metal to insulator and charge (orbital ordering). This material has potential to applied in magnetic random access memory (MRAM), spintronics, magnetic field sensors, magnetic refrigeration, etc[1–5]. Physical phenomena that occur in this material are influenced by substitution at A and Mn site. Substitution at A site can influence lattice distortion that causes changes in crystal structure and increasing double exchange (DE) interactions. DE interaction is the transfer of electrons between Mn\(^{3+}\) (3d\(^4\), t\(_{2g}\)^3 e\(_g\)\(^1\), \( S = 2\) ) and Mn\(^{4+}\) (3d\(^3\), t\(_{2g}\)^3 e\(_g\)\(^2\), \( S = 3/2\) ) ions through O\(^{2-}\) anions[6]. Besides A-site, a lot of research is done by substituting Mn-site with transition metal ions. This can modify DE interactions in Mn\(^{3+}\) and Mn\(^{4+}\) ions, and also produce other exchange interactions between Mn ions and transition metal ions. Cu substitution (Cu\(^{2+}\): t\(_{2g}\)^6 e\(_g\)\(^3\), Cu\(^{3+}\): t\(_{2g}\)^6 e\(_g\)\(^2\)) at Mn-site will reduce number of Mn\(^{3+}\) and converts it to Mn\(^{4+}\) for charge becomes neutral [3]. Several research shows that Cu substitution at \( \text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 \) perovskite can increase MR values and maximum magnetic-entropy change \( \Delta S_{\text{max}} \) with increasing Cu substitution[7,8]. The same thing is also done by Wang K. Y., substitution of Cu can also
reduce resistivity when magnetic fields are 0 and 5 T. Besides, it could be able to increase the MR values [9].

In this work, polycrystalline La$_{0.7}$Ba$_{0.291}$Ca$_{0.009}$Mn$_{1-x}$Cu$_x$MnO$_3$ were synthesized via sol-gel method. This method has been known to provide many advantages, such as homogeneous material, low temperature heating, short heating duration and high purity materials. Detailed studies on structural and effect of sintering temperature were investigated using X-ray diffractometer (XRD).

2. Experimental
Polycrystalline of La$_{0.7}$Ba$_{0.291}$Ca$_{0.009}$Mn$_{1-x}$Cu$_x$O$_3$ (x = 0 and 0.1) were synthesized using the sol-gel method. The precursors that were used namely La$_2$O$_3$ (Merck, 99.5%) Ba(NO$_3$)$_2$ (Merck, 99%) Ca(NO$_3$)$_2$.4H$_2$O (Merck, 99%), Mn(NO$_3$)$_2$.4H$_2$O (Merck, 98.5%) and Cu(NO$_3$)$_2$.4H$_2$O (Merck, 99.5%). Stoichiometric amounts of precursors were dissolved in distilled water and then added with some suitable amounts of citric acid with a ratio of 1: 1.2 to total metal ions. The resulting gel was calcined at 773 K for 4 hours to eliminate the organic material and sintered at 1173 K for 3 hours and re-sintered 1473 K for 3 hours.

The structure and phase purity were investigated by X-ray diffraction (XRD) using a PanAnalytical Expert Pro diffractometer with Cu K$_\alpha$ radiation ($\lambda = 1.56406$ Å) and data collection was done in 10° to 90° with step-size of 0.02° and a scanning time of 15 second per step.

3. Result and Discussion
The XRD study of polycrystalline La$_{0.7}$Ba$_{0.291}$Ca$_{0.009}$Mn$_{1-x}$Cu$_x$O$_3$ (x = 0 and 0.10) was carried out at room temperature and data were analysed with Rietveld refinement technique. XRD pattern of samples with heat treatment of 1173 K are shown in Figure 1(a). The samples indicate the presence of some impurities such as La$_2$O$_3$, CuO and MnO. Therefore, the samples were re-sintered 1473 K for 3 hours and a single-phase material was obtained.

The XRD pattern obtained after sintering 1473 K were shown in Figure 1(b) reveal all $hkl$ index of peak in the material. The result of refinement reveals a formation of single phase which crystallizes in the rhombohedral system with space group R3c. In this space group, the Wickoff value for La/Ba/Ca atoms are 6a at (0,0,1/4) position, (Mn/Cu) are at 6b (0,0,0) and O atom are at 18e (x,0,1/4), respectively [3,10]. There is no transition structural occurred due to Cu substitution on material and there is no identified phase of impurity. Rietveld refinement shows a good agreement between observed and calculated profile, due to excellent discrepancy factor as Goodness of Fit (GoF), Rp and Rwp, respectively, as shown in Table 1. The result of refinement and illustration of crystal structure with Virtualization of Electronic Structural Analysis (VESTA) program is shown in fig 2. Based on the XPS study, perovskite manganite substituted with Cu at site-B, will show Cu with two valences, Cu$^{2+}$ and Cu$^{3+}$ with Cu$^{2+}$ which is more dominant [3]. The change in the lattice parameter is affected by the mismatch of the ionic radius between Cu ions and Mn ions. The ionic radius of Cu$^{2+}$ (0.73 Å) is larger than radius of Mn$^{3+}$ and Mn$^{4+}$ and the ionic radius of Cu$^{3+}$ (0.54 Å) close to Mn$^{4+}$ (0.53 Å) and smaller than Mn$^{3+}$ radius (0.645 Å) [11]. Furthermore, Cu$^{2+}$ would substitute Mn$^{3+}$ ion and Cu$^{3+}$ would substitute Mn$^{4+}$ ion. Cu$^{2+}$ ions are expected to be dominant, therefore the effect of Cu substitution will lead to a change in the relative fraction of different Mn ions and will increase the amount of Mn$^{4+}$ ions. This is to maintain that the sample charge remains neutral and makes the unit cell volume decrease [3].
Figure 1. XRD patterns of La$_{0.7}$Ba$_{0.29}$Ca$_{0.009}$Mn$_{1-x}$Cu$_x$O$_3$ ($x = 0$ and 0.10), a) sintered 1173 K with impurity “*” La$_2$O$_3$, “∆” CuO and “*” MnO, b) sintered 1473 K. All peaks of the manganite phase are indexed in the rhombohedral $R-3c$ symmetry.
Figure 2. The observed and calculated XRD patterns obtained by Rietveld refinement and crystal structure of (a) La$_{0.7}$Ba$_{0.291}$Ca$_{0.009}$MnO$_3$ (b) La$_{0.7}$Ba$_{0.291}$Ca$_{0.009}$Mn$_{0.9}$Cu$_{0.1}$O$_3$.

