Preparation and crystal structure of La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{0.9}$Cu$_{0.1}$O$_3$ perovskite: a comparison between sol-gel and solid state process

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Abstract. Polycrystalline sample of La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{0.9}$Cu$_{0.1}$O$_3$ was successfully synthesized using sol-gel and solid state method. Despite the various condition employed during the process to synthesize the samples, the crystal structure of both samples show that both samples have formed a single phase without any impurities. Furthermore, in accordance with the same value of Goldschmidt factor, both samples crystallize with the same hexagonal structure and $R3c$ space group. A slight difference appears in the more detailed aspect of crystal structure which are unit cell volume, Mn-O bond length, and Mn-O-Mn bond angle. The unit cell volume is 354.797 Å$^3$ for solid state method and 352.747 Å$^3$ for sol-gel method. The bond length and bond angle are 1.967 Å and 164.026° for solid state method and 1.957 Å and 166.738° for sol-gel method.

1. Introduction
Perovskite manganite with general formula La$_{1-x}$AE$_x$Mn$_{1-y}$TM$_y$O$_3$, where AE is alkaline earth metal (Ba$^{2+}$, Sr$^{2+}$, Ca$^{2+}$) and TM is transition metal (Co, Cu, Fe), have been an interesting field of study in recent years [1-3]. This is due to the unique physical properties of the materials under the influence of external magnetic field. Magnetocaloric and magnetoresistance effect are some of the recognized example that can emerge when such materials are exposed to external magnetic field. An even interesting fact that draws many attentions from La$_{1-x}$AE$_x$Mn$_{1-y}$TM$_y$O$_3$ material is that its physical phenomenon under external magnetic field can be tuned by varying the doping levels and synthesis method used to synthesize the material [4].

La$_{1-x}$AE$_x$Mn$_{1-y}$TM$_y$O$_3$ basically is a modified material derived from parent compound which is LaMnO$_3$ that has a perovskite structure with rhombohedral crystal structure [6]. Upon partial substitution on A-site or B-site, or even on both site can cause a distortion at the crystal structure. Such distortion can cause a difference in the physical phenomenon compared to the parent compound or the undoped compound [6]. The effect of partial substitution on the crystal structure can vary from just difference in lattice parameter to a difference in crystal structure depending on the doping level [7].

Earlier investigation had been done to study the effect of doping level, which can cause a change in crystal structure, on the physical phenomenon of doped LaMnO$_3$. By partially substituting alkaline earth cation (Ba$^{2+}$, Sr$^{2+}$, Ca$^{2+}$) to the A-site of LaMnO$_3$, one can change the average A-site ionic radius of the material which can cause a difference in the curie temperature [8]. Furthermore, by partially substituting transition metal cation (Co, Cu, and Fe) to the B-site of La$_{1-x}$AE$_x$MnO$_3$ can cause a change
in the crystal structure and the ratio of Mn$^{3+}$ to Mn$^{4+}$. Such change will affect directly to the double exchange phenomenon of La$_{1-x}$AE$_{x}$Mn$_{1-y}$TM$_{2}$O$_{3}$ material [7].

It is important to choose proper method to synthesize La$_{1-x}$AE$_{x}$Mn$_{1-y}$TM$_{2}$O$_{3}$ material. As found in the previous research, different in sample preparation method will cause a different in the physical phenomenon of a doped LaMnO$_3$ system [8-9]. Although the effect of sample preparation method on the physical phenomenon had been done, a more detailed study about its effect on the crystal structure has never been done. In order to understand the effect of synthesis method on the crystal structure of doped LaMnO$_3$ system, La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{0.9}$Cu$_{0.1}$O$_3$ manganite sample are synthesized by two different methods which are sol-gel and solid state method. This article will give a detailed description of both preparation method followed by discussion on the crystal structure of the sample.