To describe the ionic match between A and B site ions in the perovskite structure compound ABO$_3$, a geometrical quantity, can be calculated using the tolerance factor of goldsmith ($t_G$). $t_G$ is defined as:

$$t_G = \frac{1}{\sqrt{2}} \frac{\langle r_A \rangle - r_O}{\langle r_B \rangle - r_A}$$  \hspace{1cm} (1)

where $r_A$ and $r_B$ represents the average ionic radius of site A and B, and $r_O$ is average ionic radius of oxygen anion. Stable oxide based manganite compound has a perovskite structure if their $t_G$ in the range $0.89 < t_G < 1.02$, and for rhombohedral structure has $t_G$ in range $0.96 < t_G < 1$ [12]. The value of $t_G$ for both of samples were estimated and listed on the Table 1. Crystalline size ($D$) was calculated based on the reflection of 2θ values of XRD profile using Scherer’s equation given as:

$$D = \frac{K\lambda}{\beta \cos \theta}$$  \hspace{1cm} (2)

where $k$ is called shape factor, which usually takes of value of about 0.9, $\lambda$ [10] is the X-ray wavelength ($\lambda = 1.54056 \text{ Å}$), $\beta$ is full width at half maximum (FWHM) of the diffraction peak and $\theta$ is Bragg diffraction angle. Substitution of Cu in B-site tends to increase the average crystallite size. Crystallite
sizes (D) are given in Table 1. DE interaction between Mn$^{3+}$ and Mn$^{4+}$ ions through anion O$^{2-}$ is depended on Mn–O–Mn angle bonds. Substitution of Cu tends to reduced DE and lead the super-exchange antiferromagnetic interaction. Decreasing of Tc corresponds to a poor overlap manganese 3d and oxygen 2p orbitals and will reduce bandwidth (W) [3]. The bandwidth described by equation:

$$W = \frac{cos \frac{1}{2} (\pi - (Mn - O - Mn))}{(Mn - O)^{3.5}}$$

where Mn–O–Mn is bond angle and Mn–O is bond length. The values of bandwidth (W) are given in Table 1. Cu substitution decrease Mn–O–Mn angle and increase Mn–O bond length, therefore electrons transfer will be more difficult.

Table 1. Parameter of structure obtained by Rietveld refinements from XRD patterns measured at room temperature for La$_{0.7}$Ba$_{0.291}$Ca$_{0.009}$Mn$_{1-x}$Cu$_x$O$_3$ (x = 0 and 0.1).

| Parameter | X = 0.0 | X = 0.1 |
|-----------|---------|---------|
| a = b (Å) | 5.53617 | 5.53509 |
| c (Å)     | 13.50642 | 13.50516 |
| V (Å$^3$) | 358.4998 | 358.3273 |
| Average Crystallite size (nm) | 48.9291 | 73.0600 |
| Discrepancy factors | | |
| Rwp (%)   | 7.8900  | 6.9206  |
| Rp (%)    | 5.9629  | 5.2928  |
| GoF       | 1.6511  | 1.0955  |
| Bond lengths and bond angles | | |
| $\theta_{Mn-O-Mn}$ (°) | 171.900 | 162.895 |
| $d_{Mn-O}$ Å | 1.960 | 1.976 |
| Bandwidth | | |
| W (10$^{-2}$) (u.a) | 9.46276 | 9.117784 |
| Tolerance factor | | |
| $t_G$ | 0.98486 | 0.980703 |

4. Conclusion
Investigation of structural polycrystalline La$_{0.7}$Ba$_{0.291}$Ca$_{0.009}$Mn$_{1-x}$Cu$_x$MnO$_3$ (x = 0 and 0.1) compound synthesized using sol-gel method have been carried out. Refinement result of XRD patterns at room temperature of both samples showed a single phase without impurities product and possess rhombohedral structure with $R3c$ space group. Cu substitution at B-site causes decreasing value of lattice parameters, unit cell volume and Mn–O–Mn bond angle, along with the increasing of crystallite size and Mn–O bond length. However, this Cu substitution did not change the crystal structure.

Acknowledgement
This work was supported by Universitas Indonesia under research grant HIBAH PIT 9 with contract NKB-0021/UN2.R3.1/HKP.05.00/2019 with the title is “Sintesis dan Karakterisasi Material Fungsional Berbasis Perovskite Manganite dan MoS$_2$ Sebagai Material Maju”.
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