2. Experimental

Bulk sample of La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{0.9}$Cu$_{0.1}$O$_3$ was prepared using two different methods which are sol-gel and solid state method. In the sol-gel method, the precursor that were used are La$_2$O$_3$ (Merck, 99.5%), Ba(NO$_3$)$_2$ (Merck, 99%), Sr(NO$_3$)$_2$ (Merck, 99%), Mn(NO$_3$)$_2$.4H$_2$O (Merck, 98.5%), Cu(NO$_3$)$_2$.3H$_2$O (Merck, 99.5%), and citric acid (C$_6$H$_8$O$_7$.H$_2$O, Merck, 99.5%). The majority of the precursor used in the sol-gel method are in metal nitrate compound. The reason being is that metal nitrate compound are easier to dissolve in the solvent used in sol-gel method. In the solid state method, the precursor that were used are La$_2$O$_3$ (Merck, 99.5%), BaCO$_3$ (Merck, 99%), SrCO$_3$ (Aldrich, 98%), MnCO$_3$ (Aldrich, 99.9%), and CuCO$_3$ (Aldrich, 95%). The majority of the precursor used in solid-state method are in oxide or carbonate form. The reason being is that it will ease the grinding process as it does not bind water vapour in the air.

2.1. Sol-gel method

Sol-gel method starts by weighing all the precursors according to the desired stoichiometry. Afterwards, precursor that have already in metal nitrate form was dissolved in double distilled water. Lanthanum oxide precursor must be converted to metal nitrate form by dissolving it in dilute nitric acid according to the following reaction:

$$\text{La}_2\text{O}_3 + 6 \text{HNO}_3 \rightarrow 2 \text{La(NO}_3)_3 + 3 \text{H}_2\text{O}$$

After every solid metal nitrate precursor have been dissolved in double distilled water, sol-gel method continues with mixing all the precursors together to synthesize La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{0.9}$Cu$_{0.1}$O$_3$ sample in solution form according to the following reaction:

$$0.7 \text{La(NO}_3)_3 + 0.1 \text{Ba(NO}_3)_2 + 0.2 \text{Sr(NO}_3)_2 + 0.9 \text{Mn(NO}_3)_2.4\text{H}_2\text{O} + 0.1 \text{Cu(NO}_3)_2.3\text{H}_2\text{O} +$$
$$\beta \text{Cu}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O} \rightarrow \text{La}_{0.7}\text{Ba}_{0.1}\text{Sr}_{0.2}\text{Mn}_{0.9}\text{Cu}_{0.1}\text{O}_3 + \delta \text{N}_2 + \gamma \text{H}_2\text{O} + \alpha \text{CO}_2$$

In this sol-gel method, citric acid was used as a fuel and chelating agent to form a perovskite structure. The amount of citric acid used can be calculated from the molar ratio of citric acid to metal nitrate which is 1.2 [11]. After all the precursor were mixed together and became a single solution, the acidity of the solution was adjusted by adding a dilute ammonia solution until it reaches 7 and a clear solution obtained. During the entire sol-gel process, the temperature of the solution was kept at constant value around 80 °C. Sample in viscous gel form will be obtained at the end of the so-gel method.

The obtained viscous gel then dried inside an oven with 120 °C overnight to decrease the water content in the sample. After a dried gel obtained, then the sample in dried gel form was grinded until a fine powder is obtained. Then sample in a form of fine powder is calcined at 500 °C for 5 hours. After the calcination process was completed, sample in black powder form will be obtained. Sample with black powder form then grinded again and pressed into a cylinder form with 2 mm thickness and 12 mm diameter using 5 tons/cm$^2$ pressure. Sample in pelletized form then sintered at 1100 °C for 12 hours.
2.2. Solid state method

Solid state method starts by weighing all the precursor according to the desired stoichiometry. Then all the precursor was mixed together in agate mortar and grinded for approximately 1 hour until the mixed powder achieved unicolor and become fine powder. The sample in powder form then calcined at 500 °C for 24 hours. Afterward, the obtained powder was pressed into a cylinder form with 2 mm thickness and 12 mm diameter using 5 tons/cm² pressure. In order to obtain average crystallite size that does not much different compared to sol-gel method, the sintering process for solid state method was carried out at 1000 °C for 24 hours which is a relatively low sintering temperature compared to the commonly known solid state method.

3. Results and Discussion

The structural and purity of both samples are determined using X-ray diffractometer (Panalitycal X’Pert Pro MPD) with Cu Kα radiation (λ = 1.5406 Å) in room temperature. The pattern was recorded in the 10 ≤ 2θ ≤ 90 angular range with a step size of 0.02°. The diffraction pattern of La0.7Ba0.1Sr0.2Mn0.9Cu0.1O3 synthesized using sol-gel and solid state method after calcination process are shown in Figure 1.

![Figure 1](image-url)

Figure 1. Diffraction pattern after calcination process of La0.7Ba0.1Sr0.2Mn0.9Cu0.1O3 sample (a) synthesized using sol-gel method and (b) synthesized using solid state method. Asterisk sign marks rhombohedral peak that belong to LaMnO3

From the result, it can be concluded that calcination temperature used during sol-gel method does not enough to form a perovskite structure. The reason being is that for doped LaMnO3 system, the perovskite structure is starting to from after the temperature of the sample reaches 600 °C [12]. Based on Figure 1(b), one can see that calcination process at 500 °C for 24 hours during solid state method was not enough to bind all the precursors into a new perovskite compound.

Although the temperature used during calcination process is relative low from solid state point of view, a few diffraction pattern that belong to LaMnO3 with rhombohedral crystal structure starting to appear with low intensity. Figure 2 shows the diffraction pattern of La0.7Ba0.1Sr0.2Mn0.9Cu0.1O3 which have been refined using rietveld analysis. Based on figure 2, it can be concluded that both sample have achieved single phase state. This is suggested by the high similarity of observed diffraction pattern compared to calculated diffraction pattern. Furthermore, based on the value of the discrepancy factor and the fit of goodness (GOF) it can also be concluded that the refinement process which have been done were already quiet good. The discrepancy factor and GOF value resulting from rietveld refinement process are listed in Table 1.
Figure 2. Rietveld analysis result from sample $\text{La}_{0.7}\text{Ba}_{0.1}\text{Sr}_{0.2}\text{Mn}_{0.9}\text{Cu}_{0.1}\text{O}_3$ synthesized using (a) sol-gel method and (b) solid state method.

Figure 3(a) shows that regardless the sample preparation method, rhombohedral structure with $R\overline{3}c$ space group was stable without any impurities. This is proved by the same miller indices on every diffraction peak from both solid state and sol-gel method. Although both diffraction pattern might look the same, there exist a slight difference in the most intense diffraction peak of both samples. A better comparison on the main diffraction pattern (highest intensity) from both samples can be seen from Figure 3(b).

One can see that the most intense diffraction peak of $\text{La}_{0.7}\text{Ba}_{0.1}\text{Sr}_{0.2}\text{Mn}_{0.9}\text{Cu}_{0.1}\text{O}_3$ which prepared using solid state method shift to lower $2\theta$ value compared to sample prepared using sol-gel method. This is an indication of a difference in the lattice parameter which also affect unit cell volume. The result obtained met an agreement with previous work which shows that a shift in lower $2\theta$ value will decrease unit cell volume of the sample [8]. The structural parameter obtained after refinement with rietveld analysis can be seen from Table 1.

The average crystal structure is calculated using scherrer formula as follow:

$$D = \frac{0.9 \lambda}{\beta_{hkl} \cos \theta}$$ (1)
where $D$ is crystallite size, $\lambda$ is Cu-$K\alpha$ radiation which is used during XRD measurement (1.5406 Å), $\beta_{hkl}$ is full-width at half maximum (FWHM) of each diffraction peak in radian unit, and $\cos \theta$ is the cosine value of each diffraction position peak.

Rietveld analysis shown that the average crystallite size of sample prepared using sol-gel method are slightly greater compared to sample prepared using solid state method. This is due to high sintering temperature which is used during preparation of sample using sol-gel method. It has been mentioned earlier that perovskite structure are starting to form after 600 °C in sol-gel method. Application of higher temperature beyond of that will improve crystallinity which cause bigger crystallite size. On the contrary, solid state method needs higher temperature and longer time to form a perovskite structure which free from impurities compared to sol-gel method. After all the precursor combined to make a new perovskite structure, a further temperature treatment will improve crystallinity which cause bigger crystallite. In solid-state point of view, usually sample without any impurities can be achieved after giving high temperature treatment above 1000 °C [7]. The fact that using 1000 °C of sintering temperature during the solid state method can achieve a single phase structure will cause a small average crystallite size and poor crystallinity. The obtained result from sample prepared using solid state method are suitable with previous expectation that low sintering temperature for solid state method will produce average crystallite size that is comparable to sample prepared using sol-gel method which commonly known could produce sample within nanometer crystallite scale.

Table 1. The structural parameter obtained from rietveld analysis for both samples after XRD measurement at room temperature.

| Structural parameter | Sol-gel | Solid state |
|----------------------|---------|-------------|
| Space group          | R3c     | R3c         |
| Lattice parameter    |         |             |
| a (Å)                | 5.5126(2) | 5.5329(3)   |
| c (Å)                | 13.4035(5) | 13.383(1)  |
| V(Å$^3$)             | 352.7446 | 354.7968    |
| Discrepancy factor   |         |             |
| GOF                  | 1.0226  | 1.1169      |
| Rwp (%)              | 7.6641  | 13.3853     |
| Rp (%)               | 6.0350  | 10.3895     |
| Average crystallite size (nm) | 56.8959 | 54.8686 |
| $<$Mn-O$>$ (Å)       | 1.957   | 1.967       |
| $<$Mn-O-Mn$>$ (degree) | 166.738 | 164.026    |

The value of Average bond length ($<$Mn-O$>$) and average bond angle ($<$Mn-O-Mn$>$) are listed in Table 1. It can be seen that sample synthesized using sol-gel method has shorter bond length and bigger bond angle compared to sample synthesized using solid state method. The result obtained also met an agreement with previous research that has been done [8]. Previous research has shown that average bond length and average bond angle can affect one of the physical phenomenon that can arise from doped LaMnO$_3$ system according to the following equation [13]:

$$W = \frac{\cos \frac{\pi}{2} (\pi - \langle Mn-O-Mn \rangle)}{d^{3/2}_{Mn-O}}$$

(2)

where $W$ is the one-electron bandwidth. Dhahri et al. have shown that Curie temperature will decrease as the value of $W$ decreases. From above equation, it can be seen that $W$ is proportional to average
bond angle $<\text{Mn-O-Mn}>$ and inversely proportional to average bond length $d_{\text{Mn-O}}$. Several research has shown that the decrease in average bond angle followed by an increase in average bond angle can cause a decrease in Curie temperature [8, 13].

4. Conclusion
In summary, La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{0.9}$Cu$_{0.1}$O$_3$ perovskite sample has successfully synthesized using two different methods. The different method does not change the crystal structure of La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{0.9}$Cu$_{0.1}$O$_3$ as it remains rhombohedral with R-3c space group in both methods. The difference in synthesis method only affect lattice parameter thus also affect unit cell volume and average bond length also average bond angle. Using a relation obtained by previous research, a different in average bond length and bond angle will cause a different in Curie temperature, thus different synthesis method will also affect Curie temperature of a doped LaMnO$_3$ system.

References
[1] Coşkun A, Taşarkuyu E, Irmak AE, Acet M, Samancıoğlu Y and Aktürk S J 2015 Alloys. Compds. 622 796
[2] Gdaiem MA, Ghodhbane S, Dahri A, Dahri J and Hlil E K J 2016 Alloys. Compds. 681 547
[3] Betancourt I, Lopez Maldonado L and Elizalde Galindo J T 2016 J Magn. Magn. Mater. 401 812
[4] Hueso L E, Sande P, Miguéns D R, Rivas J, Rivadulla F and López-Quintela M A 2012 J. Appl. Phys. 91 9943
[5] Moreno L C, Valencia J S, Landínez T D A, Arbey Rodríguez M J, Martínez M L and Roa-Rojas J 2008 J. Magn. Magn. Mater. 320 e19
[6] Ben J F, Mahmood S H, Ellouze M, Hlil E K and Halouani F C 2015 Ceram. Int. 41 8191
[7] El-Hagary M, Shoker Y A, Mohammad S, Moustafa A M, El-Aal A A and Michor H 2009 J. Alloy. Compd. 468 47
[8] Ayadi F, Cheikhrouhou-Koubaa W, Koubaa M, Nowak S, Sicard L and Ammar S 2014 Mater. Chem. Phys. 145 56
[9] Ezaami A, Nasser N O, Cheikhrouhou-Koubaa W, Koubaa M, Cheikhrouhou A and Hlil E K 2017 J. Mater. Sci. 28 3648
[10] Wang G F, Li L R, Zhao Z R, Yu X Q and Zhang X F 2014 Ceram. Int. 40 16449.
[11] Li Y, Xue L, Fan L and Yan Y 2009 J. Alloys Compd. 478 493
[12] Ravi S K and Karthikeyan A 2014 Phys. Proc. 54 45
[13] Dahri M, Zaidi A, Cherif K, Dahri J and Hlil E K 2017 J. Alloys. Compd. 691 578